# Bifunctional Catalysis to convert Synthesis Gas to Chemicals and Fuels

Jan Lennart Weber

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# Bifunctional Catalysis to convert Synthesis Gas to Chemicals and Fuels

# Bifunctionele katalyse om synthesegas om te zetten in chemicaliën en brandstoffen

(met een samenvatting in het Nederlands)

### Proefschrift

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door

## Jan Lennart Weber

geboren op 8 maart 1985 te Oldenburg, Duitsland

#### **Promotoren:**

Prof. dr. K.P. de Jong Prof. dr. P.E. de Jongh

### **Beoordelingscommissie:**

Prof. H.J. Heeres Prof. dr. W.K. Kegel Prof. X. Pan Prof. dr. D.A.M. Vanmaekelbergh Prof. dr. ir. B.M. Weckhuysen

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für Janneke und Nienke

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## **General Introduction**

Processes for the production of chemicals and liquid fuels have developed over the many decades and are well established today. These processes have a high production capacity (i.e. ~350 Mt/year C<sub>2</sub> and C<sub>3</sub> olefins, ~150 Mt/year benzene and *p*-xylene, ~760 Mt/year gasoline) <sup>1-3</sup> and are mainly based on fossil feedstocks, such as crude oil, natural gas or coal <sup>4</sup>.

As the world population increased and the society developed further, the total energy demand was 595 EJ in 2021 <sup>3</sup>. The contribution of fossil fuel to this energy consumption showed a decreasing trend, however, with 82% in 2021 still the vast majority of energy is provided from fossil sources (in 2016 85% of the energy demand came from fossil fuels).

The worldwide energy demand in combination with the high fraction of fossil resources to cover this demand causes the concentration of  $CO_2$  and other greenhouse gases in the atmosphere to increase <sup>5–9</sup>. With 411 ppm of  $CO_2$  in the atmosphere 2019, this is the highest concentration for the past 3 million years <sup>10–12</sup>. This increased concentration of greenhouse gases in the atmosphere is one of the main drivers for climate change <sup>13–15</sup> which can have catastrophic consequences for the life on this planet <sup>12,16–18</sup>.

To counteract climate change, research has moved towards replacing fossil feed stocks for the production of chemicals and fuels by renewable sources <sup>19–28</sup>. Alternatively, carbon containing waste can be used to produce chemicals and fuels directly using thermal or catalytic processes <sup>29–35</sup>. Synthesis gas (a mixture of hydrogen, carbon monoxide and/or carbon dioxide) can be derived from biomass or CO<sub>2</sub> combined with hydrogen from renewable sources (such as electrolysis using electricity from wind or solar) and allows to synthesize a variety of products in a more sustainable manner <sup>36–39</sup>.

However, the novel processes need to be developed further to be able to compete with well-established fossil-based processes in terms of economic feasibility as well as performance and production capacity <sup>40-47</sup>. Also, the impact on the environment plays an important role and must be investigated <sup>48–51</sup>. Liquid transportation fuels consist of a large number of components with well-defined concentrations <sup>52</sup>. A challenge for transportation fuel from renewable sources is to be fully compatible with fossil fuel to become a direct replacement without adjustment on current engine design or infrastructure <sup>53,54</sup>.

As part of this change, developments in technologies for the production of chemicals and fuels from synthesis gas have achieved in the past years <sup>55–58</sup>. The product distribution of the Fischer-Tropsch synthesis usually follows the Anderson-Schulz-Flory (ASF) distribution, in which polymerization of  $CH_x$  monomers on the catalyst surface takes place <sup>59</sup>. Hence, the products are distributed statistically and only depend on the rate of chain growth and chain termination. However, in 2012 an iron-carbide based Fischer-Tropsch-toolefins (FTO) catalyst was developed that enabled the deviation from this ASF distribution by the addition of sodium and sulfur as promoters <sup>60</sup>. This caused a suppressed methane formation and allowed to produce  $C_2$ - $C_4$  olefins with selectivities beyond the limitations of the Anderson-Schulz-Flory distribution of total hydrocarbons <sup>61</sup>. In 2016 a publication regarding a Fischer-Tropsch catalyst based on cobalt-carbide nanoprisms was published  $^{62,63}$ . Similar to the iron-carbide based FTO catalyst, the cobalt-carbide nanoprism catalyst allowed to deviate from the ASF distribution with reduced methane selectivity. Additionally, this catalyst system showed reduced CO<sub>2</sub> formation and a high olefin/paraffin ratio  $^{64}$ .

The addition of sodium promoters to a ruthenium-based FT catalyst also reduced the methane selectivity causing a deviation from the ASF distribution <sup>65</sup>. The content of olefins in the hydrocarbon products was high, which is uncommon for unpromoted ruthenium-based FT catalysts <sup>66</sup>.

To these olefins-producing catalysts a zeolite catalyst can be added to either convert the olefins formed on the FTO catalyst to aromatics <sup>67–70</sup> or to further increase the productivity of short olefins <sup>71,72</sup>. This strongly depends on the type of zeolite added to the FTO catalyst.

In 2016 a bifunctional catalyst consisting of a metal oxide and a zeolite (OX-ZEO) was established to convert synthesis gas to short olefins with high selectivity <sup>73</sup>. Here, modifications to the zeolites <sup>74–76</sup> or metal oxide functions <sup>77</sup> of this catalysts have a strong impact on the performance and the product spectrum. By altering the zeolite of the OX-ZEO catalysts the group of Prof. Bao achieved to convert synthesis gas to aromatics with high selectivity <sup>78–84</sup>. In 2017 and 2018, the OX-ZEO processes have been modified to directly convert CO<sub>2</sub> and hydrogen into olefins and aromatics, respectively <sup>85,86</sup>. Using zeolites with wide pore diameters, the OX-ZEO process even allowed to produce gasoline components directly from synthesis gas <sup>87</sup>.

The aim of this thesis is to examine different approaches to directly convert syngas to chemicals and fuels using bifunctional catalysts consisting of iron-based Fischer-Tropsch catalysts and zeolites. Breakthroughs have been achieved with FTO catalysts in our research group. Building on these insights, we focus on sodium and sulfur promoted and supported FTO catalysts combined with H-ZSM-5 zeolites to convert synthesis gas to olefins and aromatics. Additionally, we conducted research on bulk iron Fischer-Tropsch catalysts in combination with H-ZSM-5 zeolites to produce gasoline fuel from synthesis gas.

In **Chapter 2** we review the recent literature of bifunctional catalyst system to convert synthesis gas to dimethyl ether, short olefins, aromatics, and gasoline. Besides emphasizing the benefits and challenges of the recently developed approaches to convert synthesis gas to chemicals and fuels, we analyzed the performance of the bifunctional catalyst systems and compared it to traditional and mostly monofunctional processes connected in series.

Chapter 3 and Chapter 4 focus on the combination of iron carbide based FTO catalysts, supported on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and promoted with sodium and sulfur with H-ZSM-5 zeolites. In **Chapter 3** we describe that at low reaction pressures the aromatization of olefins formed on the FTO catalyst follows a process that involves dehydrogenation rather than a hydrogen transfer reaction. This allowed to form chemicals (short olefins and aromatics) directly from synthesis gas with high selectivities.

The effect of proximity between FTO catalyst and zeolite on the deactivation behavior was analyzed in **Chapter 4**. Using XPS measurements on fresh and spent catalyst samples we followed the migration of sodium promoters from the FTO catalyst to the zeolite causing both catalysts to rapidly decrease performance, if both catalysts are in close proximity. Using carbon nanotubes as support for the FTO catalyst prevented the migration of sodium promoter even in close proximity.

In **Chapter 5** we prepared colloidal iron oxide nanoparticles with organic ligands which were attached to H-ZSM-5 zeolite crystals. Promoters have been introduced by replacing the organic ligands with Na<sub>2</sub>S. We found that the order of attaching the nano particles to the zeolite and the introduction of promoters is crucial for the performance and stability of this bifunctional catalyst in the direct conversion of synthesis gas to chemicals.

A bulk iron oxide Fischer-Tropsch catalyst in stacked bed configuration with different amount of H-ZSM-5 zeolite downstream was analyzed in **Chapter 6** to follow aromatization, cracking, and isomerization reactions over the course of the zeolite bed. This bifunctional catalyst system allowed to produce gasoline with high octane numbers by forming a high fraction of branched isomers and a reasonable amounts of aromatics.

Finally, the conclusion of this thesis and an outlook to the future in this field of research are given in **Chapter 7**.

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# 2

## Recent advances in bifunctional synthesis gas conversion to chemicals and fuels with a comparison to monofunctional processes

In order to meet the climate goals of the Paris Agreement and limit the potentially catastrophic consequences of climate change, we must move away from the use of fossil feedstocks for the production of chemicals and fuels. The conversion of synthesis gas (a mixture of hydrogen, carbon monoxide and/or carbon dioxide) can contribute to this. Several reactions allow to convert synthesis gas to oxygenates (such as methanol), olefins or waxes. In a consecutive step, these products can be further converted into chemicals, such as dimethyl ether, short olefins, or aromatics. Alternatively, fuels like gasoline, diesel, or kerosene can be produced. These two different steps can be combined using bifunctional catalysis for direct conversion of synthesis gas to chemicals and fuels. The synergistic effects of combining two different catalysts are discussed in terms of activity and selectivity and compared to processes based on consecutive reaction with single conversion steps. We found that bifunctional catalysis can be a strong tool for the highly selective production of dimethyl ether and gasoline with high octane numbers. In terms of selectivity bifunctional catalysis for short olefins or aromatics struggles to compete with processes consisting of single catalytic conversion steps.

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#### 2.1. Introduction

Increasing worldwide demand for chemicals and transportation fuels, combined with the urgent need to move to more sustainable production processes, has spurred research towards alternatives to the traditional crude oil-based processes. Implementation is driven by geopolitical, economic, and environmental considerations. Processes such as gas-to-liquids (GTL) and coal-to-liquids (CTL) have been developed as a result of these considerations in the course of the 20<sup>th</sup> century with more recent stimuli being i.e., the shale gas revolution in the USA, and the demand for transportation fuels and chemicals in China <sup>1–3</sup>. GTL and CTL plants produce ultra-clean fuels and the possibility to shift to more sustainable feedstocks such as biomass or  $CO_2$  combined with renewable hydrogen <sup>4–6</sup>.

Another advantage is the variety of products that can be selectively obtained from synthesis gas (Figure 2-1), potentially playing a pivotal role in future chemical and energy industries. Synthesis gas can be directly or indirectly transformed to alcohols, long-chain hydrocarbons, olefins and aromatics, which constitute a sizable portion of industrial bulk chemicals and precursors for ultra-clean synthetic fuels <sup>7–9</sup>. Currently, these transformations are performed in industry by thermally catalyzed processes (although other approaches such as electrochemical or plasma driven processes are being examined <sup>10,11</sup>) and largely rely on solid catalysts<sup>7,12</sup>. A catalyst, typically a late-transition metal or metal carbide, that can hydrogenate molecules (a "hydrogenation function") can help to selectively produce chemicals such as alcohols, olefins or paraffins. Addition of a second catalyst can be employed to couple reactions and expand the diversity of products to ethers, aromatics or branched hydrocarbons <sup>9,13</sup>. Synergy between the functionalities in a catalyst mixture is particular important for the desired performance, and is feasible by selecting the appropriate chemical properties and an optimal degree of intimacy <sup>14–17</sup>. However, achieving the ideal composition while avoiding negative interference remains a challenge in these multifunctional catalytic systems.



Figure 2-1: Schematic overview of pathways to convert synthesis gas (center) to dimethyl ether (DME), olefins, aromatics, or gasoline via oxygenate or Fischer-Tropsch intermediates.

In this review, we highlight the developments over the past ten years in bifunctional catalysis systems for the transformation of synthesis gas. In particular, we compare in detail

bifunctional catalysis approaches to processes comprising two or more reactors with individual conversion steps. We start with general considerations from an academic and fundamental point of view, followed by a discussion of the relevance of bifunctionallycatalyzed processes of the most important industrial fuels and chemicals. Dimethyl ether (DME), light olefins, aromatics, and liquid fuels (gasoline, kerosene, and diesel) were selected based on their high demand and maturity of their production process. For each of these product classes background information is given, followed by discussing the recent developments concerning the catalysts for their direct production from synthesis gas and the associated challenges. The advantages and drawbacks are highlighted, considering activity, selectivity, and stability, but also taking the resulting product quality into consideration. An overview and critical analysis of yield and conversion of the latest reported data is discussed in each section, contributing to a more quantitative comparison. Finally, we summarize the key points and give a perspective for the utilization of bifunctional systems.

#### 2.1.1. Bifunctional catalysis

The process conditions and type of catalyst determine the products derived from synthesis gas. The initial products obtained after direct carbon monoxide hydrogenation (referred here as Primary conversion processes, section 2.1.4) vary according to the degree of hydrogen addition and carbon-carbon coupling. A strong hydrogenation catalyst such as nickel can vield methane, the smallest of hydrocarbons. This is interesting for the hydrogenation of captured carbon dioxide with hydrogen which is produced by electrolysis using renewable power to provide sustainable fuels <sup>18–21</sup>. A hydrogenation catalyst like iron or cobalt that removes the oxygen to form water and enables carbon-carbon coupling, leads to the formation of long-chain hydrocarbons. These hydrocarbons can be further processed to fuel-range compounds such as gasoline, kerosene, or diesel (Fischer-Tropsch route Figure 2-1), or to olefins. If the carbon-oxygen bond is maintained, for instance using a copperbased catalyst, this leads to methanol, or with polymerization to long-chain oxygenates (Oxygenates route Figure 2-1). Addition of a second functionality (typically an acid site) during reaction can further transform these initial products or intermediates. These subsequent reactions (referred here as "Secondary conversion processes", section 2.1.5) can lead to ethers, olefines, carboxylic acids, aromatics, or branched hydrocarbons. A single catalyst combining these functionalities is referred to as a bifunctional catalyst.

Applying a bifunctional catalyst or two different catalysts in a single reactor might reduce investment costs, energy requirements and complexity in comparison to two sequential reactors with individual monofunctional catalysts <sup>22</sup>. Additionally, the combination of primary and secondary conversion catalysts can boost the overall synthesis gas conversion if the primary products are removed from this equilibrium effectively by the secondary conversion step. The combination of two catalytic functions in a single reactor can, however, also pose challenges. Undesired side reactions might emerge, for instance, the

target products can further react on the primary catalytic function, or the feed might directly react on the secondary catalytic function. Examples of these side reactions are discussed in section 2.1.6, side reactions. The two catalytic functions can also negatively influence each other by electronic effects or migration of mobile species from one to the other. Another challenge is to find common reaction conditions in terms of reaction temperature, pressure, reaction atmosphere or space velocity for the two different catalysts. These challenges will be discussed more in detail throughout sections 2.2 to 2.5.

#### 2.1.2. Relevant products

One of the potential products of bifunctional synthesis gas conversion is dimethyl ether (DME), which has a total annual production capacity of 10 million tons per year and a wide variety of applications (Figure 2-2)  $^{23,24}$ . More recently, DME is increasingly used to substitute liquefied petroleum gas, or as blend in a fuel mixture. The attractiveness of DME for use as a fuel lies in its excellent ignition and combustion properties (cetane number = 55-60), and ease of storage and handling as a liquid under a pressure of only 5-6 bar. Another advantage is that no soot is formed upon combustion. Major efforts are underway mostly in Asia and North America to further develop the infrastructure and broad introduction of DME as a clean transportation fuel  $^{25}$ .

Light olefins, namely ethylene, propylene, and butylenes, are fundamental building blocks for the chemical industry <sup>22</sup>. More than 50% of ethylene and 60% of propylene produced worldwide is used for fabrication of polyolefins (Figure 2-2). Butadiene and 1-butene are used in the production of polymers and rubbers and as precursor of various chemicals <sup>26</sup>. Light olefins are currently made from fossil resources, have a high energy demand and associated emission of pollutants <sup>27,28</sup>. Several renewable alternatives to produce light olefines have been proposed<sup>22,28</sup>. Also, the increase in C<sub>1</sub> and C<sub>2</sub> feedstocks derived from shale gas has promoted alternative pathways for olefins production <sup>29</sup>.

Aromatics like benzene, toluene, xylenes, and ethylbenzene are important precursors for intermediates and polymers (Figure 2-2) <sup>26,30,31</sup>. The good anti-knocking properties of some aromatic compounds also makes them a good octane-enhancer for gasoline <sup>32</sup>. The use as anti-knocking agent depends on availability and price, for instance toluene is blended in regularly, while this is less often the case for xylene, as the latter has a higher value for other chemical applications <sup>26,33</sup>.

Recent advances in bifunctional synthesis gas conversion to chemicals and fuels with a comparison to monofunctional processes



**Figure 2-2:** Overview of possible production pathways involving synthesis gas production, primary and secondary synthesis gas conversion processes. This scheme consists of synthesis gas conversion and the production of synthesis gas (light blue), the primary hydrocarbon products (methane, naphtha, wax, and diesel; given in green), oxygenates (red), short olefins as primary and secondary products (pink), other hydrocarbon secondary products (dark blue), examples of final product groups (grey), and final chemicals (purple).

Liquid transportation fuels (diesel, kerosine and gasoline) have a total annual consumption of ~2.8 billion tons (in 2019) <sup>34</sup>. Diesel mainly consists of linear paraffins in the range of  $C_{10}$ - $C_{22}$  and a cetane number of 48-55 (the cetane number is an indicator for the willingness of diesel fuel to self-ignite) <sup>35–38</sup>. Kerosene consists of  $C_8$ - $C_{16}$  paraffins with a higher content of iso-paraffins than diesel, which decreases its freezing point and makes it suitable for application as aviation fuel <sup>39,40</sup>. Gasoline usually comprises hydrocarbons in the range of  $C_5$ - $C_{11}$  <sup>41</sup>. The specifications for gasoline are that it should have a research octane number (RON, classification number for spark-ignition characteristics) between 91 and 102, a maximum olefin content of 10-18 vol-% and maximum aromatics content of 35-40 vol-%, depending on the category of the gasoline fuel <sup>35</sup>. Liquid fuels are in general a blend to meet the needs of the transportation industry while adhering to the requirements of environmental regulations <sup>42–44</sup>. The latter are especially stringent regarding sulfur content, requiring ultralow sulfur concentrations of 10 ppm or less <sup>45</sup>. Fuels derived from synthesis gas, via the Fischer–Tropsch synthesis (FTS) process do not contain significant amounts of sulfur <sup>46</sup>. Large FTS plants with consecutive hydroprocessing have been operated for decades by Shell,

SASOL, Chevron and others, each producing yearly between 500 kt and 7.5 Mt of synthetic hydrocarbons including high quality diesel and kerosene <sup>47–51</sup>.

#### 2.1.3. Production of synthesis gas

Synthesis gas (or in short "syngas") can be produced from virtually any carboncontaining source. The present production of synthesis gas is mainly based on coal <sup>52,53</sup> and natural gas <sup>54,55</sup>. In the past years biomass-derived synthesis gas (bio-syngas) has gained significance <sup>56–59</sup>.

$$2C + \frac{1}{2}O_2 + H_2O \rightarrow 2CO + H_2$$
 Equation 2-1

$$CH_4 + CO_2 \rightarrow 2 CO + 2 H_2$$
 Equation 2-2

$$CH_4 + \frac{1}{2} O_2 \rightarrow CO + 2 H_2$$
 Equation 2-3

$$CH_4 + H_2O \rightarrow CO + 3H_2$$
 Equation 2-4

$$(C_x H_y O_z)_n + H_2 O/O_2 \rightarrow CO + H_2 + CO_2$$
 Equation 2-5  
 $CO + H_2 O \leftrightarrow CO_2 + H_2$  Equation 2-6

An important implication of the source for producing synthesis gas is the resulting  $H_2$  to CO ratio. Typically, coal is converted by gasification as shown in Equation 2-1 resulting in a 1:2 molar ratio <sup>60</sup>. The production of synthesis gas from methane yields an  $H_2$ :CO ratio between 1-3 mol/mol, depending on the process: via dry reforming (Equation 2-2) methane is converted together with carbon dioxide to synthesis gas with  $H_2$ :CO=1 mol/mol <sup>61,62</sup>, whereas via partial oxidation (Equation 2-3) and steam reforming of methane (Equation 2-4) show  $H_2$ :CO ratios of 2 mol/mol and 3 mol/mol, respectively <sup>63–66</sup>. The gasification of biomass using either steam, oxygen, or a combination of both gives a high concentration of CO<sub>2</sub> in the resulting bio-syngas (Equation 2-5). This is related to the relatively high oxygen content in the biomass feedstock <sup>67,68</sup>. The  $H_2$ :CO ratio and presence of CO<sub>2</sub> are relevant for the follow-up processes. If needed the composition of the synthesis gas can be adjusted using the (reverse) water-gas-shift reaction (Equation 2-6).

Sulfur compounds (e.g.,  $H_2S$  or COS) in synthesis gas act as a poison to most synthesis gas conversion catalysts and might result from the feedstock <sup>69,70</sup>. These can be removed using an absorber column with amine scrubbing <sup>71</sup>. In contrast, removal of sulfur from heavier hydrocarbons in conventional refinery processes requires extensive effort. Here, the feedstock needs to be treated in the hydrodesulfurization (HDS) process <sup>72</sup>.

A major challenge with the production of synthesis gas from biomass is the competition with food and the impact on the environment by the use of monocropping and

possible damage to the biodiversity <sup>73</sup>. Furthermore the availability of biomass for large scale synthesis gas production can be a hurdle considering the costs for transportation and the efficiency of land use <sup>74</sup>. A technical challenge in bio-syngas production is catalyst deactivation by the formation of tar during biomass gasification. However, the use of a suitable catalyst in the steam reforming of biomass gives a tool to reduce the formation of tar drastically <sup>68,75</sup>. Further impurities such as hydrochloric acid can be removed with amine scrubbing and an additional chloride guard bed <sup>71,76</sup>

# 2.1.4. Primary conversion processes 2.1.4.1. Methanol synthesis

Methanol is routinely produced with high selectivity from synthesis gas. The process to convert synthesis gas to methanol is typically operated at 30 - 50 bar and 220 - 300 °C. The methanol selectivity is larger than 99% <sup>77–79</sup>. Methanol can be synthetized by hydrogenation of CO or CO<sub>2</sub> (Equation 2-7 and 8) <sup>80–83</sup>. Typically, a CO<sub>2</sub>-enriched (1% - 4% CO<sub>2</sub> in the synthesis gas) synthesis gas is used <sup>84,85</sup>.

$CO + 2H_2 \leftrightarrow CH_3OH$	Equation 2-7
$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$	Equation 2-8

The main catalyst used in industry is copper based, with a typical composition of ~50–60 wt.% Cu, ~30 wt.% ZnO, and 10 wt.% Al<sub>2</sub>O<sub>3</sub> <sup>77,86</sup>. Copper in itself can catalyze the synthesis of methanol, but promotion with ZnO boosts its activity by more than an order of magnitude <sup>87–89</sup>. It is well established that in CO<sub>2</sub> enriched synthesis gas, CO<sub>2</sub> is the predominant source of methanol formation. CO<sub>2</sub> is formed during the reaction by the water gas shift reaction (Equation 2-6) from CO and H<sub>2</sub>O, keeping the water level low. <sup>84</sup> However, understanding of the nature of the synergetic interaction between Cu and ZnO remain the focus of a strong debate. <sup>90</sup> Currently two main theories are prevalent: the first proposes that the active sites emerge from structural and/or electronic interactions at the Cu-ZnO interface <sup>91–95</sup> and the second theory attributes the active sites to the presence of metallic Zn forming a Zn-Cu alloy or decorating the Cu surface <sup>96–102</sup>.

Copper-based methanol synthesis catalysts are employed by the industry due to their high activity at milder reaction conditions <sup>103</sup>. Recently, research has focused on finding a methanol synthesis catalyst for using CO<sub>2</sub> as main carbon source <sup>104</sup>. Compared to the traditional feed three challenges must be met: decreased catalyst stability due to the high-water concentrations, a less favorable equilibrium and hence driving force for the reaction, and the side reaction forming CO via the reverse water gas shift reaction. A wide variety of materials has been proposed as candidates: intermetallic compounds such as Ni-Ga <sup>105</sup> or In-

Pd <sup>106</sup>, supported metal oxide nanoparticles  $MnO_x/Co_3O_4$  <sup>107</sup> or  $In_2O_3/ZrO_2$  <sup>108</sup>, solid solutions of metal oxides ZnO- $ZrO_2$  <sup>109</sup> and transition-metal phosphide catalysts such as MoP <sup>110</sup>.

Methanol can be used as the starting point to produce DME (see Chapter 2) or hydrocarbons in processes generally known as Methanol-to-Hydrocarbons (MTH), Methanol-to-Olefins (MTO), Methanol-to-Gasoline (MTG) and Methanol-to-Aromatics (MTA)<sup>24,25</sup>.

#### 2.1.4.2. Fischer-Tropsch synthesis

Fischer-Tropsch synthesis (FTS) allows to convert synthesis gas into a mixture of hydrocarbons such as short olefins or paraffinic waxes. The mechanism involves a reaction of CH<sub>x</sub> species on the catalyst's surface, a competition between C-C coupling and hydrogenation (chain growth and chain termination, respectively). The ratio of the rates of these processes is described as the chain growth probability ( $\alpha$ ) of the Anderson-Schulz-Flory (ASF) distribution <sup>111</sup>. The ASF model allows to predict the distribution of products from the chain growth probability. A low value of  $\alpha$  means the formation of mainly light products, whereas liquid or wax products are predominantly formed at medium and high values of  $\alpha$ , respectively. The FTS always leads to a mixture of hydrocarbons with different chain lengths, with limits selectivity to certain product fractions <sup>112</sup>.

High temperature Fischer-Tropsch synthesis (HT-FTS) operates at 300-350°C and about 20 bar utilizing an iron-based catalyst to produce hydrocarbons in the gasoline range (C<sub>5</sub>-C<sub>11</sub>) and light (C<sub>2</sub>-C<sub>4</sub>) olefins (Equation 2-9) <sup>49</sup>. The active phase of catalyst is iron carbide <sup>113–117</sup>. In industry, iron-based catalysts are often promoted with alkaline metals, such as potassium or sodium to increase activity, and selectivity to olefins <sup>118</sup>. Additionally, copper is employed as promoter to increase the reducibility and SiO<sub>2</sub> can be used as structural promoter <sup>49</sup>. HT-FTS catalysts are also active in the water-gas-shift (WGS) reaction, converting CO and H<sub>2</sub>O into H<sub>2</sub> and CO<sub>2</sub> (Equation 2-6) <sup>22</sup>. Promotion with sodium and sulfur allows decreasing the methane selectivity and increasing the C<sub>2</sub>-C<sub>4</sub> olefin-paraffin ratio with respect to the ASF distribution <sup>114,119–122</sup>. This enables 72% C<sub>2</sub>-C<sub>4</sub> olefins formation, whereas according to the ASF 57% C<sub>2</sub>-C<sub>4</sub> (olefins + paraffins) at maximum would be formed <sup>121</sup>.

$$n CO + 2n H_2 \rightarrow C_n H_{2n} + n H_2 O$$
 Equation 2-9  
 $n CO + (2n+2) H_2 \rightarrow C_n H_{2n+2} + n H_2 O$  Equation 2-10

Low Temperature Fischer Tropsch Synthesis (LT-FTS, Equation 2-10) operates at 200-240°C and 25-45 bar to produce waxes, and uses either supported iron- or cobalt-based, or precipitated bulk iron catalysts <sup>49</sup>. Cobalt-based catalysts are often supported on metal oxide supports such as Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> or TiO<sub>2</sub> with weight loadings of 20-30 wt-% cobalt <sup>49,123–125</sup>. A cobalt particle size of around 6 nm is optimum for both high activity and low methane

selectivity <sup>126</sup>. For cobalt particles smaller than 6 nm the surface coverage of  $CH_x$ ,  $OH_x$  and CO intermediates decreases, while the coverage with H increases, leading to a high methane selectivity and lowered CO conversion rates. Noble metal promoters such as Pt, Re or Ru are added to increase the reducibility of the cobalt oxide precursor catalyst. LT-FTS catalysts preferentially form long-chain hydrocarbons (>95% C<sub>5+</sub> in the hydrocarbons and <3% CO<sub>2</sub> due to their limited WGS activity) <sup>125</sup>.

Ruthenium based FTS-catalysts can be operated at 140-220°C and 15-100 bar <sup>127–129</sup>. However, ruthenium is orders of magnitude more expensive than cobalt and less available. <sup>118,130,131</sup>. Nickel FTS-catalysts can display similar selectivity and activity as cobalt under similar reaction conditions <sup>132,133</sup>. However, under high carbon monoxide partial pressure volatile nickel carbonyls are formed, leading to metal particle growth and/or nickel entrainment whereby the activity of the catalyst decreases over time <sup>118</sup>. Bimetallic nickel-cobalt catalysts might be promising as they show increased activity and selectivity to C<sub>5+</sub> hydrocarbons and better stability when supported on reducible oxide support materials <sup>132</sup>.

#### 2.1.5. Secondary conversion processes 2.1.5.1. Methanol dehydration to DME, olefins, and aromatics

The conversion of methanol to other oxygenates or hydrocarbons is often associated with dehydration of methanol and the elimination of water. Dimethyl ether is mainly produced from partial dehydration of methanol (Equation 2-11), which is typically achieved at relatively low temperatures using mildly acidic sites. More details are given in Chapter 2.2.

$$2 CH_3OH \leftrightarrow CH_3OCH_3 + H_2O$$
 Equation 2-11

Additionally, methanol can be converted into hydrocarbons such as short olefins or aromatics over the acid sites of a zeolite or other strong solid acids at higher temperatures (Equation 2-12 and Equation 2-13).

$$n CH_3 OH \rightarrow (CH_2)_n + n H_2 O$$
Equation 2-12
$$n CH_3 OH \rightarrow \frac{n}{6+s} C_6 H_6 (CH_2)_s + n H_2 O + \frac{3n}{6+s} "H_2"$$
Equation 2-13

The term " $H_2$ " in Equation 2-13 describes the formation of either molecular hydrogen or the hydrogenation of an olefin molecule to the corresponding paraffin.

The conversion of methanol to olefins (MTO) and methanol to aromatics (MTA) is believed to follow the dual cycle mechanism (Figure 2-3)  $^{134-137}$ . In the alkene cycle, short olefins are alkylated by the addition of a CH<sub>2</sub> group that is transferred from methanol, forming longer chain olefins and water. The products in the alkene cycle are higher olefins

that either dealkylate forming short olefins or undergo aromatization and enter the aromatic cycle. In the aromatic cycle, light aromatics are alkylated by  $CH_2$  groups from methanol to form poly-alkylated aromatic species and water. These poly-alkylated aromatic species are protonated by the Brønsted acid sites of the catalyst, followed by dealkylation and consecutive deprotonation. During the dealkylation, short olefins are released which can either enter back into the alkene cycle or yield the final products.



Figure 2-3: Illustration of the dual cycle mechanism consisting of the aromatic and alkene cycle <sup>134</sup>.

Zeolites with 8-membered ring pores such as SAPO-34 or H-SSZ-13 show high selectivities to short olefins (70% to 96%) at full methanol conversion <sup>138,139</sup>, when operated at high temperature (300-450°C) and atmospheric pressure <sup>140,141</sup>. The zeolites used in the MTA reaction usually are 10-membered ring zeolites such as H-ZSM-5 and TNU-9 or 12membered ring zeolite such as zeolite type beta or mordenite <sup>142–144</sup> The MTA reaction yields a variety of products, ranging from 2-40% C<sub>2</sub>-C<sub>4</sub> olefins, 8-51% aliphatic hydrocarbons with more five carbon atoms (C<sub>5+</sub>) to 17-50% aromatics <sup>144,145</sup>. The strongly different product spectra of the MTO and the MTA process can be explained by the pore dimensions and topology of the zeolites <sup>146–148</sup>. The aromatic species formed during the MTO reaction are retained in the small zeolite cavities and participate in alkylation and de-alkylation in the aromatic cycle. The pores of 10- and 12-membered ring zeolites used in the MTA process are wide enough to release the aromatic molecules.

During the MTO and MTA process the zeolite is rapidly deactivated mostly by formation of coke, blocking the active sites. Catalyst lifetimes vary from 20-200 h on stream, depending on material composition, crystallite size, acid site density, porosity and reaction conditions <sup>138,141,145,149–153</sup>. Co-feeding water increases the lifetime of the catalyst, but reduces its activity due to co-adsorption on the acid sites <sup>154</sup>. Also, here promoters can play a role. Partially replacing the protons of the Brønsted acid sites with zinc-ions in H-ZSM-5, led to increased selectivity towards aromatics and reduced paraffin selectivity in the MTA process <sup>155–157</sup>.

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#### 2.1.5.2. Cracking and isomerization

Cracking is the fragmentation of long hydrocarbons into smaller molecules, whereas isomerization involves the skeletal rearrangement of hydrocarbon molecules. These reactions are often applied in the petrochemical industry to match the requirements for transportation fuels. Gasoline and diesel fuels are being used to drive spark- and self-ignition engines, respectively. By increasing branching and decreasing chain length the octane number of gasoline increases, whereas the cetane number of diesel increases with chain length and reduced number of branches <sup>158,159</sup>. The most common catalysts for cracking and isomerization are zeolites and catalysts that next to the zeolite contain a metal or metal sulfide.

The mechanism of mono-functional acid catalyzed cracking and isomerization over zeolites involves carbocations at elevated temperatures (Figure 2-4) <sup>160,161</sup>. A primary carbocation (positive charge on a carbon atom at the end of the chain) is relatively unstable and undergoes carbocation isomerization, resulting in a more stable secondary carbocation (positive charge being stabilized by two alkyl groups). Tertiary carbocations show even higher stability and are formed from skeletal rearrangement of secondary carbocations. These carbocations can be cracked at the  $\beta$ -position (one carbon atom further than positive charge, called  $\beta$ -scission) forming olefins and another carbocation. Acid cracking and isomerization yields few n-paraffins (alkanes) and gases, whereas high yields of aromatics, olefins and *i*-paraffins are produced <sup>162</sup>. The majority of the hydrocarbon products is isomerized due to the high stability of the tertiary carbocation intermediate <sup>163</sup>.



Figure 2-4: Catalytic cracking and isomerization with the formation of carbocations, isomerization and consecutive cracking with different positions of the positive charge <sup>160,161</sup>.

Alternatively, bifunctional catalysts can be used for cracking and isomerization at lower temperatures. The feed molecules are dehydrogenated on the metal sites forming olefins and hydrogen. The olefin molecules undergo carbocation formation, carbocation and skeletal isomerization, and  $\beta$ -scission to some extent similar to the mechanism of acid cracking and isomerization on the acid sites of the zeolite. The resulting olefins, however, are hydrogenated on the metal sites, forming paraffins <sup>161</sup>. This means that transport of molecules between the two different sites is very important.

Bifunctional cracking and isomerization are performed in the presence of hydrogen and at pressures between 5-150 bar <sup>14,164,165</sup>, in the so-called hydrocracking or hydroisomerization process. The product spectrum strongly depends on the reaction temperature. High reaction temperatures (between 300°C and 400°C) favor hydrocracking <sup>165–168</sup>, whereas hydroisomerization is more likely at lower temperatures (between 200°C and 260°C) <sup>14,164,169–171</sup>. The distance between the metal and acid site is crucial to achieve high yields of branched isomers in the hydroisomerization reaction. Relatively large distances, in the range of micrometers, can cause strong concentration gradients of intermediates and reactants within the catalyst <sup>172–174</sup>. Closest proximity, however, can lead to an increased degree of cracking forming more gaseous products <sup>14</sup>.

#### 2.1.6. Side reactions 2.1.6.1. Water-gas-shift reaction

The reaction of carbon monoxide and water to form carbon dioxide and hydrogen (Equation 2-6), known as the water-gas-shift (WGS) reaction, is used traditionally in industry on a scale of ~50 million tons per year <sup>175</sup>. Steam reforming of natural gas yields a mixture primarily consisting of hydrogen and carbon monoxide. This carbon monoxide is further converted using WGS to produce additional hydrogen and carbon dioxide <sup>176</sup>. The WGS reaction is also relevant to adjusting the H<sub>2</sub>/CO ratio of synthesis gas. The WGS reaction is readily catalyzed by metals and metal oxides. Catalysts based on iron oxides (previously also chromium-based catalysts) are employed at intermediate temperatures (400-500°C) and copper-based catalysts at lower temperatures (150-200°C) <sup>177,178</sup>. This reaction is moderately exothermic, favored thermodynamically at lower temperatures and kinetically at elevated temperatures <sup>179</sup>.

However, the WGS reaction is usually undesired when converting CO-based synthesis gas. Although the feed in this case does not contain water, product formation is often accompanied by water formation, especially in FT. The presence of both water and carbon monoxide can lead to the production of important concentrations of CO<sub>2</sub>, for instance in HT-FTS <sup>180</sup>. This has a negative effect on the efficiency of the process, and hence a common challenge in these processes is to limit the WGS activity of the catalyst.

#### 2.1.6.2. Olefin secondary hydrogenation

Hydrogenation of desired products or reaction intermediates (denoted as secondary hydrogenation), most notably of olefins, can decrease the final yield of the desired product. For instance, when a cobalt catalyst is used in FTS, 1-olefins can re-adsorb on the metal

catalyst surface and either participate in further chain growth or undergo secondary hydrogenation forming paraffins <sup>181</sup> <sup>182–186</sup>. The presence of alkaline promoters on iron-based FT catalysts can reduce secondary hydrogenation activity <sup>187–189</sup>. They increase the conversion of metallic iron into iron carbide <sup>113</sup>, from which it was concluded that secondary hydrogenation is predominantly catalyzed by metallic iron sites <sup>190,191</sup>.

OX-ZEO catalysts consist of metal oxides combined with zeolites and can convert synthesis gas to olefins and aromatics <sup>192</sup>. In the first step synthesis gas is converted into reactive intermediates such as methanol, dimethyl ether, or ketene over the metal oxide, followed by the formation of olefins on the zeolites. Olefins also act as intermediates in the OX-ZEO to aromatics process <sup>193,194</sup>. Metal oxide functions with a high hydrogenation activity can cause secondary hydrogenation of olefins to paraffins <sup>195</sup>. The hydrogenation of aromatics requires the presence noble metals such as platinum or palladium <sup>196,197</sup> and does not take place in the OX-ZEO process with the commonly used catalysts <sup>198</sup>. A detailed analysis of secondary hydrogenation can be found in chapter 2.3.3 and 2.4.3.

#### 2.1.6.3. Coke formation

The formation of coke is a major cause for catalyst deactivation in synthesis gas and hydrocarbon conversion reactions <sup>121,199</sup>. Either carbon or polyaromatic hydrocarbons can be formed. On metallic catalysts carbon may be formed by the disproportionation of carbon monoxide into carbon dioxide and solid carbon (Boudouard reaction, Equation 2-14) and the extent to which this may occur depends on the reaction temperature and pressure (Figure 2-5, calculated with Outotec HSC 9.6.1).



$$2 CO(g) \rightleftharpoons CO_2(g) + C(s)$$
 Equation 2-14

**Figure 2-5:** Fraction of  $CO_2 + C$  at equilibrium as a function of temperature with CO, C and  $CO_2$  at either 1 bar, 20 bar or 100 bar pressure.

Iron-based Fischer-Tropsch catalysts transform into iron-carbide species under operation conditions <sup>22,113</sup>. The formation of the active iron-carbide phase is often accompanied by the Boudouard reaction leading to carbon deposition on the active site. The presence of alkaline promoters such as K or Na increases the rate of carbon deposition, whereas the type of iron carbide does not influence the carbon deposition <sup>200</sup>. Additionally, carbon deposition in the pores of an unsupported iron-based Fischer-Tropsch catalyst or the transformation into iron-carbide can lead to fragmentation of the catalyst particles, due to strain effects <sup>22,201,202</sup>.

Alternatively, heavy hydrocarbons formed by oligomerization in acid catalyzed cracking and isomerization can condense onto and hence deactivate active sites at temperatures below 200°C <sup>203</sup>. At high temperatures (350°C and above) hydride transfer reactions take place causing the formation of polyaromatic hydrocarbons <sup>203,204</sup>. The temperature for the formation of polyaromatic hydrocarbon species is reduced for hydrocracking and hydroisomerization, because (de)hydrogenation is catalyzed by metal sites <sup>203</sup>.

The mechanism of the MTO and MTA reactions is based on the alkylation and dealkylation of light aromatic species inside zeolite crystals. The main cause for catalyst deactivation is the formation of large and heavy poly-aromatic hydrocarbons inside the zeolite pores or cavities, limiting accessibility to the acid sites of the zeolites <sup>205,206</sup>. Using an H-SSZ-13 zeolite in the MTO process, it was shown that also at lower reaction temperatures pore filling of the zeolites with methylated bicyclic aromatics plays a role, whereas at higher temperatures the deactivation is caused by the formation of 3- and 4-cyclic aromatic species <sup>207</sup>.

In the following sections we analyze the recent literature of bifunctional catalysis for the conversion of synthesis gas to DME, short olefins, aromatics, and gasoline. Additionally, we compare the performance of these catalysts with established processes consisting of sequential individual catalytic steps in terms of overall selectivity and conversion.

#### 2.2. DME

Methanol dehydration to DME is usually performed at atmospheric pressure, high space velocities and temperatures between 190°C and 400°C <sup>208–210</sup>. The catalysts most widely used are solid oxide acids such as  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> or aluminosilicates, or zeolites <sup>208,211</sup>. The active sites can be both Lewis and Brønsted acid sites <sup>212</sup>. Processes using  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts proceed at the higher end of the mentioned temperature range <sup>209,213</sup>.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> has mainly Lewis acid sites, which might adsorb the formed water particularly at low temperatures, inhibiting the reaction with methanol <sup>209</sup>. Increased reaction temperatures facilitate the

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desorption of water from the acid sites of the Al<sub>2</sub>O<sub>3</sub> catalysts, but also decrease the maximum attainable one-pass DME yield due to equilibrium limitations (Figure 2-6).



**Figure 2-6:** Equilibrium composition of methanol dehydration to DME and water as function of reaction temperature calculated at 1 bar pressure (calculated with Outotec HSC 9.6.1).

Although for methanol dehydration most commonly  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is used, other acidic compounds can also be used as catalyst. <sup>214</sup> Mixed metal oxides such as aluminosilicates and ZrO<sub>2</sub>/TiO<sub>2</sub> have Brønsted acid sites next to Lewis acid sites, and display enhanced activity and stability compared to Al<sub>2</sub>O<sub>3</sub> under the same reaction conditions <sup>208,209</sup>. Zeolites have both Lewis and Brønsted acid sites and allow lower operation temperatures. Additionally, the strong Brønsted acid sites might allow sequential olefin formation at higher temperatures <sup>214</sup>.

#### 2.2.1. Recent developments

Direct DME synthesis has attracted large interest, which is reflected by the extensive investments in direct DME synthesis pilot plants <sup>215–217</sup> and several academic reviews on DME synthesis published in the recent years <sup>211,218–223</sup>. Based on these reviews and several other publications, we give an overview of the optimal reaction conditions as well as catalysts.

Colloidal synthesis of nanoparticles has emerged as a tool to prepare and understand catalytic model systems <sup>224</sup>. Pre-forming the nanoparticles in solution and then depositing them onto a support material enables the preparation of monodisperse, single crystalline, and size-controlled nanoparticles, which is rather challenging for conventional synthesis techniques <sup>225</sup>. For bifunctional catalysts, colloidal nanoparticles have been employed as a strategy to avoid structure sensitivity effects of the metal-based methanol synthesis catalysts and control its proximity to the acid sites <sup>226</sup>. Monodisperse colloidal Cu-ZnO-based nanoparticles were either directly supported on the dehydration catalyst ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) or mixed

with the dehydration catalyst <sup>227</sup>. Directly supporting the nanoparticles on the solid acid caused partial blockage of the acid sites and a slight decrease in DME selectivity (64% to 59% DME selectivity).

The same approach has been used to study Pd-Ga-based colloidal nanoparticles, as methanol synthesis catalyst from CO and H<sub>2</sub>, supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub><sup>228</sup>. The interest in Pd-Ga systems arises from its activity in CO<sub>2</sub> hydrogenation to methanol <sup>229,230</sup>. The Pd-Ga/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> system showed good stability. However, hydrocarbon selectivity remained an issue over the whole temperature range. Methane content increased from 12% at 250°C to 43% at 300°C, while Cu-ZnO-based catalyst produced only 1.2% at 250°C and 8.8% at 300°C. High methane yields has been reported to be a general problem of Pd-based DME catalysts <sup>231</sup>.

The use of core-shell systems is a popular strategy to circumvent Cu sintering. Typically, the metal-based core is encapsulated by a solid acid shell <sup>232</sup>. This forces also the methanol formed on the core catalyst to pass through the acidic material before leaving the catalyst system, leading to a high DME selectivity <sup>233</sup>. The catalytic performance (275 °C, 35 bar, H2:COx = 3 mol/mol and TOS = 24 h) of CuO-ZnO-ZrO2 and SAPO-11 was studied for a physical mixture of the two components, and for a core-shell catalyst with the Cu-based catalyst being covered by SAPO-11<sup>234</sup>. The highest DME yields were obtained at a CuO-ZnO-ZrO2 to SAPO-11 weight ratio of 0.5. The core-shell catalyst showed a more stable catalytic performance than the physical mixture, having a relative decrease in DME yield at the end of the experiment (24 h time on stream) of 22% against 33% for the physical mixture. By comparing the acidity of the catalysts before and after reaction, it was observed that the core-shell catalysts lost around 10% of the initial acid sites after 24 h on stream, while the physical mixture lost around 26%. The loss of acid sites was identified as coke deposition, being lower for the core-shell catalyst. Physical separation of the metallic and acid functions by an intermediate silica layer contributes to reducing coke deposition on the SAPO-11, and therefore to preserve its acidity.

The strategy of a porous intermediate layer in a core-shell catalysts has been previously explored<sup>235,236</sup>; a silica layer was deposited over the Cu-based catalyst to avoid damaging the integrity of the catalyst while depositing the solid acid overlayer. Alternatively, a mesoporous alumina interlayer has been also employed, on which silicotungstic acid is deposited to improve the shell's acidity and the catalysts DME selectivity <sup>237</sup>.

However, the use of a protective silica layer can cover part of the active sites of the methanol synthesis catalyst <sup>233,238</sup>, resulting in lower CO conversion. To avoid this, a different coating method was reported in which various solvents (ethanol, water, methanol, and ethylene glycol) were used as binder to coat an H-ZSM-5 shell on a Cu-ZnO-based catalyst <sup>239</sup>. Ethanol as a solvent showed the best performance, although this could not be explained by more exposed metal sites based on the characterization results.

The use of ultra-small (< 5 nm) ZSM-5 zeolite crystals placed on a CuO-ZnO-Al<sub>2</sub>O<sub>3</sub> methanol synthesis catalyst showed better activity, selectivity to DME, and stability than the methanol synthesis catalyst combined with amorphous aluminosilicate or ZSM-5 zeolites

with 20-500 nm crystallite size <sup>240</sup>. It was concluded that the ultra-small ZSM-5 nano particles had superior diffusion properties compared to larger crystals. Additionally, the medium strength of the Brønsted acid sites resulting from the small crystallite size did not facilitate further dehydration of DME to olefins.

Electrospinning has been employed for the synthesis of various fibrous highperformance materials <sup>241,242</sup>, in this case for the design of a bifunctional catalysts. A fibrillar system has been reported which circumvents diffusion limitations while maintaining a close contact within functionalities <sup>243</sup>. The Cu-ZnO/ZrO<sub>2</sub>-ZSM-5 fibrillar bifunctional catalyst was prepared by using an electrospinning technique. The polymeric filaments after calcination, resulted in this case in homogeneous zirconia-based fibers (with a diameter of 1.5 µm) and well-distributed Cu-ZnO and zeolite aggregates throughout the fibers of the bifunctional catalyst. The catalyst showed high DME yields (59 - 63%), with a low zeolite content of 10 wt-%. This could be attributed to the high dispersion of the zeolite over the fibers, and the fact that the methanol synthesis function was not affected by the addition of the zeolite during synthesis. The pressure drop inside the fixed-bed reactor was theoretically calculated for the fibrillar structured catalyst with micrometric size and for the powder catalyst with the same effective dimension. The calculation results showed 5000 times less pressure-drop for the fibrillar packed bed than for a packed bed of spherical particles (0.3 vs. 1650 bar·m<sup>-1</sup>). Longer tests than the reported 4 hours on stream might give more insight into the stability of this material.

In-situ removal of water during DME synthesis, often referred as sorption enhanced dimethyl ether synthesis, has emerged as a relatively new approach to avoid the detrimental effects of water on the catalyst and boost the DME selectivity by inhibiting the water-gasshift reaction. This idea is promising for process intensification and can be applied to different reactions in which water is a by-product as recently reviewed  $^{244,245}$ . Water can be removed from the catalyst bed using membrane technology or selective adsorption  $^{246}$ . The former requires large H<sub>2</sub>O partial pressures differences and high permselectivity of water over the reactants, the latter is preferred at low H<sub>2</sub>O partial pressures (< 1 bar). Theoretical simulations have confirmed higher DME yields under H<sub>2</sub>O removal conditions, particularly upon addition of CO<sub>2</sub> due to an increased methanol production and preventing the water-gasshift reaction<sup>247</sup>.

Experimentally, enhanced DME production has been reported for a commercial copper-based catalyst mixed with a water absorbent material (commercial zeolite LTA-type with 3Å pore size) <sup>245,248</sup>. Adsorption of water by the zeolite during DME synthesis led to a decrease in CO<sub>2</sub> formation. The DME yield was 65% at around 70% CO conversion (275°C, 25 bar and H<sub>2</sub>:CO = 2 v/v). Upon saturation of the zeolite after some minutes of the reaction, a regeneration step was carried out by switching to nitrogen, depressurizing to 1.7 bar and heating to 400°C. More recently, the same concept has been studied using a Cu-ZnO-based catalyst in combination with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as solid acid and a zeolite 3A as water sorbent <sup>249</sup>. The methanol catalyst alone showed a carbon conversion of 9.7% and 100% selectivity to

methanol at 270°C and 25 bar with a syngas composition of  $\text{CO}:\text{CO}_2:\text{H}_2 = 1:1.9:7.7}$  (v/v/v). When the methanol synthesis catalyst was combined with the methanol dehydration catalyst and the water sorbent zeolite at 275°C, the carbon conversion increased to 83% (54% CO conversion and 97% CO<sub>2</sub> conversion) with a DME selectivity of 99% in the early stage of the reaction (~20 min). After the zeolite was saturated (after ~100 min.) the carbon conversion dropped to 19% (41% CO conversion and 8% CO<sub>2</sub> conversion) and DME was formed with 81% selectivity.

However, information on the stability of the catalysts in these studies is lacking, especially after regeneration cycles. Identifying sorbent materials that operate under DME synthesis conditions without suffering deactivation remains challenging <sup>250</sup>. Research efforts have been focused on improving the regeneration procedure <sup>251</sup>. It has been shown that a pressure swing (from 25 bar at reaction conditions to 1-3 bar) followed by purging with an inert gas can remove the water of the zeolite 3A and regenerate the activity without changing the temperature of the reactor. This swing process to remove the adsorbed water required 1 h, which is faster than the alternative thermal treatment at 400°C which can require 6 h.

The conversion of CO<sub>2</sub> or CO<sub>2</sub>-containing synthesis gas in the direct DME synthesis has attracted recently attention in research <sup>252–258</sup>. Published data has shown that 48% CO<sub>2</sub> conversion <sup>252,256</sup> and high DME selectivities up to 100% <sup>255,257</sup> can be reached. Additionally, a comparison between CO<sub>2</sub>-rich and CO-rich synthesis gas revealed that a CO:CO<sub>2</sub>-ratio of 1:4 (v/v) in the synthesis gas led to higher conversion (65.6%, sum of CO+CO<sub>2</sub>) compared to a CO:CO<sub>2</sub>-ratio of 4:1 (v/v) (35.4% conversion) The DME selectivity resulting from the CO<sub>2</sub>-rich synthesis gas was slightly lower (73.2% compared to 88.7%), however, the yield of DME was higher (48% compared to 31.4%) <sup>237</sup>. Direct CO<sub>2</sub> hydrogenation to DME also showed advantages in energy efficiency and net CO<sub>2</sub> mitigation in a techno-economic study compared to different routes (indirect route via CO or direct CO<sub>2</sub> hydrogenation) <sup>259</sup>. Compared to methanol synthesis from CO<sub>2</sub>, direct DME synthesis can result in higher CO<sub>2</sub> conversions (+20%) and higher yields of valuable products (+70%) <sup>260</sup>.

#### 2.2.2. Benefits

Figure 2-7 shows the CO conversion and yields of methanol, DME and CO<sub>2</sub> as function of reaction temperature at 40 bar total pressure for methanol synthesis (Figure 2-7-A), direct DME synthesis without WGS (Figure 2-7-B) and direct DME synthesis with WGS (Figure 2-7-C) in equilibrium (calculated with Outotec HSC 9.6.1). For the methanol synthesis the CO conversion is limited to 40% at 260°C and 40 bar. If instead of pure CO (also) CO<sub>2</sub> is added to the synthesis gas feed, the conversions are even lower. The direct DME synthesis with WGS shows a maximum CO conversion of 72%, whereas the direct DME synthesis with WGS shows a maximum CO conversion of 95% at these conditions. Removing methanol by subsequent dehydration hence increases the conversion of synthesis gas, reaching CO conversions as high as 96% and DME selectivities up to 87%  $^{261,262}$ . The additional removal

of water via the WGS reaction drives the equilibrium to even higher conversions. Although the WGS reaction compromises the selectivity to DME, it increases the DME yield per single pass, especially at higher temperatures.

Cu-based methanol synthesis catalysts display a high water-gas-shift activity  $^{263-265}$ . Water formed during dehydration can react with CO forming CO<sub>2</sub> and H<sub>2</sub> (see section 2.1.3 Equation **2-6**). This can be beneficial when using hydrogen-lean synthesis gas. Furthermore, the presence of a few percent of CO<sub>2</sub> enhances the activity of the methanol synthesis catalyst  $^{90}$ . High water concentrations result in accelerated deactivation, which can be circumvented by water removal via the WGS reaction or via a membrane  $^{266,267}$ .



**Figure 2-7:** Equilibrium composition (based on carbon atoms) and CO conversion as a function of temperature at 40 bar for carbon species involved in **A:** methanol synthesis, **B:** direct synthesis of DME without water-gas-shift reaction, and **C:** direct synthesis of DME with water-gas-shift reaction. The thermodynamic calculation considering all species in the gas phase was carried out with a synthesis gas composition of  $H_2$ :CO = 2 v/v and as possible products methanol (A) and additionally DME (B) and DME and CO<sub>2</sub> (C). HSC software from Outotec (v 7.14) was used to perform the calculations.

#### 2.2.3. Challenges

Methanol dehydration to form DME can be catalyzed by Brønsted as well as Lewis acid sites, and all acid strengths. However, particularly at high temperatures, strong acid sites can facilitate the further dehydration of DME to olefins and other hydrocarbons, compromising the DME yield <sup>209,268,269</sup>. This does not represent a problem for the dual reactor process, since the methanol dehydration step can be operated at relatively low temperatures ( $\leq 200^{\circ}$ C, Figure 2-6). At higher temperatures needed for methanol synthesis, less strong acid sites are preferred. Indeed, acid sites with a weak to medium strength have shown an excellent selectivity to DME under direct DME synthesis conditions <sup>261,270</sup> <sup>240</sup>.

Industrial methanol synthesis catalysts are copper-based <sup>86</sup>. Copper nanoparticle growth and hence loss of active metal surface area, is the main deactivation mechanism <sup>271</sup>. It is enhanced by higher water concentrations, to which it will be exposed when used in direct DME synthesis or in CO<sub>2</sub> rich feeds <sup>272,273</sup>. Faster deactivation was observed when co-feeding water using a Cu-ZnO methanol synthesis catalyst only <sup>274,275</sup>. Recently, the stability of a Cu-ZnO catalyst physically mixed with a ZSM-5 zeolite was studied under DME synthesis conditions (260°C, 20 bar, 90000 or 3600 cm<sup>3</sup>/g<sub>cat</sub>·h and H<sub>2</sub>:CO = 2 v/v) by *in-situ* synchrotron-based EXAFS and XRD experiments <sup>276</sup>. Results show an increase of the copper crystallite size from 9 nm to 12 nm during the first hours under reaction conditions, while copper remained in the metallic state within the technique's detection limit. Decreasing the gas space velocity or co-feeding water led to larger crystallite sizes, 17 nm and 20 nm respectively. The authors concluded that the water generated during DME synthesis has a detrimental effect in the stability of the Cu-ZnO catalyst mainly by particle growth.

For the methanol dehydration catalysts, the challenges vary according to the nature of the material. Zeolites in the proton form typically have strong Brønsted acid sites which can lead to further DME dehydration to hydrocarbons, although some strategies have been developed to tune the zeolite acidity and to improve DME yields <sup>277,278</sup>. Another main challenge is the microporous structure of zeolites which can limit the diffusion of reactants and products leading to hydrocarbon and coke formation, deactivating and blocking the active sites <sup>279</sup>. H-ZSM-5 in a physical mixture with Cu-ZnO catalysts showed a decrease in activity of ~20% due to accumulation of hydrocarbon species formed in the pores (250 °C, 10 bar and TOS = 100 h) <sup>280</sup>. The synthesis gas composition in this case was important for the zeolite stability, the presence of CO<sub>2</sub> directly affected the partial pressure of water and hence aided to avoid accumulation of carbonaceous species in the pores.

 $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is a very selective solid acid catalyst to produce DME due to its mild Lewis acid sites, active for methanol dehydration. However, it can loss activity in the presence of water due to competitive water adsorption on the acid sites or by recrystallization <sup>280</sup>. The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> to boehmite phase transition has been investigated in the range of 250–400 °C and H<sub>2</sub>O partial pressures up to 15 bar <sup>281,282</sup>. Results over  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at 250°C and water partial pressure of 13–14 bar led to the conversion of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> into  $\gamma$ -AlO(OH). This was linked to a decrease in catalytic activity of methanol dehydration, from ~60% methanol conversion to ~15%. However, the phase transition was reversible under more standard reaction conditions or
calcination at 350 °C, recovering its catalytic activity. Niobium oxide-based dehydration catalysts are less active but can form a stable NbO<sub>4</sub>-H<sub>2</sub>O phase and do not show water induced deactivation  $^{270,283-288}$ .

The interaction between both catalytic materials can result in activity and/or selectivity loss, therefore the distance between functionalities is a key factor for the stability of the catalyst. Two distances in the micrometer range have been studied by co-tableting powders with different sieve fractions of a Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> methanol synthesis catalyst and silica-alumina dehydration catalyst <sup>289</sup>. A fine sieve fraction of 50-100 µm of the individual catalysts and a coarse sieve fraction of 600-1000 um were used to prepare bifunctional catalysts. During direct DME synthesis (285 °C, 60 bar, TOS = 700-800 h), the finer particle catalyst deactivated faster than the catalyst pelletized from larger particles. Characterization of the used catalysts revealed migration of zinc from the methanol synthesis catalyst into the dehydration component and silicon from the dehydration component diffused into the methanol synthesis catalyst particles. The authors concluded that the faster poisoning of the more finely sieved catalyst relates to the larger contact area between the two catalyst materials. Analog, it has been observed that species exchange between the solid acid and Cu-ZnO catalyst with H-ZSM-5 as solid acid <sup>290–293</sup>. The extent of deactivation was linked to the amount of zeolite's extra-framework Al species and surface acid sites <sup>292,294</sup>. Migration of copper from the methanol synthesis catalyst to niobium-based solid acids has also been observed after DME synthesis (260 °C, 40 bar, H<sub>2</sub>:CO = 2 v/v and TOS = 120 h)  $^{270}$ .

# 2.2.4. Process comparison

The direct production of DME from synthesis gas can be effectively carried out by use of bifunctional catalysts. Combining both functionalities in a single catalyst comes with clear advantages, in particular a higher conversion of CO in a single pass, over the dual reactor process. In Figure 2-8 we have gathered experimental data for both types of processes from published literature, showing the DME yield as a function of CO conversion. The slope of the line corresponds to the overall selectivity with which CO is converted to DME. Complete data sets can be found in the supplementary information of *Catal. Sci. Technol.* **14**, 4799-4842 (2024) <sup>295</sup>. Values for the dual reactor process were obtained by combining the maximum reported conversion and selectivity values from the methanol synthesis and methanol dehydration reactions, respectively. The resulting slope of the trendline (in grey) shows an overall selectivity of 88% for the dual reactor process with the methanol synthesis being detached from the methanol dehydration reaction in separate reactors.



**Figure 2-8:** DME yield as a function of CO conversion for the dual reactor process, bifunctional process, and bifunctional process with in-situ removal of water. Data points were obtained from recent reports in which DME is the principal product, the complete data set with the corresponding references can be found in the supplementary information of *Catal. Sci. Technol.* **14**, 4799-4842 (2024) <sup>295</sup>.

For the bifunctional process, most catalysts follow a similar trend (in green) independently of the catalyst synthesis method, with a selectivity of 62%. This is lower than the dual reactor process due to the production of CO<sub>2</sub> from the water-gas-shift reaction at the expense of DME yield. Still, the bifunctional process allows to reach much higher CO conversions hence also higher DME yields in a single one-pass conversion compared to the dual reactor process. Bifunctional systems have catalysts consisting of physical mixtures or core-shell catalysts. This uniform trend also indicates that the distance between functionalities does not have a strong effect on the selectivity to DME. This might be explained by fast diffusion of chemical species in this process (i.e., methanol and DME) in contrast to species in other bifunctional processes (e.g., long-chain paraffins or aromatic compounds). This in agreement with the recent work of Li et al <sup>296</sup>. A physical mixture of methanol synthesis and dehydration catalysts displays an effective system for high DME yields. However, as discussed in the previous section, a very fine physical mixture might negatively affect the stability of the catalyst <sup>289</sup>.

Within the different catalysts' configurations for bifunctional process, the in-situ water removal strategy <sup>248–250</sup> follows a different trend (in red) and therefore has been plotted separately. Here the slope corresponds to a 98% DME selectivity, with also high CO conversion. By capturing the formed water, most of the water-gas-shift reaction is inhibited and thus CO is converted mainly to DME. This seemingly is the most attractive pathway for

an efficient DME production. However, aspects such as cost, energy consumption and ease of operation might be significant disadvantages of this method.

Unfortunately, few studies report long time-on-stream results, which makes it difficult to assess the stability of the various catalysts configurations. At least 100 h-on-stream results would give a good indication of the stability of the catalysts. Sintering of the metal functionality in the methanol synthesis catalyst and ion migration within functionalities seem to be the main phenomena responsible for activity loss. Solid acids with mild acid strength are readily active and selective for DME synthesis. Their stability seems less problematic than that of the methanol synthesis catalyst, the copper and copper-zinc interphase in these catalysts are susceptible to crystallite growth in the presence of water.

## 2.3. Olefins

## 2.3.1. Recent developments

A process called OX-ZEO, developed by the groups of Prof. Bao and Prof. Wang, to convert synthesis gas to short olefins in the range of  $C_2$ - $C_4$  can be considered a breakthrough in bifunctional catalysis <sup>192,297</sup>. The OX-ZEO catalysts consist of metal oxides (based on for instance zinc, zirconium and/or chromium oxides) and a zeolite. Synthesis gas is first converted over the CO activation catalyst (metal oxide) to reactive oxygenate intermediates such as methanol/dimethyl ether or ketene (Figure 2-9-A) <sup>298–301</sup>. These intermediates are further converted to short olefins via C-C coupling over the acid sites of a zeolite with usually 8-membered ring pores <sup>299,302–304</sup>, such as SAPO-34 or H-SSZ-13, which are well known in the methanol-to-olefins reaction for their high selectivity <sup>138,305,306</sup>.

In general, the OX-ZEO process is operated at high temperatures (300-400°C) and pressures (10-100 bar)<sup>192,195,307–311</sup>, achieving selectivities to C<sub>2</sub>-C<sub>4</sub> olefins between 63% and 87% within the hydrocarbon products (excluding CO<sub>2</sub>)<sup>299,302</sup> at 10-85% CO conversion <sup>299,302,308,309,311</sup>. These very high selectivities are well beyond the maximum predicted for a single conversion process based on the Anderson-Schulz-Flory distribution of the C<sub>2</sub>-C<sub>4</sub> fraction (sum of olefins and paraffins) of 58% <sup>312</sup>, such as the Fischer-Tropsch synthesis. This is a clear example of how using a bifunctional catalyst can improve the selectivity towards a certain product by catalyst design, as is discussed in more detail in the following paragraphs. However, it was shown that with increasing CO conversion the selectivity towards short olefins decreases and it remains a challenge to combine high selectivity with high conversion/activity, albeit that progress in that direction has been made <sup>308,309,311</sup>. The group of Prof. Bao demonstrated high CO conversion of 85%, while maintaining 83% selectivity to short olefins and reduced CO<sub>2</sub> selectivity of 32% <sup>311</sup>.

The understanding of the underlaying mechanism in OX-ZEO catalysis is still incomplete. Oxygenate intermediates are key in this process, but there is still discussion about which species is the main intermediate diffusing from the metal oxide to the acid catalyst <sup>313,314</sup>. The mechanism of the primary conversion of CO to these reactive oxygenate

intermediate species on metal oxides was studied with *in-situ* near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) and infrared (IR) spectroscopy <sup>315</sup>. It was found that upon reduction and exposure to synthesis gas, 36% of the surface lattice oxygen was removed from a manganese oxide (MnO<sub>2</sub>) catalyst, resulting in a high density of oxygen vacancies near the surface. It was proposed that CO is dissociated on these vacancies, after which oxygen is transferred to another CO molecule, forming carbonate species from which CO<sub>2</sub> is desorbed. The remaining carbon atom is hydrogenated to a CH<sub>2</sub> species, followed by insertion of CO and desorption of ethenone (C<sub>2</sub>-ketene, Figure 2-9-B). Ketenes are highly reactive molecules. The chain propagation (C-C coupling) in the zeolite is reported to follow a direct associative pathway; ketene adsorbs on the acid site of the zeolite and the CH<sub>2</sub> group is transferred to an olefin in a consecutive step, leaving a CO molecule behind <sup>316</sup>.

However, ketene intermediates are thermodynamically unstable and therefore it might be argued that methanol and/or dimethyl ether are the actual reactive oxygenate intermediate  $^{317,318}$ . The group of Prof. He proposed methanol as the intermediate from quasi-CO<sub>2</sub> hydrogenation using indium-zirconium oxide and SAPO-34 zeolite, based on DFT calculations  $^{307}$ . It was found that adsorbed CO formed an O-C-O species (quasi-CO<sub>2</sub>) on the catalyst surface with lattice oxygen, which was then hydrogenated forming the reactive intermediate. Furthermore, the pathway of side products formation such as methane and paraffins was investigated. The formation of methane was caused by hydrogenation of methanol (or surface O-C-O species) on the metal oxide catalysts. The C<sub>2+</sub> paraffins were formed after methanol traveled from the metal oxide catalyst to the zeolite forming olefins, which were then hydrogenated to paraffins in a consecutive step on the metal oxide.

The nature of the reactive oxygenate intermediate in the OX-ZEO process is hence topic of ongoing debate. Using a zinc-chromium oxide catalyst mixed with a SAPO-34 zeolite, the group of Prof. Bao identified ketene as intermediate with synchrotron vacuum ultra-violet photoionization mass spectrometry (SVUV-PIMS)<sup>192</sup>. To provide more evidence, ketene was flowed over modified mordenite zeolite with only either 8-membered ring (MR) pores or 12-MR pores accessible<sup>298</sup>. The product spectrum was similar to the spectrum obtained from experiments converting synthesis gas using a bifunctional catalyst consisting of zinc-chromium oxide and modified MOR zeolite (Figure 2-9-C).

On the other hand, methanol and dimethyl ether were identified as intermediates in the OX-ZEO process using zinc-doped zirconia catalysts mixed with SSZ-13 zeolites with various degrees of sodium ion exchange to control the density of Brønsted acid sites <sup>302</sup>. The mixture of zinc-doped zirconia with fully sodium exchanged SSZ-13 in the nano scale (~250 nm), hence without Brønsted acid sites present, showed a low CO conversion of 5% and selectivities to methanol and dimethyl ether of 65%. The CO conversion and selectivity to C<sub>2</sub>-C<sub>4</sub> olefins increased with increasing density of Brønsted acid sites, because the intermediates could be removed from the equilibrium and converted to short olefins. The influence of strength and concentration of acid sites of a ZnAlO<sub>x</sub>/CHA OX-ZEO catalyst on the conversion of synthesis gas to olefins was investigated <sup>319</sup>. With increasing Si/Al ratio of the CHA zeolite from Si/Al=20 to Si/Al=308 the selectivity to paraffins decreased (from 32% to 6%,  $CO_2$  free), while olefin selectivity increased (from 59% to 85%,  $CO_2$  free). This was attributed to the low acid site density in combination with decreased acid site strength by the addition of boron during zeolite synthesis. Additionally, it was found that a high density and strength of acid sites in a ZnCrOx/SAPO-35 zeolite accelerated the catalyst deactivation by enhanced coke formation and can cause increased paraffin selectivity in large zeolite crystals  $\frac{320-322}{2}$ .

Alternatively to the OX-ZEO process, hydrocarbon intermediates can be used to convert synthesis gas to short olefins by combining an iron (carbide) based Fischer-Tropsch core catalyst with a SAPO-34 zeolite shell <sup>323</sup>. Operating at temperatures of 325°C, the iron FTS catalyst formed typical heavy hydrocarbon products, that were cracked on the acid sites of the SAPO-34 zeolite forming  $C_2$ - $C_4$  olefins with 53% selectivity within the hydrocarbons at 55% CO conversion. Remarkably, the CO<sub>2</sub> selectivity was only 17%, which allows this approach to compete with the OX-ZEO process, although the olefin fraction in the hydrocarbon products is lower. Similar trends have been observed using a Silicalite-1 encapsuled iron-based catalyst 324,325. Additionally, an iron-based FTO catalyst capsuled with an H-ZSM-5 zeolite or a hydrophobic SiO<sub>2</sub> shell showed reduced CO<sub>2</sub> selectivity (8.5%-28%) and slightly increased  $C_2$ - $C_4$  olefins selectivity (41%-49%) compared to the FTO catalyst alone (30%-39% CO<sub>2</sub> and 25%-38% olefins) <sup>326,327</sup>. A silica-coating of a manganese promoted cobalt carbide nano-prism FTO catalyst showed increased olefins selectivity (from 40% to 59%) and reduced  $CO_2$  selectivity (from 45% to 15%) compared to the uncoated catalyst <sup>328</sup>. It was concluded that the silica-coating reduced the adsorption of water on the catalyst and promoted the diffusion of water away from the catalysts' active sites, thereby, lowering the actual concentration near the active FTO sites <sup>328,329</sup>.

In the Fischer-Tropsch to olefins process, CO activation and C-C-coupling take place on the same catalyst component, while they are spatially separated in the OX-ZEO process (Figure 2-9-C). The OX-ZEO process is operated at rather high temperatures, which shifts the equilibrium between synthesis gas and the reactive intermediates far to the side of synthesis gas (see section 2.3.2). This can partially be counteracted by operating at elevated pressures. However, it is essential to have the two functions for CO activation and C-C-coupling in optimal proximity to effectively achieve removal of the intermediates, and hence high conversion.

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**Figure 2-9: A:** General reaction scheme of the OX-ZEO process, whereas CO activation takes place on a metal oxide forming oxygenate intermediates followed by C-C coupling on a zeolite <sup>299</sup>. **B:** Proposed mechanism of CO activation over a metal oxide catalyst forming ketene intermediates <sup>315</sup>. **C:** Hydrocarbon product spectrum (CO<sub>2</sub> free) when either feeding synthesis gas to an OX-ZEO catalyst (green bars), or ketene (red bars) or methanol (grey bars) to a MOR-zeolite with 8 membered ring pores and 12 membered ring pores being accessible. For the experiments with synthesis gas feed zinc-chromium oxide particles were attached to the MOR-zeolite for synthesis gas activation. Synthesis gas over ZnCrO<sub>x</sub>/MOR gave similar products as ketene fed over MOR-zeolite with high C<sub>2</sub> selectivities<sup>298</sup>.

The group of Prof. Wang investigated the influence of the distance between the two functions on the conversion and selectivity in the OX-ZEO process, by combining a zirconium-zinc binary oxide catalyst with a SAPO-34 zeolite in different mixing modes <sup>299</sup>. Packing in stacked bed mode with the zeolite downstream of the metal oxide gave very low conversions. A physical mixture of catalyst granules with grain size of 250-600 µm (resulting distance between CO activation and C-C coupling catalyst in the range of ~500 µm) led to 7% CO conversion with 75% selectivity to  $C_2$ - $C_4$  olefins. To achieve even closer proximity, the two individual catalysts were ground in a mortar, resulting in ~500 nm distance between the two functions. The distance of the two functions could be decreased even further to ~100 nm by a ball-milling procedure for 24 h. Bifunctional catalysts prepared with closer proximity using mortar-mixing and ball-milling techniques achieved CO conversions of 10-11%, with selectivities to  $C_2$ - $C_4$  olefins slightly decreasing to 63-70%. The decrease in selectivity was assigned to secondary hydrogenation of olefins to paraffins on the metal oxide catalyst. A ZnCrO<sub>x</sub>/SAPO-34 catalyst applied in the OX-ZEO to olefins reaction showed the best performance of 60% CO conversion and 76% C<sub>2</sub>-C<sub>4</sub> olefin selectivity at medium proximity of 200-300 µm between the metal oxide and zeolite function <sup>330</sup>. The authors concluded that with greater distance between the functions the removal of reactive intermediates suffered from mass transfer limitation. However, with increasing proximity zinc species migrated from the metal oxide to the zeolite, decreasing the activity of both functions. A MnO<sub>x</sub>/SAPO-34 catalyst did not show decreasing activity with increasing proximity.

The catalysts used in the OX-ZEO process are also active for the water-gas-shift (WGS) reaction and usually show CO<sub>2</sub> selectivities between 32-45%, which is close to the equilibrium concentration of 45-49%, depending on the reaction conditions <sup>192,302,315,331</sup>. This makes it possible to also convert hydrogen-lean synthesis gas obtained from coal or biomass, because one molecule of hydrogen is formed for every molecule CO that is converted. This comes at the expense of carbon atom economy because CO<sub>2</sub> is being formed from CO. However, a high hydrogen partial pressure can also facilitate the secondary hydrogenation of olefins products over In<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub>/SAPO-34 OX-ZEO catalysts <sup>332</sup>. Hence, feeding hydrogen lean synthesis gas to the OX-ZEO process can circumvent unwanted side reactions and the WGS reaction can provide additional hydrogen further onwards in the catalyst bed.

The OX-ZEO catalysts can also be applied for the synthesis of short olefins from  $CO_2$  hydrogenation <sup>83,322,332–338</sup>. Studies on a  $Mn_2O_3$ -ZnO/SAPO-34 catalyst showed that the alkaline character and  $CO_2$  activation over oxygen vacancies of the metal oxide function favor a high activity in  $CO_2$  conversion <sup>339</sup>. By ball-milling the components together, hence decreasing the average distance between the two catalyst components, the performance of the OX-ZEO catalyst was further enhanced. The conversion of  $CO_2$  and selectivity to  $C_2$ - $C_4$  olefins increased from 20% to 30% and 49% to 80% (CO free), respectively, compared to a dual bed configuration. Additionally, the CO selectivity resulting from reverse WGS decreased from 90% to 55% upon ball-milling the catalyst.

### 2.3.2. Benefits

A clear advantage of using bifunctional catalysis to convert synthesis gas to olefins is that CO conversions can be higher than for two separate reactors for which the maximum conversion is dictated by the equilibrium between the synthesis gas and oxygenates (Figure 2-10). The thermodynamic limit for CO hydrogenation to methanol is only 0.07% (at 10 bar pressure) and 6.6% (at 100 bar pressure) at 390°C, but recently 7.5-fold to 51-fold higher conversions were reported, reaching up to 59% conversion <sup>308</sup>. These CO conversion levels are similar to those for methanol synthesis commonly operated at 260°C <sup>271,308</sup>.



**Figure 2-10:** Equilibrium CO conversion for methanol synthesis from synthesis gas (H<sub>2</sub>:CO=2 mol/mol) as function of reaction pressure at 260°C (dotted red line) and 390°C (solid green line) and reported CO conversion as a function of reaction pressure of the OX-ZEO process operated at 390°C (open green circles) exceeding the equilibrium CO conversion of the single pass methanol synthesis at 400°C <sup>308</sup>.

Another clear advantage of operating the process with two different catalytic functions, whether in a single or double reactor, is the possibility to steer the selectivity. The OX-ZEO process showed a selectivity towards short olefins of up to 87%  $^{302}$  caused by the highly selective MTO catalysts used for the C-C coupling step. In comparison, methanol or dimethyl ether feedstock in the DMTO (dimethyl ether or methanol to olefins) process also give 84-87% olefin selectivity  $^{340,341}$ . For Fischer Tropsch Synthesis only, the maximum selectivity according to the ASF distribution is limited to 58% C<sub>2</sub>-C<sub>4</sub> olefins + paraffins  $^{312}$ ), while the FTO process, being able to break the ASF distribution, reaches 61% C<sub>2</sub>-C<sub>4</sub> olefins  $^{113}$ .

Furthermore, the product spectrum can be tuned by the choice or modifications of the C-C coupling catalyst  $^{342,343}$ . The zeolite pore size is critical. SAPO-34 or SSZ-13 zeolites as C-C coupling catalyst typically give a product spectrum with 13-20% C<sub>2</sub>, 40-59% C<sub>3</sub> and 14-23% C<sub>4</sub> products  $^{192,309}$ , which is similar to the product distribution in MTO  $^{139,149}$ . A modified MOR zeolite with selectively deactivated 12-MR pores and only 8-MR pores

accessible as C-C coupling catalyst next to a  $ZnCrO_x$  catalyst for CO activation showed a remarkably high selectivity to ethene of 73% <sup>298</sup>.

A last potential advantage is related to the stability of the catalyst. For the MTO process, the SAPO-34 or SSZ-13 catalyst lifetime is only a few hours due to severe coke formation <sup>138</sup>. The OX-ZEO catalyst was reported to display much longer lifetimes, beyond 500 h <sup>308</sup>. However, no clear explanation for the high stability has been offered so far. A possibility is that the productivity of OX-ZEO is lower (~0.3 kg<sub>olefins</sub> kg<sub>catalyst</sub><sup>-1</sup> h<sup>-1</sup> <sup>308</sup>) compared to the MTO process (~2 kgolefins kgcatalyst<sup>-1</sup> h<sup>-1</sup> for micro- and pilot-scale and ~5 kg<sub>olefins</sub> kg<sub>catalyst</sub><sup>-1</sup>  $h^{-1}$  for demo- and commercial scale <sup>305</sup>) which for OX-ZEO will give rise to much longer catalyst life times expressed in hours. Cheng et al. observed a high stability of their zinc-doped zirconia catalyst (CO activation) and H-ZSM-5 zeolite (C-C coupling and aromatization) over the course of 1000 h in the conversion of synthesis gas to aromatics <sup>344</sup>. They postulated that the high silicon to aluminum ratio of the zeolite played a crucial role in its stability. Furthermore, the low partial pressure of methanol/dimethyl ether or ketene suppressed the excessive alkylation of aromatic species in the dual cycle mechanism that would eventually result in the formation of polycyclic aromatics hydrocarbons and hence catalyst deactivation <sup>345</sup>. This low partial pressure of intermediates also allows to operate the OX-ZEO process with a zeolite that has a high silicon to aluminum ratio and hence low acid site density, which is beneficial for the zeolite stability  $^{138}$ . The reaction conditions of the OX-ZEO process with high temperatures and high hydrogen concentrations compared to the MTO process limit the formation of soft coke <sup>345</sup>, which also mitigates catalyst deactivation.

# 2.3.3. Challenges

A first challenge is to realize an optimum hydrogenation activity of the metal oxide in the OX-ZEO catalyst, which is crucial for the selectivity <sup>307,346</sup>. Metal oxide catalysts with high hydrogenation activity, such as zinc oxide, showed primary overhydrogenation of surface carbon species forming methane (Figure 2-11-A) as well as secondary hydrogenation of re-adsorbed olefins (that were formed on the C-C coupling catalyst), which is detrimental to the olefin selectivity <sup>195</sup>. A Mg-HZSM-5/Al<sub>2</sub>O<sub>3</sub> catalyst applied in the DMTO reaction in the presence of synthesis gas did not show increased hydrogenation of olefins <sup>347</sup>. Hence the metal oxides' hydrogenation activity of the OX-ZEO catalyst needs to be limited, but still sufficiently high for surface CO\* species to undergo moderate hydrogenation to form the reactive oxygenate intermediates <sup>309</sup>. The hydrogenation performance of the metal oxide catalysts can be influenced by a variety of parameters, such as the nature of the oxide <sup>195</sup>, particle size <sup>331,334</sup>, nature of dopants <sup>348</sup>, promoters <sup>309</sup> and proximity to the zeolite <sup>349</sup>. Balancing the hydrogenation activity of the OX-ZEO process remains one of the main challenges for future work. Currently, zinc-chromium or zinc-zirconium binary oxide seem to be the most promising candidates as CO activation catalysts, whereas SAPO-34, SSZ-13, and ion exchanged AIPO-18 are promising solid acids <sup>302,308,311</sup>.

## 2.3.4. Process comparison

To generate a more global picture regarding attainable product selectivities, we compared the best reported catalytic performances for three different approaches to convert synthesis gas to short olefins. Figure 2-11-B shows the yield to  $C_2$ - $C_4$  olefins for the FTO process, OX-ZEO and a dual reactor process as a function of the CO conversion. For the dual reactor process, we calculated the overall yields to  $C_2$ - $C_4$  olefins that we obtained from the combination of reported data for a methanol synthesis reactor and a reactor for the methanol-to-olefins (MTO) process. The dual reactor approach is based on two consecutive reactors, separating the CO activation catalyst (methanol synthesis) from the C-C coupling catalyst (MTO). The slopes of the yields plotted against the CO conversion per pass (once-through) correspond to the overall selectivity of the process and account for the formation of CO<sub>2</sub>.

The FTO process shows a selectivity to  $C_2$ - $C_4$  olefins of ~22%. The fraction of short olefins in the hydrocarbon products of the FTO process is reported up to 61% <sup>350</sup>. However, the product stream is not only hydrocarbons, but also contains CO<sub>2</sub> formed from CO via the WGS reaction, giving 30-50% CO<sub>2</sub> in the product stream <sup>119,351</sup>. This reduces the overall selectivity to short olefins to 30-42%. A successful strategy in the case of hydrogen-rich synthesis gas might be to mitigate the WGS reaction, as illustrated by the full red square in Figure 2-11-B, which shows the yield of short olefins for a bifunctional catalyst consisting of an iron (carbide) based core and a SAPO-34 or silica shell, respectively <sup>323,327</sup>. The increased selectivity is caused by the reduced WGS activity of this catalyst system and can compete with that in the OX-ZEO process. A selectivity to short olefins to the hydrocarbon products as high as 87% <sup>299,302</sup> in combination with high CO<sub>2</sub> selectivities of 40-45% due to the WGS activity of the OX-ZEO catalysts <sup>192,307</sup>.

The approach with two separate reactors (methanol synthesis and MTO) gives an overall selectivity of ~93%. This is caused by the high selectivity of the methanol synthesis (between 97% and 99.8%  $^{352,353}$ ) and the MTO process with 94-96% selectivity to short olefins  $^{138}$ . Furthermore, in this configuration the total selectivity towards CO<sub>2</sub> from WGS (reaction of water and CO) is neglectable, because the water is mainly formed during the MTO process in the second reactor without CO being present.



**Figure 2-11: A:** Proposed pathway for primary overhydrogenation forming methane on the metal oxide catalyst and secondary hydrogenation forming paraffins from olefins by re-adsorption of olefins on the metal oxide catalyst <sup>195</sup>. **B:** Experimentally reported yields of  $C_2$ - $C_4$  olefins as function of CO conversion for a dual reactor process (single pass conversion over methanol catalyst and consecutive MTO process, gray triangles), OX-ZEO process (green circles) and FTO process (red squares, open symbols: fully WGS active, filled symbols: reduced WGS activity). The slopes of the fitted lines correspond to the overall selectivity to olefins. A detailed analysis of the catalytic data can be found in the supplementary information of *Catal. Sci. Technol.* **14**, 4799-4842 (2024) <sup>295</sup>.

Currently, a dual reactor approach to convert synthesis gas to olefins using methanol synthesis and an MTO process shows the most promising overall selectivity and carbon atom economy due to the absence of the WGS reactions and highly selective reactions. A challenge for the OX-ZEO process as well as for the FTO process is the suppression of the WGS reaction if hydrogen-rich synthesis gas is used to achieve higher yields of the desired products. This has been partially achieved with a zinc-cerium-zirconium oxide catalyst combined with a SAPO-34 zeolite <sup>354</sup>. The selectivity towards carbon dioxide was reduced

to 6% at a low CO conversion of 7%. However, the CO<sub>2</sub> selectivity increased to 26% at 12% CO conversion by increasing reaction temperature. In terms of activity the hydrogenation strength of the metal oxide needs to be finely balanced to achieve higher total activity without intensifying secondary hydrogenation of products. For this, several strategies are already available, such as choice of material <sup>355</sup>, dopants and promoters <sup>356</sup>, or intimacy between the metal oxide and zeolite <sup>357</sup>. Concerning catalysts stability important progress has been achieved with stable times on stream of 500 h and above <sup>308,344</sup>. In brief, the two-step approach cannot compete with the two-reactor approach in terms of selectivity and carbon yield but does have clear advantages, such as exceeding conversion levels of the methanol synthesis catalysts dictated by the thermodynamic limits. Additionally, as it is a relatively new method, further development can be expected.

### 2.4. Aromatics

#### 2.4.1. Recent developments

In the following paragraphs we introduce two different approaches to convert synthesis gas to aromatics (monoaromatics with a single aromatic ring) using bifunctional catalysis: (I) The combination of an FT catalyst with a zeolite and (II) the OX-ZEO process for aromatics (Figure 2-12). One of the main differences between these two approaches is the location of the C-C coupling. In the combination of the FT catalyst and the zeolite (FT+zeolite) the C-C coupling takes place on the CO activation catalyst (the FT catalyst) <sup>358</sup>, while the zeolite is responsible for further oligomerization, cyclization and aromatization. In the OX-ZEO process the CO activation catalyst (metal oxide) forms carbon monomers <sup>344,359</sup>, while the C-C coupling of these carbon monomers occurs on the zeolite <sup>348</sup>. In both approaches, H-ZSM-5 zeolites with 10 membered ring pores are typically used, due to their excellent shape selectivity for aromatics <sup>360</sup>.



**Figure 2-12:** General reaction scheme for the conversion of synthesis gas to aromatics using a combination of an FT catalyst with a zeolite (I) or the OX-ZEO process (II).

**Combination of FT catalyst and zeolite:** Iron carbide- or cobalt carbide-based FT catalysts show high selectivities to olefins <sup>119,121,361</sup> and can be combined with zeolites to convert these olefin intermediates to aromatics <sup>358,362,363</sup>. FT+zeolite is commonly operated at moderate temperatures (270-320°C) and medium pressures (10-20 bar) <sup>358,364,365</sup>, reaching aromatics selectivities up to 61% in the hydrocarbon products (excluding CO<sub>2</sub>, 9%-41% if CO<sub>2</sub> is accounted for) at 5-99% CO conversion <sup>358,365,366</sup>. The FT product spectrum usually follows the Anderson-Schulz-Flory (ASF) distribution. A wide range of products is formed, including methane and longer paraffins, that cannot be converted to aromatics under these reaction conditions <sup>367</sup>. This explains the moderate overall selectivity to aromatics. Decreasing the reaction temperature causes an increase of average chain length of the FT products and leads to a higher fraction of olefin intermediates with a chain length of C<sub>6</sub>-C<sub>10</sub>, hence suitable for aromatization.

For the aromatization of olefins over H-ZSM-5 higher temperatures (350-480°C) and lower pressures (1 bar-10 bar) are preferred <sup>359,368–370</sup>. However, operating an FT catalyst under these conditions leads to rapid deactivation due to coke formation <sup>113,121</sup>. Furthermore, more methane and less  $C_{2+}$  are formed <sup>371</sup>. For example, a bifunctional catalyst consisting of a cobalt-manganese-aluminum oxide catalyst combined with an H-ZSM-5 zeolite operated at 270°C and 10 bar led to 4% methane formation and 2%-5% aromatics, while at 320°C a 18%-21% methane selectivity and 29%-38% aromatics were formed. Alternatively, a tandem reactor design with the same cobalt-manganese-aluminum oxide catalyst upstream at 270°C and the zeolite downstream at 320°C allowed to maintain a low methane selectivity of 3% while increasing the selectivity to aromatics to 52% <sup>358</sup>, albeit at the expense of CO conversion (32-40% at 270°C compared to 65-72% at 320°C).

The aromatization of olefins often follows a pathway that involves hydrogen transfer, forming three molecules of paraffins for every aromatic molecule formed (Figure 2-13-A)  $^{359,372,373}$ . However, a high operating temperature and/or low partial pressure of olefins shifts the aromatization towards dehydrogenation instead of hydrogen transfer  $^{373}$ . For example, operating a bifunctional catalyst consisting of a Fischer-Tropsch to olefins (FTO) catalyst and an H-ZSM-5 zeolite at 400°C, 1 bar and low CO conversion (2%) facilitates aromatization of olefins via a dehydrogenation pathway with 17% aromatics selectivity and only 4% paraffins <sup>113</sup>. Alternatively, a bifunctional catalyst consisting of a pyrolyzed iron containing metal-organic-framework (MOF) promoted with sodium and a modified H-ZSM-5 zeolite has been developed for the conversion of CO<sub>2</sub> and hydrogen to aromatics  $^{374}$ . Catalytic tests performed at 320°C, 30 bar and CO<sub>2</sub> containing synthesis gas (H<sub>2</sub>:CO<sub>2</sub>=2.95 v/v) as feedstock and in granule stacking mode yielded 9.6% C<sub>2</sub>-C<sub>4</sub> paraffins and 50.2% aromatics. The authors concluded that the olefin intermediates are converted into aromatics via dehydrogenative aromatization and that adsorbed CO<sub>2</sub> on the pyrolyzed iron containing MOF acted as acceptor for hydrogen species formed during dehydrogenation  $^{374}$ .

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**Figure 2-13: A:** Aromatization of higher olefins via hydrogen transfer <sup>134</sup> (top), forming paraffins ( $C^0$ ) from olefins ( $C^{-}$ ) and via dehydrogenation <sup>373</sup> (bottom) releasing hydrogen as by-product. **B:** Overview of different bifunctional catalyst configurations showing distances between the two catalytic functions varying from the meter scale in dual reactor processes to the nano mater scale for closest proximity.

Both structure of the zeolite and acid site density have a major influence on the resulting product spectrum. For hierarchical ZSM-5 zeolites impregnated with iron, a correlation between the concentration of acid sites and the selectivity to aromatics was reported  $^{375}$ . Bifunctional catalysts with medium concentrations of acid sites (746 µmol/g) gave a higher selectivity to aromatics (15%) then with a lower or higher acid site concentration. Additionally, increasing the fraction of mesopore volume within the total pore volume from 45% to 68% increased the selectivity to aromatics from 15% to 23%  $^{375}$ .

A composite catalyst consisting of a copper-promoted bulk iron catalyst and an H-ZSM-5 zeolite was applied in the synthesis of aromatics from CO<sub>2</sub> containing synthesis gas with H<sub>2</sub>:CO<sub>2</sub> = 3 (v/v) <sup>376</sup>. At 320°C, 30 bar, and the individual catalyst granules being mixed in the catalyst bed showed 57% conversion of CO<sub>2</sub> and 57% selectivity to aromatics with only 3.5% CO selectivity resulting from the rWGS reaction. Increasing the content of copper promoter in the bulk iron catalyst from 6.25 wt-% to 50 wt-% caused the methane and short paraffin selectivity to increase (11% to 57% and 8% to 30%, respectively) and the aromatics selectivity to decrease (57% to 10%). This behavior indicates that the increasing copper content is responsible for secondary hydrogenation and methane formation of intermediate species. A similar behavior was also observed when promoting iron-based FT catalysts with copper in the conversion of CO and H<sub>2</sub> to aromatics <sup>377</sup>. With a copper content of 1.5%-wt in the iron-based FT catalyst the methane selectivity was low (8%) and aromatics selectivity

was high (42.5%). However, with lower (0.2%-wt) or higher (5%-wt) amounts of copper promoter the methane selectivity was higher (13% and 15.5%, respectively) and aromatics selectivity was lower (37% and 35% respectively).

**OX-ZEO:** Analog to the OX-ZEO process to convert synthesis gas to olefins, the OX-ZEO process to form aromatics can be regarded as an important development. The catalyst system consists of metal oxides (zirconium, zinc and chromium-based) and zeolites <sup>378–381</sup>. CO activation takes place on the metal oxide and leads to reactive intermediates, such as methanol, dimethyl ether and/or ketenes <sup>364,382–384</sup>, which can be considered as carbon monomers. These intermediates are further converted into aromatics via C-C coupling over a zeolite. Mostly zeolites with 10-membered ring pores are used, such as H-ZSM-5 and H-ZSM-11, which combine an excellent pore structure for the synthesis of aromatics with strong Lewis and Brønsted acid sites <sup>304,344,382</sup>.

The OX-ZEO process to convert synthesis gas to aromatics is usually operated at high temperatures (300-450°C) and high pressures (20-60 bar) <sup>344,355,364,380</sup>, reaching CO conversions between 3% and 55% and selectivities to aromatics of 49-86% within the hydrocarbon products (29-67% selectivity to aromatics if the CO<sub>2</sub> formation is taken into account) <sup>364,380,384</sup>, which is higher than FT+zeolite. The high temperature of the OX-ZEO process leads to a low equilibrium concentration of intermediates, which steers the aromatization towards a pathway that involves dehydrogenation rather than hydrogen transfer <sup>373</sup>. Therefore, the formation of paraffins is limited and a high selectivity to aromatics can be achieved. However, the competition between aromatization via hydrogen transfer and via dehydrogenation strongly depends on the composition of the synthesis gas <sup>364</sup>. An H<sub>2</sub>:CO ratio of 2 (v/v) showed a significantly higher C<sub>2</sub>-C<sub>4</sub> paraffin fraction of 53.1% and low aromatic fraction of 35.2% in the hydrocarbons, compared to a hydrogen lean feed gas with H<sub>2</sub>:CO=1 v/v, resulting in 20.1% C<sub>2</sub>-C<sub>4</sub> paraffins and 56.3% aromatics in the hydrocarbon products.

The nature of the reactive intermediate of the OX-ZEO process to convert synthesis gas to aromatics is under debate. Using zinc chromium oxide, zinc manganese oxide, zinczirconium oxide, or zinc alumina catalysts for CO activation, a mixture of methanol and dimethyl ether was found as reactive intermediate <sup>344,380,382,385,386</sup>. By feeding methanol and carbon monoxide over a zinc zirconium oxide catalyst mixed with an H-ZSM-5 zeolite it was found that the presence of CO showed a self-promoting effect in the conversion of methanol to aromatics, in which methanol was converted to short olefins on the zeolite. These olefins underwent aromatization via dehydrogenation, whereas the hydrogen was removed by carbon monoxide on the metal oxide catalyst resulting in the formation of methanol <sup>344</sup>.

Alternatively, ketene was proposed as reactive intermediate using zinc manganese oxide or zinc chromium oxide as CO activation catalyst <sup>379,382</sup>. The zinc chromium oxide catalyst mixed with a mesoporous SAPO-34 zeolite already has been studied in the OX-ZEO to olefins process, where ketene was identified with synchrotron vacuum ultra-violet photoionization mass spectrometry <sup>192</sup>. A cerium zirconium oxide catalyst in combination

with an H-ZSM-5 zeolite showed improved oxygen vacancies on the surface of the CO activation catalyst and assisted the formation of  $C_{2+}$  oxygenates and  $C_{6+}$  olefins. This suggested a reactive intermediate other than methanol in the conversion of synthesis gas to aromatics <sup>364</sup>.

To remove the reactive intermediates effectively and hence increase the synthesis gas conversion, close proximity between the CO activation catalyst and the C-C coupling catalyst is crucial <sup>385</sup>. With increasing proximity going from powder mixed bifunctional catalysts with ~100 nm distance between the different catalytic functions to nanocomposites, the CO conversion and selectivity to aromatics increases, whereas the methane selectivity decreases <sup>344,364</sup>. This indicates that a larger distance between the CO activation catalyst and the zeolite gives rise to secondary hydrogenation of reactive intermediates on the metal oxide catalyst, forming methane and C<sub>2+</sub> paraffins. However, a reduced zeolite crystallite size from 1.5 µm to 200 nm in a physical mixture with a ZnCrO<sub>x</sub> catalyst showed reduced selectivity to aromatics and a 1.7-fold increase of side products <sup>387</sup> which was assigned to enhanced secondary hydrogenation. Additionally, the zeolites owned different morphologies.

Generally, the formation of ortho- and meta-xylene and heavier aromatics takes place at the acid sites on the external surface of the zeolite by isomerization and alkylation <sup>388</sup>. The kinetic diameter of para-xylene is smaller than those of ortho- and meta-xylene and only para-xylene can be formed inside the micropores of H-ZSM-5 <sup>380,381</sup>. Surface modification of the zeolites forming aromatics can have a significant influence on the product distribution within the aromatics fraction (Table 2-1). These modifications can be achieved by passivation of the external surface of the zeolites or by the growth of a shell that is free of acid sites (for example a silicalite-1 shell around H-ZSM-5 crystals), and generally lead to higher fractions of p-xylene in the aromatics.

Reaction/catalyst	Zeolite modification	Aromatics selectivity		Reference
		Without modification	With modification	
MTA H-ZSM-5	chemical liquid deposition	24% p-xylene in xylenes	90% p-xylene in xylenes	389
Disproportionation of toluene H-ZSM-5	silicalite-1 shell		80% p-xylene in xylenes	390
Fe+Z Mn-promoted FT catalyst + H-ZSM-5	Zn-promotion and silicalite-1 shell	20-25% p-xylene in xylenes	65-70% p- xylene in xylenes	391
OX-ZEO CrZnO <sub>x</sub> + H-ZSM-5	Zn-promotion and silicalite-1 shell		77% p-xylene in xylenes	380
OX-ZEO SiO <sub>2</sub> -modified MnCrO <sub>x</sub> + ZSM-5	USY zeolite downstream of OX-ZEO catalyst	63% BTX in aromatics	88% BTX in aromatics	392

Table 2-1: Influence of surface modifications of zeolites for the formation of aromatics on the selectivity.

OX-ZEO catalysts often show high CO<sub>2</sub> selectivities due to their strong WGS activity. However, the group of Professor Tsubaki developed a catalyst that allows to convert CO<sub>2</sub> containing synthesis gas (CO:CO<sub>2</sub>:H2 = 6.1:1:12.8 v/v/v) into aromatics <sup>393</sup>. The rate of CO<sub>2</sub> formation and consumption was kept in balance by adjusting the feed composition, hence this reaction was operated net-CO<sub>2</sub> neutral. The OX-ZEO catalyst consisting of Cr<sub>2</sub>O<sub>3</sub> as metal oxide and H-ZSM-5, or metal ion exchanged ZSM-5 zeolite with a silica coating showed CO<sub>x</sub> conversion between 17.4% and 24.6% (CO conversion: 18.3%-28.4% and CO<sub>2</sub> conversion: 1.5%-13.1%, respectively) and aromatics selectivity between 65% and 76%. It is worth mentioning that Cr<sub>2</sub>O<sub>3</sub> combined with a gallium exchanged and silica coated ZSM-5 zeolite performed with the highest Co<sub>x</sub> conversion (24.6% Co<sub>x</sub>, 28.4% CO, 1.5% CO<sub>2</sub>) and simultaneously with the highest selectivity to aromatics (76.4%) of the tested bifunctional catalysts. Additionally, the silica coating of the ZSM-5 zeolite reduced the alkylation of aromatics on the external acid sites of the zeolite, hence increasing the C<sub>6</sub>-C<sub>8</sub> aromatics selectivity to 55%. *p*-Xylene was formed with 38.6% selectivity.

Analog to the OX-ZEO to olefins reaction, the production of aromatics can also be achieved by CO<sub>2</sub> hydrogenation and reach CO<sub>2</sub> conversion levels between 9% and 41% and selectivities to aromatics of up to 76% <sup>394</sup>. Using a chromium-doped ZrO<sub>2</sub> aerogel catalyst combined with an H-ZSM-5@SiO<sub>2</sub> zeolite CO<sub>2</sub> conversion of 14% was achieved with 77% aromatics selectivity, of which 2/3 were light aromatics (C<sub>6</sub>-C<sub>8</sub>) <sup>395</sup>. The methane selectivity was low with only 1.1%.

### 2.4.2. Benefits

**Combination of FT catalyst and zeolite:** The performance of the CO activation catalyst (FT catalyst) does not depend on the equilibrium between synthesis gas and the reactive intermediate. This gives more freedom in the catalyst bed and reactor design. Hence a range of different configurations is reported, from iron nano particles directly anchored on the zeolite <sup>396</sup>, and mixing individual catalyst grains in the catalyst bed, to stacked bed and tandem reactor design in which the individual catalysts are spatially separated (Figure 2-13-B)<sup>358</sup>.

Interestingly, combining a sodium and sulfur promoted FTO catalyst and an H-ZSM-5 zeolite in a physical mixture caused a 1.8-fold activity enhancement of the FTO catalyst compared to the FTO catalyst without zeolite or in stacked bed mode, where the two functions are spatially separated <sup>113</sup>. Although not fully understood, Mößbauer spectroscopy measurements revealed an enhanced formation of iron carbide, which is the active phase in the FTO reaction for the physical mixture of FTO catalyst and zeolite. Here, 83% of the iron was transformed into an iron carbide phase after a 1 h carburization step at 290°C and atmospheric pressure, whereas the FTO catalyst without zeolite only showed 57% carbide formation. Hence unexpected benefits can arise from the close coupling of the two functions <sup>397</sup>.



**Figure 2-14:** Equilibrium CO conversion for methanol synthesis from synthesis gas (H<sub>2</sub>:CO=2 mol/mol) as function of reaction pressure for 260°C (dotted red line) and 400°C (solid green line) and reported CO conversion as function of pressure for the OX-ZEO process operated at 400°C (open green circles) exceeding the equilibrium CO conversion of the single pass methanol synthesis at 400°C  $^{355,378,380}$ .

**OX-ZEO:** A clear asset of the OX-ZEO process is the enhanced conversion with the bifunctional catalyst system, which exceeds the equilibrium CO conversion in a single pass over a CO activation catalyst alone. Taking methanol as an intermediate, the CO conversion would be thermodynamically limited to 1.4% at 50 bar or 1.9% at 60 bar, when operating at 400°C (Figure 2-14). In the OX-ZEO process the intermediates are effectively

removed from this equilibrium by the aromatization reaction, resulting in CO conversions as high as 55% at 50 bar or 22% at 60 bar <sup>355,380</sup>. This corresponds to an 11-fold to 40-fold activity enhancement at the same temperature and allows the OX-ZEO process to operate at 400°C with similar CO conversions as methanol synthesis typically operated at 260°C (Figure 2-14 - dotted red line) <sup>271</sup>.

Furthermore, the OX-ZEO process has a high fraction of aromatics in the hydrocarbon products compared to FT+zeolite. The formation of aromatics from methanol follows a dual cycle mechanism in which higher olefins are formed in the alkene cycle that undergo aromatization to enter the aromatic cycle as shown in Figure 2-3  $^{134}$ . The aromatization of higher olefins is based on the following steps: formation of dienes, cyclization to cyclic olefins, formation of cyclic dienes and formation of aromatics (Figure 2-13-A). Commonly reported, the formation of dienes, formation of cyclic dienes and the aromatization is based on hydrogen transfer, in which also paraffins are formed at the expense of olefins. However, operating the OX-ZEO process at high temperatures and low reactive intermediate concentrations facilitates the aromatization via dehydrogenation, forming molecular hydrogen instead of paraffins <sup>373</sup>. Therefore, the OX-ZEO shows higher selectivity than FT+zeolite, which operates at lower temperatures and higher concentrations of reactive intermediates. In FT+zeolite, the aromatization is more likely to follow hydrogen transfer and form undesirable paraffins <sup>358,365</sup>. Furthermore, the product spectrum of the CO activation catalyst (FT catalyst) depends on the ASF distribution and the maximum selectivity of suitable intermediate products to be converted into aromatics is limited <sup>398</sup>.

The OX-ZEO process shows stabilities that exceed the stability of the methanol-toaromatics process. The group of Prof. Wang presented an OX-ZEO catalyst system consisting of a zinc zirconium oxide catalyst and H-ZSM-5 zeolite, which showed stable performance with 80% selectivity to aromatics and CO conversion of 20% over the course of 1000 h at 400°C and 30 bar <sup>344</sup>. In the methanol-to-aromatics reaction the activity in methanol conversion drops significantly after 5-200 h, when operated at the same reaction temperature <sup>155,399,400</sup>. Due to the low partial pressure of reactive intermediates, zeolites with high siliconaluminum ratios and hence low density of strong acid sites can be used in the aromatization reaction, which is beneficial for the zeolite stability. <sup>278,344</sup>. Additionally, the low partial pressure of intermediates and the high reaction temperature contribute to the catalyst stability albeit at the expense of activity of the metal oxide catalyst <sup>373</sup>. Another explanation for the stability expressed in hours could be the low productivity of the OX-ZEO catalysts (~0.04 kg<sub>aromatics</sub> kg<sub>catalyst</sub><sup>-1</sup> h<sup>-1</sup>) compared to the MTA process (~0.4-1.4 kg<sub>aromatics</sub> kg<sub>catalyst</sub><sup>-1</sup> h<sup>-1</sup>), which leads to a lower rate of coke formation <sup>155,344,399</sup>.

# 2.4.3. Challenges

**Combination of FT catalyst and zeolite:** A great challenge for the FT+zeolite approach is to find optimum reaction conditions. High temperatures generally give a high

methane and lower olefin production in the first step, not allowing aromatization. Hence a high temperature FT catalyst with a suitable alpha value, low methane selectivity and high olefin to paraffin ratio is needed to be combined with an H-ZSM-5 zeolite in a high temperature process. Alternatively, a zeolite or another solid acid capable of converting olefins at low temperatures into aromatics needs to be identified. Dopants such as gallium or zinc can increase the performance at lower temperatures, as it was shown for the aromatization of propane <sup>401</sup>. Furthermore, these dopants can lead to increased dehydrogenation activity, shifting the aromatization pathway away from hydrogen transfer towards dehydrogenation <sup>402,403</sup>. However, the dehydrogenation activity of the dopants incorporated in the zeolites can also facilitate secondary hydrogenation of the olefins intermediates that are formed on the FT catalyst.

The addition of sodium and sulfur promoters to a supported iron carbide based Fischer-Tropsch to olefins (FTO) catalyst decreased the methane production from synthesis gas and gave a high selectivity towards short olefins <sup>404,405</sup>. Combining this promoted FTO catalyst with an H-ZSM-5 zeolite enabled the direct synthesis of aromatics from synthesis gas <sup>113</sup>. However, in close proximity of the FTO catalyst to the zeolite, higher methane selectivities (15% in stacked bed mode and 30-35% in close proximity) and lower aromatics selectivities (12% in stacked bed mode and 5% in close proximity) were observed, probably due to migration of alkaline promoters from the FTO catalyst to the zeolite, which led to neutralization of the acid sites on the zeolite <sup>15,406</sup>. The migration of promoters and the accompanying effects on the catalytic performance could be circumvented by placing the zeolite downstream of the FTO catalyst in a stacked bed mode. Alternatively, by using carbon nanofibers as support material, the migration of promoters was suppressed, despite close proximity of the two catalytic functions <sup>15</sup>. This shows that controlling the mobility of mobile species, such as promoters or dopants, is crucial for the design of bifunctional catalysts for this process.

**OX-ZEO:** For effective OX-ZEO catalysts, optimizing the hydrogenation activity of the metal oxide) is crucial. It needs to be low enough to avoid significant secondary hydrogenation, but still provide sufficient activity to convert synthesis gas into reactive intermediates. The hydrogenation activity of the metal oxide can be controlled among others by the molar composition of mixed oxides <sup>344</sup>. Using a zinc zirconium oxide catalyst in combination with an H-ZSM-5 zeolite, it was shown that zinc oxide is mainly responsible for hydrogen activation in the metal oxide catalyst. A low zinc content of Zn:Zr = 1:1000 mol/mol resulted in low CO conversion (14%) in combination with high selectivity to aromatics (76%), whereas the CO conversion increased (43%) and the selectivity to aromatics decreased (7%) with increasing zinc content (Zn:Zr = 1:5 mol/mol). Furthermore, the selectivity to short paraffins increased from 18% to 52% with the same change in zinc fraction, indicating that a high zinc content enables secondary hydrogenation of reactive intermediates. Hence, a high hydrogenation activity towards aromatics.

This hypothesis was supported by experiments performed with a cerium zirconium oxide catalyst mixed with an H-ZSM-5 zeolite, for which the selectivity towards aromatics and olefins decreased with increasing hydrogen content in the synthesis gas <sup>364</sup>. Operating at 450°C and 20 bar, the OX-ZEO catalyst showed 13.3% olefins in the range of C<sub>2</sub> to C<sub>4</sub> and 56.3% aromatics selectivity at a hydrogen to carbon monoxide ratio of 1 (v/v). Increasing the hydrogen content of the synthesis gas to H<sub>2</sub>:CO = 2 (v/v) led to decreased selectivity to short olefins of 3.4% and aromatics of 35.2%. This shows that for the OX-ZEO catalyst the hydrogenation activity needs to be carefully optimized.

### 2.4.4. Process comparison

In this section we focus on the overall selectivity to aromatics. Figure 2-15-A shows the best reported aromatic yields as function of the CO conversion for the OX-ZEO process and for FT+zeolite. To compare, we added the aromatic yields of a dual reactor process in Figure 2-15-B, calculated from a combination of reported data for a methanol synthesis reactor  $^{352,353}$  and a reactor for the methanol-to-aromatics (MTA) process  $^{155,399,403,407}$ . The slopes of the yields plotted against the CO conversion correspond to the overall selectivity of the processes (taking the formation of CO<sub>2</sub> as one of the alternative products into account).



**Figure 2-15:** A: Reported yields of aromatic hydrocarbons as function of CO conversion for the OX-ZEO process (green circles) and combination of FT catalyst and zeolite (red squares). The filled green circles show the yield to aromatics as function of CO conversion of the OX-ZEO process with reduced WGS activity B: Calculated overall aromatic selectivity resulting from the combination of a methanol synthesis reactor and a reactor for methanol aromatization via hydrogen transfer (open gray triangles) and dehydrogenation (solid gray triangles) in a dual reactor process. The slopes of the fitted lines correspond to the overall selectivity of the process. A detailed analysis of the catalytic data can be found in the supplementary information of *Catal. Sci. Technol.* **14**, 4799-4842 (2024) <sup>295</sup>.

The combination of an FT catalyst with a zeolite showed an average selectivity to aromatics of ~26%. The results are distributed over a range of 9%-41%. Li *et al.* found that in the conversion of synthesis gas to aromatics the intimacy within the bifunctional catalysts played a crucial role for the selectivity, which can explain these wide-spread selectivities <sup>408</sup>. The overall selectivity is rather low which can be explained by limited selectivity to suitable olefinic intermediates in the first step. Furthermore, the temperature needed for the CO activation catalyst favors the aromatization to follow the hydrogen transfer pathway, forming three molecules of paraffins from olefins for every aromatic molecule being formed <sup>373</sup>.

The OX-ZEO process for aromatics showed a higher overall selectivity of 41% to aromatics, resulting from a high fraction of aromatics in the hydrocarbon products between 49% and 86% but also high selectivities to CO<sub>2</sub> in the range of 17% to 49% <sup>364,379</sup>. The high aromatics fraction can be explained by the low partial pressure of reactive intermediates and the high reaction temperature, shifting the aromatization towards dehydrogenation <sup>373</sup>. The OX-ZEO process shows a selectivity to paraffinic hydrocarbon side products as low as 6% <sup>344,379</sup>. The high CO<sub>2</sub> selectivity is caused by the WGS activity of the OX-ZEO catalysts and is in the same range as for the FT+zeolite systems, showing 16-49% CO<sub>2</sub> selectivity <sup>365</sup>. However, tailoring an OX-ZEO catalyst to reduced WGS activity and adapted feed compositions showed that selectivities to aromatics of ~70% are possible (Figure 2-15-A) <sup>393,409</sup>.

The calculated overall aromatic selectivity resulting from the combination of a methanol synthesis reactor and a reactor for the MTA process shows a selectivity to aromatics of ~41% (Figure 2-15-B, open triangles), which is higher than FT+zeolite and in the same range as the OX-ZEO process. We based these calculations on reported catalytic data of single pass conversions of synthesis gas over methanol synthesis catalysts with CO conversion ranging from 9% to 47% and methanol selectivities of 97-99.8% 352,353. Consecutively, methanol is converted into aromatics via suitable zeolite catalysts in a separate MTA process. A moderate selectivity to aromatics from methanol was reported between 33% and 50%, which is in good agreement with the dual cycle mechanism in combination with hydrogen transfer, in which a substantial amount of paraffins of usually ~40% is formed  $^{155,399,403,407}$ . This decreases the overall selectivity to aromatics, despite the absence of WGS activity and therefore no significant formation of  $CO_2$  in this approach. However, a zinc doped H-ZSM-5 zeolite operated at high temperature of 475°C showed a selectivity to aromatics of 96% in the conversion of methanol, due to aromatization via dehydrogenation <sup>156</sup>. The theoretically calculated maximum overall selectivity to aromatics from the combination of methanol synthesis and aromatization via only dehydrogenation in a dual reactor process was ~95% (Figure 2-15-B, solid triangles).

The high CO<sub>2</sub> production in both the OX-ZEO process and FT+zeolite presents a great challenge for the conversion of hydrogen-rich synthesis gas to aromatics. According to the proposed reaction mechanism for the OX-ZEO process to form olefins with ketene intermediates, the formation of CO<sub>2</sub> is inevitable, since the oxygen from carbon monoxide is

removed from the surface of the metal oxide catalyst via CO oxidation <sup>315</sup>. Iron carbide-based FT catalysts with high olefin selectivity commonly show high WGS activity and CO<sub>2</sub> selectivities between 21% and 50% <sup>351,410</sup>. The WGS of cobalt carbide-based FT catalysts is slower and leads to CO<sub>2</sub> selectivities between 2% and 13% <sup>361</sup>. However, for the cobalt carbide-based catalysts the selectivity to short olefins is rather low (17-30% in the hydrocarbons). Hence, an important challenge for bifunctional catalysis is the suppression of CO<sub>2</sub> formation and the combination of cobalt carbide-based FT catalysts (with increased olefin selectivity) with a zeolite seems to have the potential to achieve this <sup>411</sup>.

However, selectivity is not the only important factor determining the feasibility of a process. To analyze the economic feasibility of a process for the direct conversion of synthesis gas to aromatics, technical-economical aspects were simulated by Song et al. using ASPEN software <sup>412</sup>. Here, the direct conversion of synthesis gas to aromatics was compared to a dual reactor process, whereas synthesis gas was first converted to methanol and the methanol was further converted to aromatics. The simulation did not only include the reaction unit, but also units for quenching the reaction mixture, compression, distillation, cyclic absorption separation and pressure swing absorption. The catalytic data were based on 70% CO conversion per pass over the methanol synthesis catalyst and a fraction of 70-80% aromatics in the liquid products after passing an H-ZSM-5 zeolite. It was shown that a low CO conversion resulted in a low yield of aromatics and therefore low partial pressure, which gave additional challenges in product condensation and separation. To compete with a dual reactor approach with separate methanol synthesis and aromatization at individual reaction conditions, a novel bifunctional process needs to give a minimum of 66% CO conversion per pass with an aromatic fraction of 70-80% in the liquid products and very low  $CO_2$ selectivities. Both approaches, the OX-ZEO process and FT+zeolite, are currently not meeting these requirements.

### 2.5. Liquid Fuels

The products formed in the Fischer-Tropsch synthesis are always a mixture of hydrocarbons with various chain lengths. The maximum selectivity to C<sub>5</sub>-C<sub>11</sub> products in the Fischer-Tropsch synthesis is 48% for a chain growth probability of  $\alpha = 0.76$  according to the ASF distribution (Figure 2-16-A) <sup>382</sup>. Increasing the production of liquid transportation fuels requires operating at higher  $\alpha$ -values and cracking the resulting Fischer-Tropsch products with a too high chain length to the desired fraction.

Chapter 2



**Figure 2-16 A:** Anderson Schulz-Flory distribution of Fischer-Tropsch products showing a maximum selectivity to the C<sub>5</sub>-C<sub>11</sub> fraction of 48% at chain growth probability of  $\alpha = 0.76^{-382}$ ; **B:** Equilibrium distribution of C<sub>5</sub>-C<sub>11</sub> paraffin isomers at 250°C and 20 bar. This represents the thermodynamic limitation for isomerization of *n*-paraffins. (Calculated with Outotec HSC 9.6.1)

The octane number is relevant for gasoline and strongly increases with a smaller size and a higher degree of branching of hydrocarbons <sup>413</sup>. In general, the octane numbers of a hydrocarbon molecule with the same number of carbon atoms follow the trend of paraffins < olefins < aromatics (e.g., n-hexane: 19, 1-hexene: 85 and benzene: 108) <sup>158,414-416</sup>. Figure 2-16-B shows the thermodynamic distribution of isomers according to the ASF distribution at 250°C and 20 bar for C<sub>5</sub>-C<sub>11</sub> paraffins, grouped by degree of branching. The maximum conversion of linear paraffins in the secondary isomerization is between 75% and 91%, leaving 9% - 15% *n*-paraffins un-isomerized. The main products are mono- or di-branched paraffins with 45% - 68% and 19% - 42% shares, respectively <sup>413</sup>. The highly branched paraffins are key for a high-octane number, but only constitute 2% - 4% of the product mixture for tri-branched and 0.1% - 0.2% quad-branched paraffins. To convert paraffinic FT waxes into suitable gasoline fuels with octane numbers of ~90 by the formation of aromatics, temperatures above 500°C are applied <sup>417</sup>.

## 2.5.1. Recent developments

Different bifunctional catalysts, in particular for the direct production of gasoline from synthesis gas have been developed over the past years. These catalysts consist of ironor cobalt-based Fischer-Tropsch catalysts, methanol or DME catalysts, or (mixed) metal oxides as the primary functional group and zeolites for the secondary conversion to gasoline. Some studies have also employed noble metals supported on zeolites, since these are industrially used as hydrocracking catalysts to upgrade paraffines by isomerization and cracking <sup>418</sup>.

Fischer-Tropsch catalysts can be combined with different zeolites, such as H-ZSM-5, SAPO-11, SSZ-13, mordenite, Y or beta, in order to overcome the limitations for the selectivity to  $C_5$ - $C_{11}$  products according to the ASF model <sup>419–422</sup>. Both pore structure and acidity of these zeolites play a crucial role in the final product distribution <sup>419,423–425</sup>. Acidity plays a major role for primary cracking and isomerization, whereas porosity affects the secondary olefin isomerization by micropore diffusion limitations <sup>426</sup>. Larger pore sizes of zeolites facilitate the formation of multi-branched isomer products and strong acidity can cause over-cracking to lighter products <sup>427</sup>. Hydrocracking catalysts such as Pt/ZSM-5 were also effective for the secondary conversion of the Fischer-Tropsch products <sup>418,428</sup>.

Co/SiO<sub>2</sub> catalysts with different average pore diameters (10 nm and 50 nm) were used as silicon source for a Co containing zeolite catalyst with a hierarchical pore structure for the direct conversion of syngas to gasoline fuel <sup>41</sup>. The resulting catalysts with the zeolite in Na-form showed high selectivities towards C<sub>5</sub>-C<sub>11</sub> of 65-68% and 14-25% iso-paraffins in the hydrocarbon products, whereas the Co/SiO<sub>2</sub> catalyst alone displayed 48-49% selectivity to C<sub>5</sub>-C<sub>11</sub> products with 11-19% iso-paraffins. After ion-exchange to convert the zeolite into the proton form, the C<sub>5</sub>-C<sub>11</sub> selectivity remained at the same level, but the fraction of isoparaffins increased to 35-37%. The selectivity to C<sub>5</sub>-C<sub>11</sub> products was further increased by the introduction of mesopores to the catalyst <sup>429</sup>. Additionally, the presence of mesopores in an H-ZSM-5 support can increase the dispersion of the Co nanoparticles and hence the overall activity <sup>430</sup>. Co/Al<sub>2</sub>O<sub>3</sub> catalyst with multimodal porosity in a dual bed configuration with a Pt/nano-ZSM-5 hydrocracking catalyst showed a 2-fold increase of hydrocarbon products in the middle distillate fraction (C<sub>10</sub>-C<sub>24</sub>) compared to the configuration with a mono-modal Co/Al<sub>2</sub>O<sub>3</sub> FT catalyst <sup>428</sup>.

Experiments with different average distances between Co and acid sites of an H-ZSM-5 zeolite showed a maximum selectivity to  $C_5$ - $C_{11}$  products for proximity in the µm-range <sup>431</sup>.  $C_5$ - $C_{11}$  products were formed with 89.5% selectivity and 35.5% isomers in the  $C_{5+}$  products at 270°C, 20 bar and conversion between 71% and 92%. Additionally, mesoporous H-ZSM-5 zeolite coated with a pyrolytic carbon layer prior to impregnation with Co precursor showed enhanced reducibility of the cobalt oxide, low CH<sub>4</sub> selectivity and higher selectivity to  $C_5$ - $C_{11}$  than the catalyst system without carbon layer, due to reduced metal-support-interaction. <sup>432</sup>

The influence of the amount of acid sites has also been studied. Co/MCF and nanosized H-ZSM-5, with different mass ratios in the physical mixture, showed that with increasing zeolite mass content, the selectivity to  $C_{12+}$  products decreased from 50% (Co/MCF alone) to 6% for Co/MCF:Z = 1:4 m/m <sup>433</sup>. Also, the C<sub>2</sub>-C<sub>4</sub> selectivity increased from 6% to 23% and the sum of iso-paraffins and olefins increased from 17% to 52% in the hydrocarbon products. The C<sub>5</sub>-C<sub>11</sub> selectivity showed a plateau at medium zeolite content (34% for Co/MCF, 54% for Co/MCF:Z = 1:1 m/m, 45% for Co/MCF:Z = 1:4 m/m).

Iron-based Fischer-Tropsch catalysts allow to form a larger fraction of olefins in the products and are usually operated at higher temperatures compared to cobalt-based Fischer-Tropsch catalysts <sup>434</sup>. The addition of a zeolite to an iron-based Fischer-Tropsch catalyst can promote the formation of aromatics, which significantly raises the octane number of the C<sub>5</sub>-C<sub>11</sub> product fraction. A co-precipitated iron-based Fischer-Tropsch catalyst containing Cu, Mg and K as promoters showed 53% selectivity to C<sub>5</sub>-C<sub>11</sub> products of which 4% were aromatics (300°C, 10 bar, CO conversion 70-90%) <sup>435</sup>. The addition of an H-ZSM-5 with medium concentration of acid sites (Si/Al=240) by physical mixing increased the selectivity to C<sub>5</sub>-C<sub>11</sub> products to 67% with 73% aromatics in this fraction. A physical mixture of the iron-based Fischer-Tropsch catalyst with an H-ZSM-5 with high acid site concentration (Si/Al=40) increased content of aromatics in the C<sub>5</sub>-C<sub>11</sub> hydrocarbon fraction to 90%, however, the total C<sub>5</sub>-C<sub>11</sub> fraction decreased to 58% due to over-cracking and increased formation of C<sub>1</sub>-C<sub>4</sub> products. Additionally, the olefins/paraffin ratio increased 3-7-fold upon zeolite addition compared to the Fischer-Tropsch catalyst alone. All experiments showed high water-gas-shift activities with 40 - 44% CO<sub>2</sub> formed.

Coating the iron-based catalyst with a hydrophobic methylated silica layer decreased the formation of  $CO_2$  <sup>436</sup>. Further addition of an HZSM-5 zeolite packed below the FTS catalyst in the reactor led to a high C<sub>5</sub>-C<sub>11</sub> selectivity (62.5% at 260°C, 20 bar and 50% CO conversion) and low CO<sub>2</sub> selectivity (14.3%). The authors showed that the diffusion of water through the hydrophobic layer was unidirectional, which led to a reduced CO<sub>2</sub> formation by hampering the water-gas shift reaction on the iron-based catalyst.

An Fe/SiO<sub>2</sub> core/shell catalyst was tested in the direct conversion of synthesis gas to gasoline <sup>437</sup>. The silicalite-1 membrane applied onto the core catalyst served as protection as well as anchor point for the functional H-ZSM-5 membrane. This catalyst showed similar CO conversions (55 – 60%) and C<sub>5</sub>-C<sub>11</sub> selectivities (49 – 53%, CO<sub>2</sub>-free) as the base core catalyst or the core catalyst in physical mixture with H-ZSM-5 at 280°C and 10 bar. The selectivity to iso-paraffins was 30% higher for the core/shell catalyst than for the core catalyst alone and the physical mixture with hereof, which was ascribed to hydrogenation and isomerization of olefins, next to hydrocracking and isomerization of C<sub>12+</sub> hydrocarbons.

Combining a zinc-manganese-oxide catalyst with different 10-membered ring zeolites revealed that the OX-ZEO process allows to form  $C_5$ - $C_{11}$  products with a high selectivity of up to 77% <sup>382</sup>. The product spectrum of the ZnMnOx catalyst mixed with SAPO-11 showed only 6% *n*-paraffins in the  $C_5$ - $C_{11}$  aliphatics as well as 16% aromatics in

 $C_5-C_{11}$ . The CH<sub>4</sub> selectivity was remarkably low (2.3%). Introducing mesopores into an H-ZSM-5 zeolite of a zinc-chromium-oxide containing OX-ZEO catalyst enhanced the selectivity to  $C_{5+}$  from 20% to 61%, while maintaining the low CH<sub>4</sub> selectivity <sup>194</sup>. Conversion of ketene, which is thought to be an intermediate in OX-ZEO catalysts, using H-SAPO-11 has been studied to elucidate the reaction mechanism to form C<sub>5</sub>-C<sub>11</sub> hydrocarbons <sup>438</sup>. The authors showed by in situ IR and quasi-in situ ssNMR spectroscopy that ketene transforms via either an acetic acid ketonization pathway or an acetoacetic acid decarboxylation pathway to acetone, butene, and C<sub>5</sub>-C<sub>11</sub> hydrocarbons.

A DME catalyst (Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>+ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) allows to convert synthesis gas to DME with 90% selectivity (CO<sub>2</sub> free) at 300°C, 30 bar and 65% CO conversion <sup>439</sup>. In a physical mixture with a nano-sized H-ZSM-5, a DME-to-gasoline (DTG) catalyst, the CO conversion increased to 75%,  $C_5$ - $C_{11}$  products were formed with 26% selectivity and  $C_1$ - $C_2$  products with a selectivity of 20%. Figure 2-17 illustrates the difference between the dual bed and dual reactor configurations. The dual bed configuration can have dedicated temperatures for the individual catalyst beds applied in a single reactor. The dual reactor configuration consists of two consecutive reactors with removal of intermediates between the reactors <sup>358,439</sup>. Placing the two different catalysts in a dual bed configuration (Figure 2-17-A) with the DME catalyst upstream led to an increase of  $C_5$ - $C_{11}$  selectivity to 76% and only 5%  $C_1$ - $C_2$ . When the dual bed configuration was operated with dedicated temperatures for each catalyst (DME catalyst at 260°C and DTG catalyst at 320°C) the CO conversion increased to 87% and the  $C_1$ - $C_2$ selectivity decreased to 1.7%. C<sub>5</sub>-C<sub>11</sub> products were formed with 79% selectivity, of which 34% were aromatics. It was also found that C<sub>5</sub>-C<sub>11</sub> aliphatics consisted of 95% isomerized products. Increasing the temperature of the DTG catalyst bed caused the  $C_5$ - $C_{11}$  and aromatics selectivity to decrease. Additionally, nano-sized H-ZSM-5 DTG catalysts with medium Si/Al ratio and medium acid sites concentration show superior stability in the DME conversion to  $C_5$ - $C_{11}$  products, compared to zeolites with a higher acid site concentration due to reduced coke formation on the zeolite.



Figure 2-17: Illustration of bifunctional catalysis performed in (A) dual bed and (B) dual reactor configuration.

### 2.5.2. Benefits

In the following paragraphs we illustrate the potential benefits of bifunctional catalyst systems for the direct production of fuels compared to the operation in multiple individual reactors.

An OX-ZEO catalyst capable of converting synthesis gas into gasoline showed a high content of 95% of branched isomers in the C<sub>5</sub>-C<sub>11</sub> aliphatics (non-aromatic molecules) fraction <sup>382</sup>. In the OX-ZEO process branched molecules are predominantly by the alkylation of hydrocarbons with oxygenates such as MeOH, DME, or ketene <sup>440–442</sup>. The dual bed process with a methanol synthesis or FTO catalyst in the first bed and zeolite at high temperature (320°C) in the bed downstream showed a low selectivity to linear C<sub>5</sub>-C<sub>11</sub> paraffins of 3% and 4%, respectively <sup>358,439</sup>. At high temperatures, in the zeolite bed oligomerization of short iso-olefins acts as an additional source of C<sub>5</sub>-C<sub>11</sub> branched molecules next to isomerization of linear aliphatics, which also holds for medium- and high-temperature operation of iron-based Fischer-Tropsch catalysts combined with zeolites <sup>398</sup>.

Fischer-Tropsch catalysts can form a liquid product layer around the metal particles, inside the support's pores or in the void space between the catalyst particles. This may result in H<sub>2</sub> and in particular CO profiles as a function of distance to the catalyst surface as schematically illustrated in Figure 2-18<sup>443-450</sup>. Hydrogen diffuses 2-3 times faster through FT wax than carbon monoxide <sup>451-453</sup>, although the latter has a ~20% higher solubility <sup>454-457</sup>. As a result, the H<sub>2</sub>/CO ratio at the catalyst surface can be significantly higher than in the bulk of the reactor, leading to lower C<sub>5+</sub> and higher CH<sub>4</sub> selectivities with increasing catalyst particle size and liquid layer thickness <sup>458-460</sup>. Experiments with a core/shell catalyst consisting of a Co/SiO<sub>2</sub> core and H-ZSM-5 shell showed a reduced CH<sub>4</sub> selectivity compared

to the Co/SiO<sub>2</sub> alone (10.3% vs. 25.7%) together with a reduced selectivity to  $C_{11+}$  (0.3% vs. 15.3%) at 280°C, 10 bar and full conversion <sup>236</sup>.



**Figure 2-18:** Illustration of the concentration profile of hydrogen and carbon monoxide through the gas phase and the liquid product layer to the catalyst surface with different liquid product layer thicknesses. **A:** A thick layer of liquid products increases the effective  $H_2$ :CO ratio on the catalyst surface. **B:** Reduction of the liquid layer thickness leads to a lower  $H_2$ :CO ratio on the catalyst surface.

An often claimed benefit for the conversion of synthesis gas to gasoline using bifunctional catalysis is the lower investment costs for a single reactor <sup>431</sup>. However, Fischer-Tropsch reactors may have higher costs per installed unit compared to a dedicated reactor filled with a hydrocracking/isomerisation catalyst <sup>461</sup>. Hence, the lower investment costs for a larger Fischer-Tropsch reactor (to accommodate the Fischer-Tropsch catalyst and the zeolite) compared to two separate reactors seems to be limited.

### 2.5.3. Challenges

Catalysts containing noble metals for hydrocracking are widely employed and their performances maximized. However, when employed for *in-situ* hydrocracking of Fischer-Tropsch products in bifunctional catalysts, poisoning of the noble metal with carbon monoxide reduces the hydrotreating performance of these catalysts  $^{418,462-464}$ . The conversion of long chain paraffins is reduced 4.3-fold over a Pt/ZSM-5 catalyst in the presence of synthesis gas compared to H<sub>2</sub> atmosphere  $^{418}$ . Olefins still undergo isomerization and cracking on the acid sites of the zeolite.

The liquid wax filling the FT catalyst pores can reduce catalyst activity by causing mass transfer limitation for synthesis gas <sup>443–450</sup>. Removal or reduction of this product layer by operating alternatingly at Fischer-Tropsch and hydrogenolysis conditions can lead to enhanced activity and stability of the Fischer-Tropsch catalysts <sup>465</sup>. However, a combination of Fischer-Tropsch catalyst with a zeolite to reduce the product layer by cracking did not show significant activity enhancement and displayed a similar turn-over-frequency as the FT catalyst alone <sup>423,430,466,467</sup>, despite an altered ASF distribution <sup>432</sup>.

#### 2.5.4. Process comparison

Figure 2-19-A and Figure 2-19-B show the yield to  $C_5-C_{11}$  products for the bifunctional catalysts consisting of Co-based Fischer-Tropsch catalysts and solid acids (Co+Z), iron-based Fischer-Tropsch catalysts with zeolite (Fe+Z), the OX-ZEO process for the synthesis of gasoline (OX-ZEO) as function of CO conversion. Additionally, the C<sub>5</sub>-C<sub>11</sub> yield of dual bed approaches is shown. Furthermore, Figure 2-19-B contains the yield of C<sub>5</sub>-C<sub>11</sub> hydrocarbons as function of CO conversion of two separate processes (dual reactor process, Figure 2-17-B) that involves methanol synthesis and separation in the first process and the methanol to gasoline (MTG) as the second process. <sup>358,439</sup> The slopes for the individual approaches correspond to the overall C<sub>5</sub>-C<sub>11</sub> selectivity and take the formation of CO<sub>2</sub> into account. As a reference the maximum yield as function of CO conversion resulting from the ASF distribution (48% selectivity for C<sub>5</sub>-C<sub>11</sub>) is shown as well.

Co+Z, Fe+Z and OX-ZEO show overall selectivities to  $C_5$ - $C_{11}$  of 54%, 22% and 39%, respectively. The dual bed process allows to produce  $C_5$ - $C_{11}$  products with 51% selectivity. The scattering is due to the fact that the  $C_5$ - $C_{11}$  selectivity is influenced by many parameters, such as reaction conditions, type of bifunctional catalyst, and nature of the zeolite. Fe+Z shows a low overall selectivity to  $C_5$ - $C_{11}$  products (22%) resulting from a moderate fraction of  $C_5$ - $C_{11}$  (10-55%) in the hydrocarbon products and much CO<sub>2</sub> production due to the high WGS activity <sup>375,398</sup>. Inhibiting the WGS can increase the  $C_5$ - $C_{11}$  selectivity (62%) <sup>436</sup>. Cobalt-based FT catalysts show low WGS activity, (only 1%-4% CO<sub>2</sub>) thus Co+Z can have a higher overall selectivity to  $C_5$ - $C_{11}$  products (56%) <sup>421</sup>. The OX-ZEO process displays a large fraction of  $C_5$ - $C_{11}$  in the hydrocarbons (67%-77%), but with a high WGS activity (~50% CO<sub>2</sub>) the overall selectivity is reduced to 39% <sup>306,382</sup>.



**Figure 2-19: A:** Yield of  $C_5$ - $C_{11}$  hydrocarbons as function of CO conversion for Co+Z and Fe+Z; **B:** Yield of  $C_5$ - $C_{11}$  hydrocarbons as function of CO conversion for OX-ZEO, dual bed configuration and separated dual reactor processes **C:** the calculated octane number and **D:** methane selectivity for the combination of cobalt-based FT catalysts with zeolites (Co+Z), whereas zeolites were 12-membered ring or 10-membered ring zeolites or non-microporous solid acids (NMPA), iron-based FT catalysts with zeolite (Fe+Z), the OX-ZEO process and the combination of DME or FTO catalysts with zeolites in a dual bed configuration. The solid diamond in A indicates a combination

of iron-based FT catalyst with zeolite showing reduced CO<sub>2</sub> selectivity of 14.3% <sup>436</sup>. A cobalt-carbide based FTO catalyst combined with a zeolite is shown in C and D as red triangle (first point of the Fe+Z series) <sup>411</sup>. The horizontal grey bars in C and D highlight the octane numbers needed to use the  $C_5$ - $C_{11}$  fraction directly as gasoline fuel and the typical methane selectivities of the HT-FTS for comparison, respectively.

The dual bed processes show a C<sub>5</sub>-C<sub>11</sub> selectivity of 51%, which is comparable to the highest possible selectivity predicted by the ASF distribution. This selectivity results from a high fraction of C<sub>5</sub>-C<sub>11</sub> in the hydrocarbon products (70%-78%) and a significant WGS activity (32%-38% CO<sub>2</sub> formed) which reduces the overall C<sub>5</sub>-C<sub>11</sub> selectivity <sup>358,439</sup>. A combination of separate processes (MeOH synthesis, MeOH recovery, MTG process) could potentially show much higher overall selectivity of 96-99%, due to high selectivities of the MeOH synthesis (97-99%) <sup>352,353</sup> and the MTG process (up to 99%) <sup>442</sup> (Data can be found in the supplementary information of *Catal. Sci. Technol.* **14**, 4799-4842 (2024) <sup>295</sup>).

Based on reported catalytic performance of bifunctional catalysts for the direct conversion of synthesis gas to gasoline we calculated the octane number of the corresponding  $C_5-C_{11}$  fraction (Figure 2-19-C) for different approaches: Co+Z, Fe+Z and OX-ZEO. Additionally, we added dual bed processes with direct DME synthesis or FTO catalyst in the first bed and a zeolite in the bed downstream. These processes have different temperatures for the individual catalyst beds but do not separate the intermediate products after the first catalytic conversion from unreacted reactants or formed side products. The detailed analysis and calculation of the octane numbers can be found in Appendix A.

The linear C<sub>5</sub>-C<sub>11</sub> paraffin products of a Co-based FTS catalyst with ASF product distribution at  $\alpha$ =0.76 without zeolite have a low octane number (~1.5). The combination of Co-based Fischer-Tropsch catalysts and a zeolite increases octane numbers to between 13 and 72. The use of zeolites with different pore dimensions, namely 10- or 12-membered-ring pores, does not affect the resulting octane number significantly. Iron-based Fischer-Tropsch catalyst mixed with zeolites show higher octane numbers of the C<sub>5</sub>-C<sub>11</sub> products of 65-91. Also, the OX-ZEO process allows high octane products with an octane number of 73-89. The dual bed processes with different temperatures for the catalyst beds exhibit high octane numbers between 88 and 96. The horizontal grey bar in Figure 2-19-C highlights the octane numbers needed to use the C<sub>5</sub>-C<sub>11</sub> fraction directly as gasoline fuel. However, the octane number is often boosted by fuel additives, such as MTBE or ethanol.

The relatively low octane number of Co+Z can be explained by the mainly paraffinic products of Co-FTS, which hardly undergo isomerization, oligomerization or aromatization under typical reaction conditions <sup>468–470</sup>. Fe+Z on the other hand is usually applied at higher temperatures, hence iron-based Fischer-Tropsch catalysts produce a higher fraction of olefins, allowing to form aromatics, boosting the octane number of the C<sub>5</sub>-C<sub>11</sub> fraction drastically. OX-ZEO is not thermodynamically limited in the iso-paraffin fraction in the product and can additionally form aromatics and olefins with moderate selectivity. The analyzed OX-ZEO catalysts showed selectivity to iso-paraffin of 52%-78%, olefin of 17%-28% and aromatics of up to 16% in the C<sub>5</sub>-C<sub>11</sub> hydrocarbon fraction <sup>306,382</sup>. The dual bed

process allows to operate the first bed (CO activation) at lower temperatures ( $260^{\circ}C-270^{\circ}C$ ), reducing CH<sub>4</sub> selectivity and boosting CO conversion to 88% for the DME or FTO catalysts. Operating the second catalyst bed accommodating the zeolite (for gasoline synthesis) at higher temperatures of  $320^{\circ}C$  enables the formation of aromatics, oligomerization of short olefins and eventually produce high-octane gasoline with high yields <sup>439</sup>.

Next to the octane number, the methane content is also important. In the past decades, Fischer-Tropsch catalysts and their process conditions have been optimized to reduce the CH<sub>4</sub> selectivity. However, the addition of a zeolite leads to more methane <sup>375,420,422,433,471,472</sup>. In Figure 2-19-D the reported methane selectivities for Co+Z, Fe+Z, OX-ZEO and the dual bed processes are shown. The horizontal grey bar shows the typical methane selectivities of the HT-FTS for comparison. Co+Z and Fe+Z catalysts show high methane selectivities (7-30%), 2- to 3-fold higher than without the zeolite <sup>433</sup> <sup>437</sup>. OX-ZEO and the dual reactor processes only produce 2-3% methane similar to the values obtained for high-alpha FT catalysts.

The higher operating temperature and the resulting shift to lower alpha-values in the ASF distribution contributes to the high methane selectivity of FT+Z. For Co-based catalysts, the (acidity of the) support plays an important role <sup>473</sup>. Methane production increases 3–4-fold than that predicted by the ASF model for catalysts supported on oxides with higher acidic character <sup>474</sup>. XPS studies revealed that cobalt supported on a zeolite showed higher binding energy for Co 2p3/2 electrons compared to cobalt on a zeolite that has been covered with a layer of carbon prior to Co impregnation <sup>432</sup>. Hence, the increased methane selectivity for cobalt catalysts supported directly on a zeolite might be explained by electronic effects <sup>475</sup>. A reduced electron density of the cobalt particles causes weaker binding of hydrogen and stronger bonds between carbon and hydrogen of adsorbed CH<sub>x</sub> species <sup>476</sup> making the hydrogenation of CH<sub>x</sub> species to CH<sub>4</sub> energetically favored. Alternatively, the increased methane formation can be explained by a decreased reducibility of cobalt particles supported on zeolites <sup>477,478</sup> or by small cobalt particles inside the zeolite pores, which also give rise to high methane selectivity <sup>479,480</sup>.

Co+Z shows the highest selectivity to the  $C_5$ - $C_{11}$  fraction (55%). However, the resulting octane number of this fraction is very low, hence it cannot be used as gasoline fuel directly. It has to be blended with a high fraction of additives. In terms of octane number for bifunctional processes, OX-ZEO and Fe+Z are the most promising, as they allow  $C_5$ - $C_{11}$  products with high octane numbers of up to ~91 to form. Regarding the methane selectivity, only OX-ZEO and the dual bed processes can compete with the low methane selectivities achieved in FTS which are necessary for industrial application. In summary, the OX-ZEO process can form  $C_5$ - $C_{11}$  fuels with high octane number and little methane. If the WGS activity can be further reduced, this bifunctional catalyst has potential for the direct conversion of synthesis gas to gasoline fuel.

### 2.6. Summary and perspective

The transition to a more sustainable society is forcing a change in the current production processes of chemicals and fuels. A key step is the use of alternative feedstocks to the traditional fossil-based ones. Synthesis gas plays a crucial role due to the versatility of its sources and the various products it can create. In this regard, carbon sources from feedstocks such as CO<sub>2</sub>, organic waste, or biomass, together with the implementation of hydrogen production from renewable energy sources, can become central in this transition <sup>481</sup>. Additionally, synthesis gas operation (production and conversion) is also feasible on a smaller scale, allowing a targeted production in remote locations <sup>76</sup>. The use of bifunctional catalysts can expand the variety of products directly obtained from these sources.

In the past years, great progress has been realized in the field of synthesis gas conversion using bifunctional catalysts. A major advantage is that when combining different catalytic functions in a single reactor, synthesis gas conversion levels can lay far beyond the thermodynamic limitations of a first conversion step in a two-reactor system (Figure 2-10 and Figure 2-14).

In many cases in the first conversion step (e.g., in methanol synthesis) no water is formed. Combining with a second conversion step can enhance the water content in the proximity of the CO activation catalyst, which can lead to the formation of CO<sub>2</sub> via the WGS reaction. This has been observed for the OX-ZEO process and DME synthesis, leading to  $CO_2$  selectivities up to 50% and 33%, respectively. The degree to which this happens is an important parameter. On the one hand  $CO_2$  formation lowers the carbon atom economy. On the other hand, the removal of water by the WGS reaction can also increase the catalyst lifetime and facilitate *in-situ* production of additional hydrogen, favoring the utilization of carbon-rich synthesis gas over bifunctional catalysts. For the use of hydrogen-rich synthesis gas, the water-gas-shift activity of the OX-ZEO catalysts should be reduced, for example by recycling CO<sub>2</sub>. Our detailed analysis of recently published data for the direct synthesis of DME using bifunctional catalysts revealed an average DME selectivity of 62%. In contrast, a process consisting of two consecutive reactors (methanol synthesis and methanol dehydration) can achieve an overall DME selectivity of 88%. The lower selectivity for the bifunctional catalysts relates to the formation of CO<sub>2</sub>. In-situ water removal by adsorption has proven an effective strategy to circumvent this limitation. The DME selectivity of bifunctional catalysts can be enhanced to 98% by in-situ water removal by adsorption. Although the application in an industrial production scale still needs to be demonstrated, the Netherlands Organization for Applied Scientific Research (TNO) has taken the first steps in 2022 by building a containerized pilot reactor for sorption enhanced DME synthesis (SEDMES) <sup>245,251,482–484</sup>.

In terms of  $C_2$ - $C_4$  olefins selectivity, neither OX-ZEO nor FTO can compete with a dual reactor process with methanol or DME synthesis in the first reactor and (D)MTO in a consecutive reactor (93% to  $C_2$ - $C_4$  olefins). The OX-ZEO process allows to form a high olefin

fraction in the hydrocarbon products, but the high WGS activity and hence  $CO_2$  production reduces the overall selectivity to short olefins to 43% on average. FTO catalysts enable the production of short olefins with an average selectivity of 22% due to the high WGS activity and a limited high fraction of short olefins in the hydrocarbon products. Specific reduction of the WGS activity of FTO catalysts can increase the overall selectivity to 44%.

The situation is different for direct synthesis of aromatics from synthesis gas. OX-ZEO and the combination of iron-based Fischer-Tropsch catalysts with a zeolite (FT+Z) show selectivities to aromatics of 41% and 26%, respectively. Especially for the OX-ZEO process, this is only slightly lower than for the dual reactor process that comprises the synthesis of methanol or DME accompanied by aromatization based on hydrogen transfer (41%). This can make OX-ZEO competitive to this type of dual reactor process based on hydrogen transfer. A dual reactor process with aromatization based on dehydrogenation could theoretically achieve selectivities as high as 95%.

Three factors were considered for the analysis of the direct production of gasoline fuels using bifunctional catalysts: the overall selectivity to hydrocarbons in the gasoline range  $(C_5-C_{11})$ , the methane selectivity and the octane number of the resulting  $C_5-C_{11}$  fraction. The combination of cobalt-based Fischer-Tropsch catalysts and zeolites (Co+Z) showed C5-C11 selectivities of 54%, which is beyond the maximum predicted by the ASF distribution. However, the methane selectivity was between 7% and 30% and octane numbers were rather low (30-50). Iron-based Fischer-Tropsch catalysts combined with zeolites (Fe+Z) yielded higher octane numbers (65-91). However, the methane selectivity was high (7%-28%) and the overall selectivity to  $C_5$ - $C_{11}$  hydrocarbons was reduced to 22%, due to the high WGS activity. OX-ZEO produced a high-octane number of 73-89, low methane selectivity (only 1%-2%) and medium overall selectivity to C<sub>5</sub>-C<sub>11</sub> hydrocarbons (39%). This is slightly less than for a dual bed process with a zeolite downstream of a DME or FTO catalyst and dedicated reaction conditions for every catalyst bed: octane numbers between 88 and 96, methane selectivity 2%-3% and medium C<sub>5</sub>-C<sub>11</sub> selectivity (51%). Further efforts are then necessary to make gasoline production with bifunctional catalysis more attractive, particularly by reducing the water gas shift activity (and hence CO<sub>2</sub> production).

Interest for bifunctional catalysts at industrial scale has been leaning towards DME and C<sub>2</sub>-C<sub>4</sub> olefins production. The synthesis of DME from synthesis gas is mainly performed via the indirect route with a total annual production capacity of  $10^7$  t per year <sup>23</sup>. In 2003 the JFE Group in Japan finished the construction of a pilot plant designed for the direct DME synthesis with a capacity of  $3.6 \times 10^4$  t per year in Shiranuka-cho, Hokkaido, Japan using a slurry phase reactor <sup>485,486</sup>. The Korea Gas Corporation launched a demonstration plant for the direct synthesis of DME with a capacity of 10 t per day already in 2004 at the Incheon KOGAS LNG terminal based on the KOGAS DME process <sup>23,222,487</sup>. After successful operation, the design of a commercial production plant with 3 x 10<sup>5</sup> t per year is in progress <sup>487</sup>.

From 2002 to 2007, a 100 ton/day demonstration plant project was successfully conducted by DME Development Corp. funded by 10 companies. Process performance analysis, catalyst life and long-term stable operation were assessed. Building on the technical data, the feasibility studies of commercial scale DME production from natural gas or coal were explored. Total Energies, JAPEX, INPEX and Toyota Tsusho, former members of the DME Development Corp., developed the technology in 2010. In 2016, those four companies transferred the technology patents to RenFud Corporation, which licenses the DME synthesis process technology and supplies proprietary catalysts. The first demonstrating operations with coke oven gas feed showed promising results, with 96% synthesis gas conversion, 93% selectivity to DME and 99.6% purity of DME.

In September 2019, the Dalian Institute of Chemical Physics and the Bureau of Major R&D Programs (Chinese Academy of Science) announced a cooperation between the Dalian Institute of Chemical Physics, the Chinese Academy of Sciences and Shaanxi Yanchang Petroleum (Group) Co., Ltd to perform industrial pilot trials with the aim to produce short olefins via the OX-ZEO process (Figure 2-20). The capacity of this demonstration plant was 1000 t of short olefins per year and it is located in Shaanxi, China <sup>488,489</sup>. In a first step synthesis gas is produced from coal, followed by the OX-ZEO process, converting 50% of the synthesis gas to  $C_2$ - $C_4$  olefins with 75% selectivity in a single pass.



**Figure 2-20:** Photo of the industrial pilot plant to produce short olefins via the OX-ZEO to olefins (OXZEO<sup>®</sup>-TO) process, located in Shaanxi, China <sup>490</sup>.

At the moment research also focuses increasingly on the direct conversion of  $CO_2$  to chemicals and fuels <sup>491–496</sup>. Bifunctional heterogeneous catalysts can be key to integrating  $CO_2$  activation and subsequent conversion to chemicals and fuels in an efficient way, contributing to carbon capture and utilization efforts. Despite the challenges for applications such as high costs, development of bifunctional catalysts for effective  $CO_2$  conversion is a promising topic with potentially beneficial environmental effects <sup>497</sup>.
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## 3

### Bifunctional Catalysis for the Conversion of Synthesis Gas to Olefins and Aromatics

The conversion of synthesis gas (a mixture of hydrogen and carbon monoxide) to chemicals has attracted significant attention in the past years. Strong emphasis has been on enabling a process that allows the production of short olefins from synthesis gas, which can be derived from coal, biomass, or natural gas. Here we introduce bifunctional catalysis to tailor the selectivity towards aromatics next to olefins by combining an iron-based Fischer-Tropsch to olefins catalyst with the acid function of a zeolite. Olefins were formed from synthesis gas on an iron-based catalyst and partly converted to aromatics on the acid sited of the zeolite. Surprisingly, this aromatization did not follow the pathway of hydrogen transfer, whereby three paraffin molecules are produced for every aromatic molecule formed, which allowed us to obtain carbon selectivity towards chemicals (sum of lower olefins and aromatics) of ~70-80 % at 1 bar reaction pressure. Increasing the partial pressure of hydrogen led to substantial hydrogenation of olefins towards paraffins.

Weber, J. L., Dugulan, I., de Jongh, P. E. & de Jong, K. P. Bifunctional Catalysis for the Conversion of Synthesis Gas to Olefins and Aromatics. *ChemCatChem* **10**, 1107–1112 (2018).

#### **3.1. Introduction**

In the past few years, the conversion of synthesis gas to chemicals has often been aimed at the production of lower olefins from a wide range of feedstocks other than crude oil. Recent publications have shown that Fischer-Tropsch to olefins (FTO) allows the formation of lower olefins with high selectivity, using promoted iron-based and cobaltcarbide-based catalysts, which give rise to deviation from the Anderson-Schulz-Flory (ASF) distribution <sup>1–3</sup>. Another approach to form olefins and/or aromatics with high selectivity is the combination of a methanol synthesis catalyst with an acid function of a SAPO34 or H-ZSM-5 zeolite in a single reactor <sup>4–8</sup> or multiple reactors <sup>9,10</sup>. To extend the product spectrum of the Fischer-Tropsch synthesis, acid sites can be appended to the metal catalyst, and the proximity of those two sites can have a major effect on selectivity and activity <sup>4,5,11</sup>. Cobaltcatalyzed low-temperature Fischer-Tropsch synthesis provides a wide range of products from methane (C<sub>1</sub>) to waxes (C<sub>20+</sub>) <sup>12,13</sup>. The supplement of an H-ZSM-5 zeolite facilitates cracking of the C<sub>12+</sub> fraction to hydrocarbons in the gasoline range (C<sub>5</sub>-C<sub>12</sub>) with a total carbon selectivity of close to 60% <sup>14–16</sup>.

Combining an unpromoted iron-based FTS catalyst forming olefins with a zeolite enables the formation of aromatics to a certain degree <sup>17,18</sup> related to the higher reactivity of olefins compared with paraffins and the variability in reaction temperature of iron catalysts <sup>19–21</sup>. According to the hydrogen transfer mechanism, three paraffin molecules are produced from olefins for every aromatic molecule that is formed <sup>9,17,22–24</sup>. This decreases the carbon utilization towards valuable chemicals.

In this study, we will show that extending the product spectrum of the FTO process by aromatics by the combination of a promoted FTO catalyst with an H-ZSM-5 zeolite not only increases the activity of the former but also the selectivity to aromatics compared with an iron-based FTS catalyst. Furthermore, we will show the influence of reactor bed configuration and composition of synthesis gas on the catalytic performance and the product spectrum. Moreover, the formation of paraffins from olefins during aromatization was negligible and we introduce an alternative pathway for the aromatization of FTO olefins that involves dehydrogenation rather than hydrogen transfer.

#### **3.2. Experimental Section**

The iron catalysts were prepared by using incipient wetness impregnation of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (BASF, AL4196E, 7 m<sup>2</sup>/g, pore volume: 0.4 cm<sup>3</sup>/g) with a solution that contains ammonium ferric citrate ((NH<sub>4</sub>)<sub>x</sub>Fe<sub>y</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>, 34.880 g) per 100 mL for the unpromoted iron catalyst and ammonium ferric citrate ((NH<sub>4</sub>)<sub>x</sub>Fe<sub>y</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>, 34.880 g), ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, 0.165 g), and trisodium citrate dihydrate (Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub> x 2 H<sub>2</sub>O, 1.225 g) per 100 mL for the promoted iron catalyst. The support was dried under vacuum at 120°C for 2 h. Three impregnation steps were necessary to achieve an iron loading of 5.5 wt-%. The subsequent calcination was performed at 250°C for 4 h in static air. Inductively coupled

plasma (ICP) analysis showed an iron loading for the unpromoted catalyst of 5.60 wt-% with a Na/Fe ratio of 0.015 at/at, owing to impurities in the iron precursor, whereas the promoted iron catalyst featured an iron loading of 5.51 wt-% with Na/Fe ratio of 0.144 at/at and S/Fe ratio of 0.0093 at/at (Table B2 in Appendix B). The calcined catalysts were pelletized, ground, and sieved to a fraction of  $75-150 \,\mu\text{m}$ . The iron particle sizes of the calcined catalysts were measured by transmission electron microscopy (TEM, Figure B3 in Appendix B), which showed an average iron oxide particle size of 10 nm, whereas FeP displayed 14 nm iron oxide particles after calcination. To determine the crystal phase of the catalysts, X-ray diffraction (XRD) patterns (Figure B4 in Appendix B) were recorded with a Bruker D2 Phaser powder diffractometer (CoK<sub>a</sub> source: 1.79 Å). After calcination at 250°C, the crystal structure of both Fe and FeP was maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>). To transform the commercial zeolite (NH<sub>4</sub>-ZSM-5, Zeolyst, Si/Al ratio: 15 at/at) from the ammonium form to the proton form, calcination was performed at 500°C for 4 h in static air. Ammonium temperatureprogrammed desorption (TPD) data are shown in Figure B5 in Appendix B. Afterwards, the zeolite was pelletized, ground, and sieved to a fraction of 75-150 µm. The iron catalysts were either mixed with the zeolite in a mixed bed or placed in a stacked-bed configuration with the zeolite downstream of the iron catalyst. The catalyst bed was diluted with silicon carbide in a volume ratio of  $V_{\rm SiC}/V_{\rm total catalyst} = 2$  to avoid heat transfer limitation phenomena. Prior to being subjected to the reaction conditions, the iron catalysts were reduced *in-situ* in a stream of hydrogen and nitrogen (H<sub>2</sub>/N<sub>2</sub> = 2 v/v, GHSV=18,000 h<sup>-1</sup>, gas hourly space velocity (GHSV) was always normalized for the volume of the iron catalyst only) at 350°C for 2 h, in which the space velocity is based on the volume flow per volume of iron catalyst. A consecutive carburization was performed at  $290^{\circ}$ C in a stream of synthesis gas (CO/H<sub>2</sub> = 1, 1 bar, GHSV=7200 h<sup>-1</sup>) for 1 h. The catalytic testing was performed at 400°C in a stream of synthesis gas with a GHSV of 7200  $h^{-1}$  at ambient pressure, in which the CO/H<sub>2</sub> ratio of the synthesis gas was varied between  $CO/H_2 = 0.5$  and 3. The CO conversion was kept below X(CO) = 5%. The products were analyzed with an online gas chromatograph (GC) equipped with a flame ionization detector (FID). The activity was determined based on iron time yield (FTY), which represents CO converted to hydrocarbons per second and gram of iron. Selectivities were calculated on the basis of carbon atoms within hydrocarbons formed (CO<sub>2</sub> free). CO conversions in the low pressure experiments were based on CO converted to hydrocarbons ( $CO_2$  free). The selectivity to  $CO_2$  is expected to be according to the thermodynamic equilibrium of CO, H<sub>2</sub>, H<sub>2</sub>O, and CO<sub>2</sub> in the water-gas shift reaction  $(S(CO_2) \approx 47\%)$  Experiments at elevated pressure were performed in a Avantium Flowrence 16-port parallel fixed-bed reactor setup. Prior to being exposed to the reaction conditions, the iron catalysts were reduced *in-situ* in a stream of 30 vol-% hydrogen in helium (GHSV=15,000 h<sup>-1</sup>) at 350°C for 2 h at 3 bar. A consecutive carburization was performed at  $290^{\circ}$ C in a stream of synthesis gas (CO/H<sub>2</sub> = 1, 3 bar, GHSV=28,000 h<sup>-1</sup>) for 1 h. The catalytic testing was performed at 400°C in a stream of synthesis gas with a GHSV of 24,000 h<sup>-1</sup> at a pressure of 5 bar, where the CO/H<sub>2</sub> ratio of the synthesis gas was varied

between CO/H<sub>2</sub> = 0.5 and 2. The products were analyzed with an online gas chromatograph (GC) equipped with a flame ionization detector (FID) and thermal conductivity detector (TCD). The activity was determined based on iron time yield (FTY), which represents CO converted to hydrocarbons per second and gram of iron. Selectivities towards hydrocarbon products were calculated on the basis of carbon atoms within hydrocarbons formed (CO<sub>2</sub> free). Transmission <sup>57</sup>Fe Mössbauer absorption spectra were collected *in-situ* at 300 K with a conventional constant-acceleration spectrometer using a <sup>57</sup>Co(Rh) source. Velocity calibration was performed by using an  $\alpha$ -Fe foil.

#### 3.3. Results

We prepared an unpromoted (5.6 wt-% iron on alpha-alumina, Na/Fe = 0.015 at/at, denoted as Fe) and a promoted iron catalyst (5.5 wt-% iron on alpha-alumina, Na/Fe = 0.144 at/at, S/Fe = 0.0093 at/at, denoted as FeP) by incipient wetness impregnation (Table S2 in Appendix B). The calcined iron catalysts were than combined with the pelletized H-ZSM-5 zeolite (Si/Al = 15 at/at) in different volumetric ratios of zeolite to iron catalyst in a quartz fixed-bed reactor. Here, experiments were conducted in different reactor configurations, namely mixed bed, and stacked bed.

To investigate the influence of proximity of the zeolite to the iron catalysts on activity and selectivity, mixed bed experiments were conducted. All catalysts first were tested under the reaction conditions 400°C, 1 bar,  $CO/H_2 = 1 v/v$ , CO conversion <5% to introduce a benchmark for the experiments in which the iron catalysts were mixed with the zeolite. The promoted iron catalyst (FeP) showed higher activity compared with unpromoted (Fe; Figure 3-1-A), whereas the selectivity to methane was decreased (Figure 3-1-C). Furthermore, the  $C_2$ - $C_4$  fraction (olefins and paraffins) of the promoted catalyst was higher than expected based on the limitation by the ASF distribution (maximum selectivity of  $C_2$ - $C_4$ -fraction: 58% c<sup>1</sup>) with 63% (61% colefins and 2% paraffins). This was not the case for the unpromoted catalyst (49%c olefins and 2%c paraffins). When mixed with the zeolite in a ratio of  $V_{\text{zeolite}}/V_{\text{iron-catalyst}} = 2 \text{ v/v}$  as a physical mixture of the pelletized catalyst particles, the activity of the mixture of the promoted iron catalyst and the zeolite (FeP-2Z) was enhanced significantly, whereas the activity for the mixture of the unpromoted iron catalyst and the zeolite (Fe-2Z) decreased slightly (Figure 3-1-A). In the first 15 h on stream, the selectivity towards methane of both iron catalysts was not influenced strongly by the addition of the zeolite. In the case of the promoted iron catalyst mixed with the zeolite, the total selectivity to chemicals is 68% (51% C<sub>2</sub>-C<sub>4</sub> olefins and 17% c aromatics), whereas the promoted iron catalyst alone showed 61% C<sub>2</sub>-C<sub>4</sub> olefins without aromatics formed. The mixtures of both iron catalysts with the zeolite showed similar selectivities towards  $C_2$ -C<sub>4</sub> paraffins (2%<sub>C</sub> for Fe-2Z and 4% for FeP-2Z) compared with the iron catalysts only (2% for Fe and FeP). Figure 3-1-B shows that the selectivity to olefins within the  $C_{5+}$  fraction decreased when the zeolite was added (from  $8\%_C$  for Fe to  $2\%_C$  for Fe-2Z and from  $12\%_C$  for FeP to  $3\%_C$  for

FeP-2Z), whereas the selectivity towards paraffins in this fraction remained constant ( $2\%_{C}$  for Fe,  $1\%_{C}$  for Fe-2Z,  $3\%_{C}$  for FeP, and  $3\%_{C}$  for FeP-2Z).



**Figure 3-1:** Activity and product distribution for the mixed bed experiments. **A:** Activity during the initial phase of the reaction for the two iron catalysts with and without zeolite present in a physical mixture at 400 °C, CO:H<sub>2</sub> = 1, GHSV: 7200 h<sup>-1</sup>, total pressure: 1 bar with CO conversion levels of 0.50% (Fe), 0.26% (Fe-2Z), 1.1% (FeP) and 2.0% (FeP-2Z). The addition of the zeolite has influence on the activity of the iron catalysts, **B:** Distribution of olefins and paraffins within the C<sub>5+</sub>-fraction of mixed bed experiments at 400°C, CO:H<sub>2</sub> = 1, GHSV: 7200 h<sup>-1</sup>, total pressure: 1 bar and after 4 h on stream. C<sub>5+</sub> olefins are also converted to aromatics, **C:** Carbon selectivity in the hydrocarbon products for the mixed bed experiments at 400°C, CO:H<sub>2</sub> = 1, GHSV: 7200 h<sup>-1</sup>, total pressure: 1 bar and after 4 h on stream. C<sub>5+</sub> olefins are also converted to aromatics, **C:** Carbon selectivity in the hydrocarbon products for the mixed bed experiments at 400°C, CO:H<sub>2</sub> = 1, GHSV: 7200 h<sup>-1</sup>, total pressure: 1 bar and after 4 h on stream. C<sub>5+</sub> olefins at 400°C, CO:H<sub>2</sub> = 1, GHSV: 7200 h<sup>-1</sup>, total pressure: 1 bar and after 4 h on stream.

This behavior is not consistent with the hydrogen transfer mechanism, in which the formation of aromatics coincides with the formation of paraffins from olefins with comparable carbon selectivity. The carbon selectivity towards aromatics was three times higher than towards total paraffins (4-5 times higher compared with C<sub>2</sub>-C<sub>4</sub>-paraffins). Furthermore, we expect paraffins to be inert under these reaction conditions and not to be converted to aromatics <sup>25</sup>. These observations led to the following questions: does the proximity of the zeolite have an influence on the activation and performance of the iron catalysts <sup>9</sup>, and does the aromatization of olefins follow the hydrogen transfer pathway?



**Figure 3-2:** Degree of reduction and carburization of mixed bed experiments. **A:** Degree of carburization of the two iron catalysts with and without zeolite present in a physical mixture after the *in-situ* carburization step at 290 °C for 1 h in CO:H2 = 1 with GHSV: 7200 h-1, at 400 °C, CO:H2 = 1, GHSV: 7200 h-1 and total pressure of 1 bar after 5 h and at 400 °C, CO:H2 = 1, GHSV: 7200 h-1 and total pressure of 1 bar after 15 h. The presence of promoters and zeolite enhance the carburization, **B:** Degree of reduction of the two iron catalysts to Fe<sup>0</sup> with and without zeolite present in a physical mixture after *in-situ* reduction at 350°C for 2 h in H2:N2 = 2 with GHSV: 18000 h-1 and total pressure of 1 bar. The presence of zeolite has a greater effect on the reduction than the promoters, **C:** Fraction of Fe<sup>2+</sup>-oxide and iron carbides within the total iron atoms after 15 h at 400°C, CO:H2 = 1, GHSV: 7200 h-1 and total pressure of 1 bar. The presence of the zeolite has influence on the iron carbide phases for the promoted iron catalyst. For detailed data see Tables S3-S6 in Appendix B.

To investigate the differences in activity of the iron catalysts when mixed with the zeolite, Mössbauer spectroscopy was performed, which is shown in Figure 3-2 A-C. The presence of the zeolite enhanced the reduction in a more pronounced way than the presence of promoters (Figure 3-2-B), whereas promotion showed a greater influence on the carburization (Figure 3-2-A). After 15 h time on stream, the unpromoted iron catalyst with and without the zeolite present were not fully carburized, whereas we observed a large fraction of superparamagnetic Fe<sub>x</sub>C (56%<sub>Fe</sub> at/at) for FeP-2Z and Hägg carbide ( $\chi$ -Fe<sub>5</sub>C<sub>2</sub>, 67%<sub>Fe</sub> at/at) for FeP. It is not yet fully understood to what extent the different iron phases

contribute to the catalytic performance <sup>26–28</sup>. However, it was shown that the degree of carburization has a major influence on the activity and selectivity of iron catalysts in the Fischer-Tropsch to olefins reaction <sup>29</sup>. Hereafter, experiments were performed in a stacked-bed configuration to exclude this influence of the zeolite on the iron carbide function.



**Figure 3-3:** Atomic ratio of hydrogen and carbon in the hydrocarbon products  $(C_1-C_{16})$  and selectivity towards olefins, paraffins and aromatics as function of zeolite/FTO catalyst ratio at 400°C, CO:H<sub>2</sub> = 1, GHSV: 7200 h<sup>-1</sup>, total pressure: 1 bar and after 4 h on stream with CO conversion levels of  $1.2 \pm 0.1\%$ . The lower hydrogen-carbon ratio at zeolite/FTO of two indicates dehydrogenation. The selectivity towards aromatics stayed constant independent from the amount of zeolite added, while olefins were hydrogenated to form paraffins with increasing amount of zeolite present. This resulted in an increase of the hydrogen-carbon ratio.

To investigate the pathway of aromatization of olefins, the promoted iron catalyst was combined with the zeolite in a stacked-bed configuration with the zeolite downstream of the iron catalyst. The activity of the promoted iron catalyst (FeP) alone was comparable with the activity of the stacked-bed experiments (FeP-xZ-SB, x represents the ratio of zeolite to FTO catalyst, v/v), which shows that the iron catalyst is not influenced, owing to the spatial separation to the zeolite (Figure S1 in Appendix B). The zeolite to iron catalyst ratio was varied from V<sub>zeolite</sub>/V<sub>iron-catalyst</sub>=2-20 v/v (denoted as FeP-2Z-SB, FeP-10Z-SB, and FeP-20Z-SB). When combining the FTO catalyst with a low amount of zeolite in stacked-bed configuration (FeP-2Z-SB), aromatics were formed with 18% c selectivity, whereas olefins remained with 55% selectivity (Figure 3-3). This gives a total selectivity to chemicals of  $73\%_{\rm C}$ . Surprisingly, paraffins were formed with only  $4\%_{\rm C}$  selectivity. With ascending quantity of zeolite, the selectivity towards aromatics remained constant, whereas the selectivity to olefins decreased from 55% to 29%. At the same time, more paraffins were formed and the selectivity increased from  $4\%_{\rm C}$  to  $25\%_{\rm C}$ . Increasing the amount of zeolite downstream of the FTO catalyst resulted in a decrease of selectivity to chemicals from 73% C to 47%<sub>C</sub>. Subsequently, the composition of synthesis gas was altered from hydrogen-rich  $(CO/H_2 = 0.5 \text{ v/v})$  to carbon-rich  $(CO/H_2 = 3 \text{ v/v})$  for the FeP-10Z-SB experiment (Figure 3-4). Here, the methane selectivity dropped from 28% c to 13% c, whereas olefins selectivity

increased from  $29\%_{\rm C}$  to  $41\%_{\rm C}$ . Surprisingly, the selectivities for paraffins and aromatics behaved contrary. The paraffin selectivity decreased from  $27\%_{\rm C}$  to  $10\%_{\rm C}$ , whereas aromatics selectivity increased from  $12\%_{\rm C}$  to  $27\%_{\rm C}$ . By raising the CO/H<sub>2</sub> ratio of the synthesis gas, the total selectivity to chemicals was increased from  $41\%_{\rm C}$  (CO/H<sub>2</sub> = 0.5) to  $68\%_{\rm C}$  (CO/H<sub>2</sub> = 3). Seemingly, the formation of paraffins and aromatics were not linked. The ratio of hydrogen and carbon of the total hydrocarbon products (C<sub>1</sub>-C<sub>16</sub>) as function of the zeolite to iron catalyst ratio shows a decrease of hydrogen content in the products for a low quantity of zeolite in respect to the FTO catalyst (Figure 3-3). For higher quantities of zeolite, the hydrogen/carbon ratio increased.



**Figure 3-4:** The product distribution of FeP-10Z-SB with a variation of the feed composition from  $CO:H_2 = 0.5 - 3$  v/v at 400°C, GHSV: 7200 h<sup>-1</sup>, total pressure: 1 bar and after 4 h on stream. Even though the hydrogen-carbon ratio of the hydrocarbon products at  $CO:H_2 = 1$  v/v corresponds to the ratio of the promoted iron catalysts (Figure 3-3) it can be seen that the selectivities of paraffins and aromatics behave contrariwise.

#### 3.4. Discussion and Conclusion

The low selectivities towards paraffins when the iron catalysts were mixed with the zeolite implies that the pathway of aromatization of FTO olefins does not follow the hydrogen transfer pathway. According to the hydrogen transfer mechanism, lower olefins oligomerize to form olefins in the range C<sub>6</sub>-C<sub>10</sub>. Hydrogen from these longer olefins is passed on to another olefin molecule (hydrogen transfer), resulting in dienes and paraffins. The dienes cyclize, forming cyclic olefins, which undergo two consecutive hydrogen transfer steps resulting in cyclic dienes and aromatics, respectively (Equation 3-1). For each of these hydrogen transfer steps, one paraffin molecule is formed <sup>22</sup>, which would lead to a decrease in carbon utilization in terms of formation of desired chemicals (C<sub>2</sub>-C<sub>4</sub> olefins and aromatics).

$$6 C_2 H_4 \rightarrow C_6 H_{12} + 3 C_2 H_4 \rightarrow C_6 H_6 + 3 C_2 H_6$$
 Equation 3-1

However, the selectivity to paraffins was surprisingly low for twice the volume of zeolite added to the iron catalysts in both mixed-bed (2.2%) for Fe-2Z and 3.7% for FeP-2Z, Figure 3-1-C) and stacked-bed configurations (3.7%c for FeP-2Z-SB, Figure 3-3), whereas aromatics were formed with a substantial selectivity (9.4%) for Fe-2Z, 17.4% for FeP-2Z, and 18.3%<sub>C</sub> for FeP-2Z-SB). In the stacked-bed experiments, a lower hydrogen/carbon ratio of the hydrocarbon products was found for a zeolite/FTO ratio of two (H/C = 2.23 at/at) than the FTO catalyst without zeolite (H/C = 2.43 at/at), which suggests dehydrogenation takes place. The selectivity towards aromatics showed an independent behavior from the amount of zeolite downstream of the FTO catalyst, however, increasing the zeolite/FTO catalyst ratio led to an increase in hydrogen/carbon ratio. This increase can be attributed to the hydrogenation of olefins to paraffins with increasing zeolite/FTO ratio (Figure 3-3). The selectivities towards paraffins and aromatics even showed an opposite behavior when the synthesis gas composition was altered from hydrogen-rich to carbon-rich for an experiment with zeolite/FTO ratio of 10 v/v (Figure 3-4). This led to less extensive hydrogenation of olefins next to a shift of the equilibrium of dehydroaromatization to the side of aromatics and hydrogen (Figure S2 in Appendix B) and shows that the increase in hydrogen/carbon ratio in the hydrocarbon products to the initial value of the promoted iron catalyst cannot be attributed to the hydrogen transfer pathway. Therefore, we propose that the aromatization does not follow the hydrogen transfer pathway, but rather dehydroaromatization, which involves dehydrogenation instead of formation of paraffins (Equation 3-2, Figure 3-5). However, increasing the partial pressure of hydrogen led to more extensive hydrogenation of olefins towards paraffins (Equation 3-3). This could be shown in experiments at 1 bar by altering the synthesis gas composition (Figure 3-4) as well as performing experiments at a pressure of 5 bar, where a significant fraction of olefins was hydrogenated whereas aromatics were formed with low selectivity of up to 3.1% (Table S7 in Appendix B).

This pathway of olefin aromatization allows us to convert synthesis gas to chemicals with selectivities as high as  $73\%_{C}$  (55%<sub>C</sub> lower olefins and 18%<sub>C</sub> aromatics for FeP-2Z-SB) without giving rise to the formation of undesired paraffins at low pressure. By adjusting the reaction conditions, the fraction of aromatics within the chemicals can be altered from 25%<sub>C</sub> (mixed bed, CO/H<sub>2</sub> = 1 v/v, zeolite/FTO=2 v/v, 1 bar) to 40%<sub>C</sub> (stacked bed, CO/H<sub>2</sub> = 3 v/v, zeolite/FTO=10 v/v, 1 bar).



Figure 3-5: Proposed pathway for the conversion of synthesis gas to aromatics: Conversion of synthesis gas to olefins on the FTO catalyst, dehydroaromatization of olefins to aromatics on the zeolite.

Furthermore, the decrease in selectivity to  $C_2$ - $C_4$ -olefins (from 61%<sub>C</sub> for FeP to 51%<sub>C</sub> in FeP-2Z) as well as olefins within the  $C_{5+}$  fraction (from 12%<sub>C</sub> for FeP to 3%<sub>C</sub> in FeP-2Z) when the zeolite was present shows that aromatics (17%<sub>C</sub> for FeP-2Z) are not exclusively formed from  $C_2$ - $C_4$  olefins but also from  $C_{5+}$  olefins. Mixing the iron catalysts in close proximity with the zeolite, the catalytic activity was influenced. The activity of the unpromoted iron catalyst decreased slightly in the initial phase of the reaction, whereas the addition of zeolite to the promoted iron catalyst enhanced activity by a factor of two. This behavior can be attributed to the degree of reduction and carburization of the iron catalysts, which is influenced by the presence of the zeolite. Also, the type of iron carbide formed during activation and reaction depends on the presence of promoters <sup>29</sup> and zeolite and has an influence on the catalytic activity.

The addition of sodium and sulfur as promoters to an iron-based Fischer-Tropsch synthesis catalyst led to enhancement of activity and selectivity to lower olefins <sup>1,2,29</sup>. Now, we show that the combination of such a catalyst with a zeolite shows increased selectivity to chemicals of up to  $73\%_{\rm C}$ , whereas the product spectrum is extended to aromatics. Furthermore, the proximity of two functions in a bifunctional catalyst can have a significant influence on the activity and selectivity, which also applies in fields other than synthesis gas conversion.

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# 4

### Effect of Proximity and Support Material on Deactivation of bifunctional Catalysts for the Conversion of Synthesis Gas to Olefins and Aromatics

Synthesis gas conversion to short olefins and aromatics using bifunctional catalysts has gained high attention in recent years. Here, we study the interaction between the components of bifunctional catalysts to design a more stable catalyst system. Mixing  $\alpha$ -alumina supported iron (-carbide) promoted with sodium and sulfur with an H-ZSM-5 zeolite to convert synthesis gas to aromatics and short olefins we observed selectivity loss of the iron (-carbide) catalyst as well as the acid function. This was displayed by increasing methane and decreasing aromatics selectivity when the two individual catalysts were mixed in close proximity. We introduced different approaches to understand this selectivity related deactivation. Larger spatial separation of the iron and zeolite allowed a more stable system with constant methane and aromatics selectivity loss was caused by migration of sodium ions that were used next to sulfur as promoters on the iron catalyst over the  $\alpha$ -alumina support to the zeolite, which was supported by XPS model experiments. This migration seems hindered on carbon supported iron catalysts.

Weber, J. L., Krans, N.A., Hofmann, J.P., Hensen, E.J.M., Zecevic, J., de Jongh, P.E., de Jong, K.P. Effect of Proximity and Support Material on Deactivation of bifunctional Catalysts for the Conversion of Synthesis Gas to Olefins and Aromatics. *Catal. Today* **342**, 161–166 (2020).

#### 4.1. Introduction

Synthesis gas (a mixture of carbon monoxide/carbon dioxide and hydrogen) can be derived from coal <sup>1</sup> and natural gas <sup>2</sup> as well as from biomass <sup>3</sup> and can be converted to valuable chemicals such as short olefins and aromatics. This has received significant interest in the past years in academia and industry <sup>4,5</sup>. Recent publications have shown that bifunctional catalyst systems consisting of a metal oxide catalyst and a zeolite enable direct conversion of synthesis gas towards chemicals such as short olefins <sup>6,7</sup> and aromatics <sup>8</sup>. The intermediates in this reaction are reported to be oxygenates like methanol and dimethyl ether <sup>9,10</sup> or ketene <sup>11</sup>.

Alternatively, cobalt carbide catalysts with certain crystal facets exposed or promoted iron (-carbide) based Fischer-Tropsch to olefins (FTO) catalysts can be used to convert synthesis gas to short olefins  $^{12-18}$ . These catalysts show a selective suppression of methane formation next to an increase in olefins to paraffin ratio in the products and allows to form olefins in the range of C<sub>2</sub>-C<sub>4</sub> beyond the Anderson-Schulz-Flory (ASF) distribution. In the case of iron (-carbide) based FTO catalysts, the presence of both sodium and sulfur promoters on the iron (-carbide) particles is essential for the decrease in methane selectivity  $^{19-21}$ .

In order to further convert the olefins formed on the iron (-carbide) based catalyst to aromatics the iron catalyst can be combined with a solid acid such as H-ZSM-5 zeolites in a single reactor  $^{22-26}$ . The group of Ding successfully combined iron catalysts with H-ZSM-5 zeolite to convert synthesis gas to aromatics with high CO conversion (85%) and aromatics selectivity (70% in C<sub>5+</sub>). This was achieved by either impregnation of the zeolite with iron precursor or powder mixing of bulk iron catalysts with H-ZSM-5 zeolites  $^{23,26}$ . Additionally, the group of Dabydurjor studied the effect of addition of H-ZSM-5 zeolite to carbon supported iron catalysts in different catalyst bed designs and observed catalyst deactivation in mixed bed mode, which was assigned to metal migration  $^{24,25}$ .

Typically, deactivation of supported metal catalysts has been reported as a result of particle growth, which decreases the number of active sites but does not change their nature <sup>27–30</sup>. However, in bifunctional catalysts other deactivation mechanisms might play a role. For instance, a short distance between the iron (-carbide) and the acid sites of a bifunctional catalyst system may facilitate migration of alkali metal ions from the iron (-carbide) catalyst towards the zeolite <sup>31</sup> due to high mobility of alkali metal ions <sup>32,33</sup>. This could not only lower the activity and selectivity of the FTO catalyst but also neutralize the acid sites of the zeolite with alkali metal ions leading to a decreased selectivity to aromatization of olefins <sup>34</sup>.

Here, we want to gain fundamental understanding of the mechanism of selectivity loss, with the final aim to allow design of more stable bifunctional catalysts. Therefore, we combined a Fischer-Tropsch to olefins (FTO) catalyst based on iron promoted with sodium and sulfur with an H-ZSM-5 zeolite to convert synthesis gas to aromatics with short olefins as intermediates <sup>35</sup>. This work focuses on both the influence of proximity <sup>6,8,36</sup> of the two

catalytic functions as well as of the nature of the support on the stability. We show how the migration of promoters from the iron catalyst to the zeolite is affected and the resulting increase in methane selectivity and decreased selectivity to aromatics.

#### 4.2. Experimental 4.2.1. Catalyst Preparation

The promoted iron catalyst was prepared via incipient wetness impregnation of  $\alpha$ -alumina (BASF, Al4196E, 7 m<sup>2</sup>/g surface area, 0.4 mL/g pore volume (determined by water wetting). Prior to impregnation, the alumina powder was dried in a two-neck flask equipped with a vacuum valve adapter and a septum under vacuum and 120°C for 2 h. After the flask was allowed to cool to 25°C in vacuum the valve was closed, and the impregnation solution was added with a syringe and needle through the septum while stirring. The impregnation solution was prepared by dissolving ammonium ferric citrate (6.002 g, brown, Acros), sodium citrate monobasic (380.0 mg, Sigma Aldrich) and sulfuric acid (180.4 mg. 10 wt.-% solution in demineralized water) in demineralized water (20 mL). Three impregnation steps were necessary to achieve an iron loading of ~6 wt.-%. Between the impregnation steps the material was dried under vacuum for 2 h at 60°C. After the third impregnation step the samples were dried at 60°C for 16 h in static air followed by calcination at 250°C in static air for 4 h. The calcined iron catalyst was pelletized, ground, and sieved to a fraction of 425 – 630 µm or 75 - 150 µm.

For the CNT supported iron catalyst, iron nano-crystals (Fe-NC) were prepared via colloidal synthesis. 1,2-hexadecandiol (350.9 mg), oleyl amine (214.9 mg), oleic acid (433.1 mg) and 1-octene (10 mL) were mixed in a 3-neck flask, equipped with a reflux condenser, septum and vacuum adapter connected to a Schlenk-line. Vacuum was applied, and the mixture was heated to 120°C for 30 min. A mixture of iron pentacarbonyl (20.85 mg) and 1-octadecene (1 mL) was prepared in a nitrogen glovebox. The 3-neck flask was flushed with nitrogen three times followed by injection of the iron pentacarbonyl solution at 90°C. The mixture was heated to 290°C and kept there for 1 h. Afterwards the mixture was allowed to cool to 25°C it was transferred to a vial, to further process in air, and mixed with an equal volume of *iso*-propanol. The Fe-NC were placed in a centrifuge (2700 rpm, 15 min) and the supernatant was decanted. 5 drops of toluene were added, and the mixture was sonicated for 30 s, followed by a treatment in the centrifuge (2700 rpm, 15 min). The toluene-washing procedure was repeated one more time. The as-synthesized Fe-NC were diluted with 10 mL 1-octadecene.

To attach the Fe-NC to the support the support material (CNT, Bayer BayTubes, 800 mg, surface area 230 m<sup>2</sup>/g, pore volume 1.6 mL/g) was added into a 100 mL three-neck flask, which was connected to a Schlenk line through a reflux condenser. The suspended Fe-NC were added to the support material by pipetting while simultaneously magnetically stirring at 400 rpm. The mixture was brought under vacuum for 30 min at 120°C to evaporate

the toluene, and subsequently purged with nitrogen. The temperature was increased to 200°C within 10 min under nitrogen flow and maintained for 30 min. Afterwards, the mixture was allowed to cool down to  $25^{\circ}$ C and further processed in air. Finally, the iron Fe-NP supported on the carbon materials were washed five times with hexane and acetone (hexane/acetone = 1:3 v/v) and dried at 60°C for 1 h under static air, at 120°C for 3 h under static air, and at 80°C for 3 h under vacuum.

The addition of promoters to the CNT-supported Fe-NC was achieved using incipient wetness impregnation of the unpromoted Fe-NC after attachment to the CNT. The unpromoted Fe-NC on CNT were placed in a two-neck flask equipped with a septum and a vacuum valve adapter and heated to  $60^{\circ}$ C under vacuum for 1 h. Afterwards the flask was allowed to cool to  $25^{\circ}$ C (under vacuum) and the valve was closed. Sodium sulfide nonahydrate (212.5 mg) was dissolved in demineralized water (5.7 mL) and 1 mL of this solution was diluted with a mixture of water and *iso*-propanol (1:1 v/v, 9 mL of mixture). 1.2 mL of the final solution was added per gram of catalyst. The impregnated catalyst was dried under vacuum at  $25^{\circ}$ C for 16 h and pelletized, ground and sieved to a fraction of  $425 - 630 \,\mu$ m.

The ZSM-5 zeolite was transformed from the ammonium form (NH<sub>4</sub>-ZSM-5, Zeolyst, Si:Al = 15 at/at) to the proton form H-ZSM-5 by calcination at 550°C for 4 h in static air (the temperature programmed desorption profile of ammonia can be found in Appendix C, Figure C1). Afterwards, the powder was pelletized, ground, and sieved to a fraction of 425-630  $\mu$ m or 75-150  $\mu$ m, respectively.

The iron catalyst and the zeolite were combined with different proximities. In the stacked bed configuration (denoted as AFe+Z) the zeolite was placed downstream of the iron catalyst with a thin layer of silicon carbide in between. Mixed bed experiments were prepared by physically mixing the iron catalyst and the zeolite in the reactor using sieve fractions of 75-150  $\mu$ m (denoted as AFe/Z-100) and 425-630  $\mu$ m (denoted as AFe/Z-500), respectively. To prepare composite catalysts consisting of the iron catalyst supported on alumina (denoted as AFeZ) and CNT (denoted as CFeZ), respectively, and the zeolite, the powders of the iron catalysts and the calcined zeolite were mixed in a mortar for 5 min to achieve an appropriate distribution within the final grains. The iron catalyst supported on alumina was mixed with the zeolite in a ratio of Fe/Al<sub>2</sub>O<sub>3</sub>:zeolite = 3:5 m/m, whereas the CNT-based iron catalysts were mixed with a ratio of Fe/CNT:zeolite = 4:5 m/m to compensate for the lower iron loading of the iron catalysts supported on CNT. Subsequently, the mixed powders were pelletized, ground, and sieved to a fraction of 425 – 630  $\mu$ m.

#### 4.2.2. Characterization

The elemental composition of the calcined alumina-supported iron catalysts and the dried CNT-supported iron catalysts was determined with ICP analysis (Appendix C, Table C1). Transmission electron microscopy (TEM) images were acquired using a FEI Talos
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F200X transmission electron microscope in bright field mode operating at 200 kV (Appendix C, Figure C2-C4). To analyze the porosity and surface area of the support materials, nitrogen physisorption was measured at liquid nitrogen temperature using a Micromeritics TriStar 3000 surface area and porosity analyzer. Prior to physisorption measurements, the alumina support was dried in nitrogen flow for 16 h at 300°C and CNT support at 150°C, respectively (isotherms and physisorption data can be found in Appendix C, Figure C5 and Table C2).

X-ray photoelectron spectroscopy (XPS) measurements were carried out on a K-Alpha XP spectrometer (Thermo Scientific) equipped with a monochromatic small-spot (400  $\mu$ m) X-ray source operating at 72 W, a 180° double focusing hemispherical analyzer with a 128-channel delay line detector and an Al anode (*E*(Al K<sub>a</sub>) = 1486.6 eV). The background pressure inside the analysis chamber was kept below 8×10<sup>-8</sup> mbar reaching maximum of 3×10<sup>-7</sup> mbar during the measurements due to the flow of low energy Ar<sup>+</sup> ions involved in the charge neutralization process. Samples were handled in ambient air and were fixed on the XPS sample holder by conducting carbon tape. High-resolution spectra of core levels (Al 2p, C 1s, Fe 2p, Na 1s, O 1s, Si 2p) and wide-range survey spectra were recorded with a pass energy of 50 eV and 200 eV, respectively. Binding energy calibration of the spectra was done by setting the C 1s peak of sp<sup>3</sup> adventitious carbon to 284.8 eV.

#### 4.2.3. Catalytic Performance

To analyze the catalytic performance of the  $\alpha$ -alumina supported iron catalyst without zeolite, 15 mg of the calcined and sieved iron catalyst were loaded into a stainless-steel reactor with 2.6 mm ID after dilution with 100 mg of silicon carbide. The stacked bed configuration was achieved by first loading 25 mg of calcined and sieved H-ZSM-5 zeolite diluted with 100 mg of silicon carbide into the reactor followed by a layer of silicon carbide to avoid direct contact between the iron catalyst and the zeolite. Afterwards, 15 mg of calcined and sieved iron catalyst was diluted with 100 mg of silicon carbide and loaded upstream of the zeolite into the reactor.

Mixed bed configurations were prepared by mixing 15 mg calcined and sieved iron catalyst, 25 mg calcined and sieved H-ZSM-5 zeolite, and 200 mg silicon carbide in a glass vial, followed by loading the mixture into the reactor.

For the composite experiments of the  $\alpha$ -alumina supported iron catalyst and zeolite, 40 mg of the sieved composite mixture was diluted with 150 mg silicon carbide and loaded into the reactor, whereas 45 mg of the composite of CNT supported iron catalyst and zeolite was loaded after dilution with 150 mg of silicon carbide.

The catalysts were tested in a 16-channel high throughput fixed bed reactor setup (Avantium Flowrence) by *in-situ* reduction of the calcined catalysts in a flow of 30% hydrogen in helium (v/v) at 350°C for 2 h at 1 bar and a gas hourly space velocity (GHSV) of 10,500 h<sup>-1</sup> followed by carburization in synthesis gas (CO/H<sub>2</sub> = 1 v/v, 5%<sub>vol</sub> He as internal standard) at 290°C for 1 h at 1 bar and GHSV of 14,400 h<sup>-1</sup>. The reaction conditions were

400°C in synthesis gas (CO/H<sub>2</sub> = 1 v/v, 5%<sub>vol</sub> He as internal standard), 1 bar and GHSV of 14,400 h<sup>-1</sup>. The GHSV is calculated based on the gas flow and the volume of the iron catalyst only. The C<sub>1</sub>-C<sub>9</sub> hydrocarbon products as well as the permanent gases were analyzed with an online gas chromatograph equipped with a flame ionization detector (FID) and thermal conductivity detector (TCD). The reported selectivities were based on carbon atoms (%<sub>C</sub>) within hydrocarbon formed and were calculated excluding CO<sub>2</sub>. The selectivity to CO<sub>2</sub> was in the range of the thermodynamic equilibrium of ~47% for all experiments.

A heat treatment to simulate a spent catalyst without the formation of coke on the surface for XPS measurements was performed by heating the calcined catalysts to  $350^{\circ}$ C with 5 K/min and hold for 2 h in a nitrogen flow with a GHSV of  $10,500 \text{ h}^{-1}$ , followed by  $290^{\circ}$ C (5 K/min) for 1 h in nitrogen flow with GHSV=14,400 h<sup>-1</sup> and  $400^{\circ}$ C (5 K/min) for 15 h in nitrogen flow with GHSV=14,400 h<sup>-1</sup>.

# 4.3. Results and Discussion 4.3.1. Effect of proximity on catalyst stability

The sodium and sulfur promoted iron catalyst supported on  $\alpha$ -alumina with an iron loading of 5.75 wt.-% (Na/Fe = 0.097 at/at, S/Fe = 0.0091 at/at) and 6.2 nm iron oxide particles was combined with an H-ZSM-5 zeolite in different configurations to vary the proximity between the iron catalyst and the zeolite (Figure 4-1-A). The iron time yield (moles of carbon monoxide converted per gram of iron and second) as a function of time can be found in Figure 4-1-B. The iron catalyst without zeolite (AFe) showed an iron time yield of  $1.8 \times 10^{-5}$  mol CO g<sub>Fe</sub><sup>-1</sup> s<sup>-1</sup> at the beginning of the reaction decreasing to  $1.2 \times 10^{-5}$  mol CO g<sub>Fe<sup>-1</sup></sub> s<sup>-1</sup> after 40 h on stream. The experiment performed in the stacked bed configuration (AFe+Z) showed similar activity, whereas the mixed bed configuration with large grain size (AFe/Z-500) had slightly higher FTY of  $2.2 \times 10^{-5}$  mol CO  $g_{Fe}^{-1}$  s<sup>-1</sup> at the beginning of the reaction, decreasing to  $1.7 \times 10^{-5}$  mol CO g<sub>Fe</sub><sup>-1</sup> s<sup>-1</sup> after 40 h. In the experiment of the mixed bed configuration and small grain size (AFe/Z-100) a higher activity of  $3.4 \times 10^{-5}$  mol CO g<sub>Fe</sub><sup>-1</sup> s<sup>-1</sup> was observed in the early stage of the reaction increasing to 3.9 ×10-5 mol CO gFe-1 s-1 after 40 h. The composite mixture (AFeZ) showed an even higher activity in the beginning of  $3.8 \times 10^{-5}$  mol CO g<sub>Fe</sub><sup>-1</sup> s<sup>-1</sup>, decreasing to  $2.7 \times 10^{-5}$  mol CO g<sub>Fe</sub><sup>-1</sup> s<sup>-1</sup> after 40 h.

In this set of experiments, we observed the trend that the initial activity increased with increasing proximity between the iron catalyst and the zeolite. In our previous work we found that this is caused by enhanced carburization of the iron catalyst when the iron catalyst is mixed with the zeolite in close proximity and observed full formation of iron carbide after 15 h under similar conditions <sup>35</sup>. The iron catalyst with the zeolite in a mixed bed configuration with small grains showed an increase in activity over time, in contrast to the other experiments that showed a gradual decrease. Using small grains in this experiment

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might have led to partial clogging of the catalyst bed due to coke formation under these conditions and therefore a gradual build-up of pressure of after ~10 h on stream.



**Figure 4-1: A:** Illustration of proximity between the iron catalyst and the zeolite. AFe: Iron catalyst without zeolite, AFe+Z: stacked bed with the zeolite downstream of the iron catalyst and a layer of silicon carbide between the two catalysts, AFe/Z-500 and AFe/Z-100: mixed bed configuration with the iron catalyst and the zeolite being mixed as a physical mixture with and average grain size of 500  $\mu$ m and 100  $\mu$ m, respectively and AFeZ: composite mixture of the iron catalyst and the zeolite. **B:** Iron time yield (FTY) of the iron catalyst as function of time on stream for samples with variable proximity between iron catalyst and zeolite. The higher the proximity between the inon catalyst and the zeolite, the higher the initial iron time yield. Reaction conditions: 400°C, 1 bar, CO:H2 = 1 (v/v), GHSV: 14,400 h<sup>-1</sup>.

The experiments performed with low proximity (AFe+Z and AFe/Z-500) showed a selectivity to  $C_2$ - $C_4$  olefins of 49-59%<sub>C</sub>, similar to the iron catalyst without zeolite (Figure 4-2-A). On the other hand, the experiments with higher proximity (AFeZ and AFe/Z-100) had lower  $C_2$ - $C_4$  olefin selectivity of 41-49%<sub>C</sub>. The composite mixture of iron catalyst and zeolite showed a low selectivity to  $C_6$ - $C_8$  aromatics of 5-6%<sub>C</sub> (Figure 4-2-B). The stacked bed and mixed bed experiments performed with lower proximity (AFe+Z and AFe/Z-500) displayed a decrease in selectivity to  $C_6$ - $C_8$  aromatics from 12%<sub>C</sub> to 9%<sub>C</sub> and 11<sub>C</sub> to 8%<sub>C</sub> in the first 40 h of the experiment, respectively. The iron catalyst mixed with the zeolite in a

mixed bed configuration and small grain size (AFe/Z-100) showed a strong decrease in C<sub>6</sub>-C<sub>8</sub> aromatic selectivity from 10%<sub>C</sub> to 6%<sub>C</sub> in the first 18 h followed by further decrease to 5%<sub>C</sub> after 40 h on stream. The methane selectivity of the iron catalyst without zeolite (AFe), the stacked bed configuration (AFe+Z) and the mixed bed with large grain size (AFe/Z-500) was between 14%<sub>C</sub> and 19%<sub>C</sub> throughout the whole experiments (Figure 4-2-C). The composite mixture (AFeZ) had high methane selectivity of 31%<sub>C</sub> to 35%<sub>C</sub>, whereas the methane selectivity of the mixed bed mixture of iron catalyst and zeolite with small grain size (AFe/Z-100) increased from 15%<sub>C</sub> to 25%<sub>C</sub> after 40 h.

In Figure 4-2-D and Figure 4-2-E the ASF-distribution for (aliphatic)  $C_1$ - $C_5$  hydrocarbons as a function of time on stream of the mixed bed experiment with small grain size (AFe/Z-100) and the stacked bed experiment (AFe+Z) can be seen, respectively. Here, the natural logarithm of the molar product fraction per carbon number was plotted versus the corresponding carbon number as a function of time on stream. The ideal ASF distribution would show a straight line. However, the presence of sodium and sulfur on an iron catalyst can break the ASF-distribution by selectively suppressing the methane formation as well as increase the olefin/paraffin ratio in the product distribution <sup>19,37</sup>.

The mixed bed experiment with small grain size (AFe/Z-100) showed this suppression of methane formation in the beginning of the reaction. As the reaction progressed, the product distribution converged towards the ideal ASF-distribution. The experiment with the stacked bed configuration (AFe+Z) showed the altered product distribution with suppressed methane formation throughout the whole experiment.

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**Figure 4-2: A:** Selectivity to  $C_2-C_4$  olefins as function of time on stream (TOS) for the alumina supported iron catalyst mixed with the zeolite in different proximities. **B:** Selectivity to  $C_6-C_8$  aromatics as function of time on stream for the alumina supported iron catalyst mixed with the zeolite in different proximities. **C:** Selectivity to methane as function of time on stream for the alumina supported iron catalyst mixed with the zeolite in different proximities. **D:** Anderson-Schulz-Flory distribution as function of time on stream for the iron catalyst mixed with the zeolite in a mixed bed configuration with small grain size (AFe/Z-100). **E:** Anderson-Schulz-Flory distribution as function of time on stream for the iron catalyst mixed with the zeolite in a stacked bed configuration (AFe+Z). Reaction conditions: 400°C, 1 bar, CO:H<sub>2</sub> = 1 (v/v), GHSV: 14,400 h<sup>-1</sup>. The selectivity to C<sub>2</sub>-C<sub>4</sub> paraffins as a function of time can be found in Figure C6 in Appendix C.

These data show that the proximity between the iron catalyst and the zeolite has a limited influence on the selectivity of the bifunctional catalyst for olefins whereas the effects on aromatics and methane selectivities are significant. The ASF-distribution as function of time on stream for the mixed bed experiment with small grain size (Figure 4-2-D) suggests a gradual loss of the effect of sodium and sulfur promoters on the iron catalyst over time, whereas this loss of promoter effect was not observed for the spatially separated stacked bed experiment (Figure 4-2-E). This is in line with the selectivity of methane and  $C_2$ - $C_4$  olefins over time, where the stacked bed experiment showed stable selectivities in the range of the

iron catalyst without zeolite for methane as well as for  $C_2$ - $C_4$  olefins and the mixed bed experiment with small grains displayed an increasing methane selectivity over time as well as a lower  $C_2$ - $C_4$  olefin selectivity. Furthermore, the decrease over time in selectivity to  $C_6$ - $C_8$  aromatics for AFe/Z-100 indicates a gradual migration of sodium ions from the iron catalyst to the zeolite resulting in neutralization of acid sites in the zeolite. The composite mixture of the iron catalyst and the zeolite displayed a low selectivity to  $C_6$ - $C_8$  aromatics from the beginning of the reaction, which suggests fast migration of sodium ions from the iron catalyst to the zeolite due to the close proximity of the iron and the zeolite. This is also in agreement with the high methane selectivity for the composite mixture from the beginning of the reaction.

To provide spectroscopic evidence for the migration of sodium ions from the iron catalyst to the zeolite, we performed X-ray photoelectron spectroscopy (XPS) measurements on the calcined iron catalyst without zeolite and the mixed bed mixture of the iron catalyst and zeolite with small grains after heat treatment. The catalysts were treated using the same temperature profile as for the catalytic performance measurement (5 K/min to 350°C, 2 h; 5 K/min to 290°C, 1 h; 5 K/min to 400°C, 15 h). However, we used an inert nitrogen flow to avoid carbon formation on the surface of the catalysts during catalysis, which would interfere with the XPS measurement due to screening of photoelectrons. A sodium ion exchanged ZSM-5 zeolite (denoted as Na-ZSM-5) was analyzed as a reference for sodium ions being located in the zeolite. The calcined iron catalyst initially showed a Na 1s signal in XPS at 1071.4 eV, whereas the position of this peak did not change after performing the heat treatment (Figure 4-3). However, the mixed bed mixture of the iron catalyst and the zeolite after the heat treatment showed a shift of the Na 1s signal to 1073.0 eV, which is in the range of the sodium ion exchanged zeolite (1072.8 eV). This shift towards higher binding energy of the signal for the Na 1s electrons after the heat treatment supports our hypothesis of migration of sodium ions from the iron catalyst to the zeolite, resulting in loss of promotion effect on the iron catalyst as well as decreased acidity of the zeolite.

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**Figure 4-3:** X-ray photoelectron spectra of the Na 1s core level region of (a) the  $\alpha$ -alumina supported iron catalysts without zeolite, (b) the  $\alpha$ -alumina supported iron catalysts without zeolite after heat treatment, (c)  $\alpha$ -alumina supported iron catalysts and zeolite in mixed bed configurations with 75-150 µm grains size after heat treatment, and (d) sodium ion exchanged ZSM-5 zeolite.

#### 4.3.2. Effect of support material on catalyst stability

To study the effect of support material on the stability, an iron catalyst supported on carbon nano-tubes (CNT) was prepared by attaching colloidal iron nano-crystals (Fe-NC) onto CNT <sup>38,39</sup>, followed by incipient wetness impregnation of a solution that contained sodium and sulfur promoters (resulting in 2.96 wt.-% Fe, Na/S=0.073 at/at, S/Fe=0.036 at/at, 8.4 nm iron oxide particles). The iron loading was limited to 3 wt-% to avoid fast deactivation due to sintering of Fe-NC <sup>39</sup>. This CNT supported iron catalyst was used to prepare a composite mixture with the H-ZSM-5 zeolite (denoted as CFeZ). This composite catalyst demonstrated a lower overall stability (Appendix C, Figure C7) but constant selectivity to

methane of  $19\%_{C}$  throughout the runtime of 50 h (Figure 4-4-A). In comparison, the alumina supported iron catalyst in a mixed bed configuration with the zeolite and small grain size showed that the methane selectivity increased from  $15\%_{C}$  to  $27\%_{C}$ . The ASF distribution of these two experiments after 50 h on stream for the alumina supported iron catalyst in a mixed bed configuration with the zeolite and small grains and after 100 h on stream for the composite with the CNT-supported iron catalyst and zeolite can be seen in Figure 4-4-B, respectively. The CNT-supported iron catalyst as composite with the zeolite showed a strong deviation from the ASF distribution with lower methane selectivity, whereas for the alumina supported iron catalyst in a mixed bed with the zeolite this deviation was much less pronounced. This constant selectivity of the composite mixture of the CNT-supported iron catalyst and the zeolite indicates that the migration of sodium ions over the surface of the support towards the zeolite is hindered, despite the close proximity of iron and zeolite. We hypothesize that the migration of sodium ions over the CNT surface was hindered due to the limited capability of the CNT material for charge compensation of the sodium ions moving from the iron (-carbide) to the zeolite.



**Figure 4-4:** A: Methane selectivity of the sodium and sulfur promoted iron catalyst supported on CNT in a composite mixture with the zeolite (CFeZ) and the  $\alpha$ -alumina supported sodium and sulfur promoted iron catalyst in a mixed bed configuration with the zeolite and 75-150 µm grain size (AFe/Z-100) as a function of time on stream, **B:** Anderson-Schulz-Flory distribution for the sodium and sulfur promoted iron catalyst supported on CNT in a composite mixture with the zeolite (CFeZ) after 100 h on stream and the  $\alpha$ -alumina supported sodium and sulfur promoted iron catalyst in a mixed bed configuration with the zeolite and 75-150 µm grain size (AFe/Z-100) after 50 h on stream. Reaction conditions: 400°C, CO/H<sub>2</sub>=1, GHSV=7200 h<sup>-1</sup>, 1 bar.

An increased methane selectivity due to the loss of promotion effect on the iron (carbide) function as well as decreased selectivity to  $C_6$ - $C_8$  aromatics caused by neutralization of acid sites of the zeolite by sodium ions was observed when the iron catalyst was mixed with the zeolite in close proximity. The migration of sodium ions from the iron catalyst to the zeolite was confirmed using XPS. Mixing the iron catalyst and the zeolite in lower proximity could circumvent this loss of promotion effect and decrease in acidity of the zeolite, due to the spatial separation of the two catalysts. Furthermore, we could support our hypothesis of sodium ion migration from the iron catalyst to the zeolite by using carbon as support material for the iron catalyst, which is suggested to lack the capability of charge compensation for diffusing sodium ions.

# 4.4. Conclusions

We combined an  $\alpha$ -alumina supported iron catalyst promoted with sodium and sulfur with an H-ZSM-5 zeolite to convert synthesis gas to olefins and aromatics in a single reactor. The presence of both sodium and sulfur on the iron catalyst led to a deviation from the Anderson-Schulz-Flory distribution with decreased methane selectivity. However, when the iron catalyst was mixed with the zeolite in close proximity, the deviation from the ASF-distribution vanished over time and the selectivity to methane increased, whereas the selectivity to aromatics decreased. We attributed this behavior to the migration of sodium ions from iron to zeolite, resulting in a loss of promotion effect of iron and neutralization of acid sites in the zeolite. The migration of sodium ions as a result of heat treatment was confirmed using XPS. Catalysis with lower proximity of iron and zeolite circumvented the migration of sodium ions. Furthermore, using carbon material as support for the iron catalyst supported our hypothesis of sodium ions, their migration was hindered over the carbon support. These findings are important for future development of more stable bifunctional catalyst systems.

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# 5

# Influence of Promotion on the Growth of Anchored Colloidal Iron Oxide Nanoparticles during Synthesis Gas Conversion

Using colloidal iron oxide nanoparticles with organic ligands, anchored in a separate step to supports, has been shown beneficial to obtain homogeneously distributed metal particles with a narrow size distribution. Literature indicates that promoting these particles with sodium and sulfur creates an active Fischer-Tropsch catalyst to produce olefins, while further adding an H-ZSM-5 zeolite is an effective way to obtain aromatics. This research focused on the promotion of iron oxide colloids with sodium and sulfur using an inorganic ligand exchange followed by the attachment to H-ZSM-5 zeolite crystals. The catalyst referred as FeP/Z, which consisted of iron particles with inorganic ligands attached to a H-ZSM-5 catalyst, was compared to an unpromoted Fe/Z catalyst and an Fe/Z-P catalyst, containing the colloidal nanoparticles with organic ligands, promoted after attachment. A low CO conversion was observed on both FeP/Z and Fe/Z-P, originating from an overpromotion effect for both catalysts. However, when both promoted catalysts were washed (FeP/Z-W and Fe/Z-P-W) to remove the excess of promoters, the activity was much higher. Fe/Z-P-W simultaneously achieved low selectivity towards methane as part of the promoters were still present after washing whereas for FeP/Z-W the majority of promoters was removed upon washing, which increased the methane selectivity. Moreover, due to the addition of Na+S promoters, the iron nanoparticles in the FeP/Z(-W) catalysts had grown considerably during catalysis, while those in Fe/Z-P(-W) and Fe/Z(-W) remained relatively stable. Lastly, as a large broadening of particle sizes for the used FeP/Z-W was found, where particle sizes had both increased and decreased, Ostwald ripening is suggested for particle growth accelerated by the presence of the promoters.

Krans, N. A., Weber, J. L., Van Den Bosch, W., Zečević, J., De Jongh, P. E., & De Jong, K. P. Influence of Promotion on the Growth of Anchored Colloidal Iron Oxide Nanoparticles during Synthesis Gas Conversion. *ACS Catal.* **10**, 1913–1922 (2020).

## 5.1. Introduction

Over recent years, research has focused on the exploration of alternative pathways to produce fuels and chemicals which are nowadays mainly obtained from oil. As a suitable replacement for oil, synthesis gas (a mixture of  $H_2$  and CO) can be used, as it can be derived from natural gas, coal, CO<sub>2</sub>, renewable hydrogen gas and biomass <sup>1–5</sup> and can be converted to a wide range of products via monofunctional <sup>6–8</sup> and bifunctional catalysts <sup>9–11</sup>.

Recently, a bifunctional catalyst system has been introduced by the group of Prof. Bao consisting of a metal oxide and a zeolite (OX-ZEO) to convert synthesis gas to short olefins via reactive oxygenate intermediates such as methanol, dimethyl ether, or ketene <sup>9,12–14</sup>. The choice of zeolite material is crucial to control the resulting product spectrum of the OX-ZEO process. The reactive oxygenate intermediates can be converted to olefins using zeolites with small pore diameters such as SAPO-34 and SSZ-13. However, the use of a ZSM-5 zeolite owning a larger pore diameter allowed the formation of aromatics from these intermediates <sup>10,15</sup>.

Alternatively, synthesis gas can be converted in the Fischer-Tropsch synthesis (FTS) to ultraclean hydrocarbons in the range from methane to waxes <sup>6,16</sup>. Operating cobalt-based catalysts in the low-temperature Fischer-Tropsch process (LT-FTS) results in the formation of linear paraffins with high molecular weight, whereas the high-temperature Fischer-Tropsch synthesis (HT-FTS) using iron-based catalysts produces light olefins <sup>6,11,17,18</sup>.

The product spectrum of the FTS usually follows the Anderson-Schulz-Flory (ASF) distribution, a statistical distribution of products of surface polymerization reactions. However, adding promoters to an iron-based Fischer-Tropsch catalyst can lead to a deviation from the ASF distribution in the so-called Fischer-Tropsch to olefins (FTO) process <sup>19–22</sup>. The presence of both sodium and sulfur promoters on the iron catalyst is essential for a decreased selectivity to methane and increased olefins/paraffin ratio <sup>23–25</sup>. This allows the formation of C<sub>2</sub>-C<sub>4</sub> olefins with 65%<sub>C</sub> selectivity <sup>26</sup>, more than the ASF predicted distribution of 58%<sub>C</sub> selectivity for the C<sub>2</sub>-C<sub>4</sub> fraction (olefins plus paraffins) <sup>27</sup>.

These short olefins being formed on the FTO catalyst with high selectivity can be further converted to aromatics on an H-ZSM-5 zeolite  $^{28-30}$  not only starting from syngas but also using CO<sub>2</sub> as a reactant  $^{31}$ . In this process, the Brønsted acid sites (BAS) of the zeolite enable the aromatization of olefins that are formed on the FTO catalyst. However, combining the zeolite and FTO catalyst promoted with sodium and sulfur can facilitate the migration of sodium ions from the FTO catalysts to the BAS of the zeolite. This results in zeolite acid sites neutralization and a loss of the promotion effect of the FTO catalysts thus increasing methane selectivity  $^{32}$ .

Metal catalysts are typically prepared via methods such as incipient wetness impregnation (IWI) or precipitation <sup>33,34</sup>. These methods, however, can offer limited control over the metal particle size, shape, and distribution, which is of the utmost importance for catalyst activity, selectivity and stability <sup>35–37</sup>. Therefore, research in academia has focused

on colloidal synthesis methods which can controllably yield iron oxide nanoparticles (Fe-NP) of various sizes. Here, an iron precursor is decomposed at higher temperatures in a solvent in the presence of organic ligands, resulting in ligand stabilized Fe-NP in suspension. Colloidal particles are subsequently attached to different support materials, obtaining relatively sinter resistant catalysts <sup>38–42</sup>.

Furthermore, model catalysts composed of colloidal iron nanoparticles supported on carbon nanotubes (CNT) were used to study the FTO reaction <sup>41,43</sup>. These colloidal particles were promoted with sodium and sulfur using an inorganic ligand exchange method <sup>44–46</sup>. Here, the organic ligands stabilizing the Fe-NP are (partially) replaced with inorganic ligands that can also act as promoters, such as Na<sub>2</sub>S <sup>45,46</sup>. When applied in the FTO process, this exchange was performed after the Fe-NP were attached to the support material <sup>44</sup>. However, so far it has been challenging to direct the promoters so that they specifically attach to the iron particles and not to the support material.

Since the colloidal method has the advantage of controlling the particle size distribution, it means that it is easier to discern particle growth mechanisms <sup>24</sup>. Particle growth can be divided into two distinctively different mechanisms, namely Ostwald ripening, where the transport of mobile species happens over the support or in the gas phase, growing larger particles at the expense of smaller ones and coalescence and growth which involves particle migration over the surface, coalescing to form larger particles <sup>47</sup>.

In this study, we prepared colloidal Fe-NP and attached these in a separate step onto an H-ZSM-5 zeolite in order to convert synthesis gas to olefins and aromatics. This advanced synthesis method allows for uniform particle distributions where the particles are located on the exterior surfaces of the zeolite crystals. Using this method allows to create a catalyst which not only uses the ZSM-5 as a support but additionally to convert syngas into aromatics. To introduce sodium and sulfur promoters, inorganic ligand exchange with Na<sub>2</sub>S was performed on the Fe-NP either before or after attachment onto the zeolite. These materials were used in the Fischer-Tropsch reaction to obtain olefins, which are further converted to aromatics. We show the influence of the synthesis sequence of Na+S promoted Fe-NP on H-ZSM-5 on the activity, selectivity, and stability. Using ligand exchange prior to the attachment (FeP/Z) compromised the catalyst stability when compared to ligand exchange after attaching the particles (Fe/Z-P). A washing step was used (FeP/Z-W and Fe/Z-P-W) to remove the excess of inorganic ligands which led to a more active catalyst for both promoted catalysts. Finally, analysis of the used catalyst revealed that particles from the promoted FeP/Z-W catalyst partially shrunk to smaller sizes than the fresh catalyst, giving a strong indication of the Ostwald ripening process.

# 5.2. Experimental 5.2.1. Catalyst Preparation

Synthesis of 6 nm iron oxide nanoparticles (Fe-NP). All chemicals were obtained from Sigma-Aldrich unless stated otherwise. To synthesize the colloidal iron oxide nanoparticles, 0.43 g oleic acid (90% purity), 0.21 g olevlamine (70% purity), 0.35 g 1,2hexadecanediol ( $\geq$  98% purity) and 10 mL 1-octadecene (90% purity) were added to a threeneck round-bottom flask.<sup>43</sup> The reactants were degassed under vacuum in a Schlenk-line setup for 30 minutes at 120°C while magnetically stirring at 650 rpm. The stirring bar used in the preparations were glass-covered magnetic stirring bars to prevent contamination by iron uptake into the PTFE of conventional stirring bars. The suspension was subsequently purged with nitrogen gas, after which the temperature was lowered to  $90^{\circ}$ C and a solution of 0.21 g iron pentacarbonyl (99.99%) in 1 mL 1-octadecene was injected. The temperature was then increased to 290°C in 10 minutes and the mixture was refluxed for 1 h. Subsequently, the obtained suspension of iron nanoparticles (Fe-NP) was cooled down to room temperature and further processed in air. The iron Fe-NP suspension was washed thrice, where the suspension was centrifuged in about 10 mL isopropanol at 2700 rpm for 15 min, and re-dispersed in five drops of toluene. Finally, particles were suspended in 2.4 mL of toluene by sonication for 5 minutes.

Attachment of Fe-NP onto H-ZSM-5. As-synthesized Fe-NP suspended in toluene were diluted with 10 mL 1-octadecene. 800 mg of powdered zeolite (H-ZSM-5, Zeolyst CBV 3024E, Si/Al = 15 at/at, calcined for 5 h at 550°C in static air) was added to a 100 mL three-neck round-bottom flask, which was connected to a Schlenk line through a reflux cooler.<sup>43</sup> The suspended Fe-NP were added to H-ZSM-5 by pipetting while simultaneously magnetically stirring at 400 rpm. The mixture was brought under vacuum for 30 minutes at 120°C to evaporate the toluene, and subsequently purged with nitrogen. The temperature was increased to 200°C in 10 minutes under nitrogen flow and maintained for 30 min. Afterward, the mixture was cooled down to room temperature and further processed in air. Finally, the Fe-NP supported on the zeolite were washed five times with a mixture of *n*-hexane and acetone (1:3 v/v) and dried at 60°C for 1 h under static air, at 120°C for 3 h under static air, and at 80°C for 3 h under vacuum. This method allowed to synthesize Fe-NP attached to H-ZSM-5 zeolite with 3 wt.% iron loading. These samples are referred to as Fe/Z.

**Inorganic ligand exchange of Fe/Z.** A 0.05 M sodium sulfide stock solution was obtained by sonicating 0.24 g sodium sulfide nonahydrate ( $\geq$  98% purity) in 20 mL formamide ( $\geq$  99.5% purity) for 1 h. 2.2 mL of the stock solution was added to 350 mg of Fe/Z and stirred at 400 rpm for 10 minutes.<sup>44</sup> The promoted catalysts were first washed with ethanol, followed by four times washing with a mixture of ethanol and acetone (1:3 v/v), and finally washed with acetone. In every step, the supernatant was carefully decanted and pipetted off. Finally, the catalyst was dried at 60°C for 1 h under static air, at 120°C for 3 h

under static air and at 80°C for 3 h under vacuum. This promoted catalyst is designated as Fe/Z-P.

**Inorganic ligand exchange of Fe-NP with Na<sub>2</sub>S.** For the direct promotion by inorganic ligand exchange, a method was adapted from Nag, *et al.*<sup>45</sup> The as-synthesized Fe-NP suspended in toluene were added to 2.4 mL of a 0.5 M Na<sub>2</sub>S  $\cdot$  9H<sub>2</sub>O solution in formamide. This formed two layers with the Fe-NP in toluene on top and the formamide solution at the bottom. The solution was vigorously stirred for 1 hour. Afterward, the particles had transferred to the formamide layer. The particles were washed with acetonitrile, centrifuged at 2700 rpm for 15 min and re-dispersed in five drops of methanol three times. Finally, particles were suspended in 2.4 mL of methanol. These particles are denoted as FeP-NP.

Attachment of FeP-NP onto H-ZSM-5. FeP-NP suspended in methanol were added to 800 mg of the zeolite (H-ZSM-5, Zeolyst CBV 3024E, Si:Al = 15 at/at, calcined for 5 h at 550°C in static air) in the Schlenk-line set-up while stirring at 400 rpm. Slowly, the vacuum was applied to the suspension, and it was heated to 50°C to evaporate the methanol. The suspension was kept at these conditions for 1 h to ensure the FeP-NP had attached to the support. The catalyst was dried at 60°C for 1 h under static air, at 120°C for 3 h under static air, and at 80°C for 3 h under vacuum. This catalyst is referred to as FeP/Z.

**Washing procedure.** To remove the excess of sodium and sulfur promoters from the Fe-NP and to recover acidity of the zeolite by ion exchange, the catalysts (Fe/Z, Fe/Z-P and FeP/Z) were washed with an ammonium nitrate solution. 400 mg catalyst was added to a 2 mL ammonium nitrate solution (1 mol/L in demineralized water) and stirred at 400 rpm and 25°C for 1 h. Afterward, the catalysts were washed six times with a mixture of water and acetone (1:3 v/v), centrifuged and dried at 60°C for 16°h. Catalysts will be referred to as Fe/Z-W, FeP/Z-W and Fe/Z-P-W. After this procedure, the H-ZSM-5 had been converted into an NH<sub>4</sub>-ZSM-5. However, during the *in-situ* reduction at elevated temperatures the ammonia fully desorbed and the proton form of the zeolite was recovered, as evidenced by TPD (Figure D1, Appendix D). Moreover, the sample codes and descriptions of all catalysis have been explained in Table D1 in Appendix D.

# 5.2.2. Characterization

**Inductively Couple Plasma Atomic Emission Spectrometry.** The elemental composition of the catalysts was determined with a Thermo Jarrell Ash model ICAP 61E trace analyzer inductively-coupled plasma atomic emission spectrometer (ICP-AES).

(Scanning) Transmission Electron Microscopy. To determine the size distribution and the spatial distribution of iron nanoparticles on the support, before and after catalytic testing, (scanning) transmission electron microscopy ((S)TEM) was used. Images were recorded with an FEI Talos F200X transmission electron microscope, operated at 200 kV in bright field (TEM) or dark field mode (STEM). The samples were prepared on Formvar carbon film, 200 mesh copper grids. The samples were dispersed in pure ethanol, sonicated, and drop casted on the TEM grids.

**Ar-physisorption.** Ar-physisorption at -196°C was carried out on a Micromeritics TriStar 3000 to determine the specific surface area and pore volume of the parent zeolite. Prior to measurement, the material was dried in a nitrogen flow at 300°C for 16 h.

**Temperature programmed ammonia desorption.** Temperature programmed ammonia desorption (NH<sub>3</sub>-TPD) was done to determine the total amount of acid sites on all catalysts with around 50 mg per sample. Drying was carried out with a heating ramp of 10 K/min until a temperature of 600°C was reached for 15 min. The samples were cooled down to 100°C and ammonium gas (10% NH<sub>3</sub> in He) was dosed to the samples. Ammonium desorption was performed by heating again to 600°C with 10 K/min.

**Pyridine Infrared spectroscopy.** Pyridine Infrared (IR) measurements were done as an addition to the NH<sub>3</sub>-TPD. Around 20 mg of sample was pelletized into IR pellets with a diameter of 1.3 cm. IR spectra were taken with a Perkin-Elmer System 2000 instrument in the spectral range of 4000–400 cm<sup>-1</sup> (32 spectra were acquired per sample). Background spectra were recorded on an empty cell under vacuum (~10<sup>-5</sup> mbar). Drying of the pellet was done under the same pressure with a heat ramp of 5 K/min until a temperature of 350°C was reached and held for 3 h. The samples were cooled down to room temperature and pyridine gas was introduced ( $p_{Py}$  ~15 mbar) for 30 min. Thereafter, desorption was performed at vacuum (~10<sup>-5</sup> mbar) by heating with a heat ramp of 5 K/min until a temperature of 150°C was reached and held for 30 min. The pyridine was desorbed by heating up to 150°C while taking spectra every 25°C. When 150°C was reached, the temperature was held for 30 minutes, and spectra were recorded every 10 minutes. Complete desorption of the pyridine was achieved by heating to 550°C (5 K/min) and maintaining that temperature for 2 h. The acid sites were calculated following methods originating from both Emeis, *et al.* and Hernández-Giménez, *et al.* <sup>48–50</sup>.

**Thermogravimetric analysis Mass spectrometry (TGA-MS).** TGA was performed to analyze the organic ligands present on the particles. The ligand content of samples ZSM-5 (support), Fe/Z and FeP/Z was measured using a Perkin Elmer TGA8000, hyphenated with a Hiden HPR-20 mass spectrometer. Catalysts were heated from  $30^{\circ}$ C -  $800^{\circ}$ C (5 K/min) in 20% O<sub>2</sub> in Ar (16 mL/min). Additionally, ZSM-5 treated with the organic liquids using the procedure *Attachment of Fe-NP onto H-ZSM-5* without suspended iron particles present was measured. Lastly, Fe/Z was measured as well by using a reduction procedure (5 K/min to  $350^{\circ}$ C for 2 h, 5% H<sub>2</sub> in Ar, 25 mL/min) to find if the ligands were removed during the *in situ* reduction in the FTO reaction. To verify the removal of the ligands, the reduced Fe/Z was again measured by heating from  $30^{\circ}$ C -  $800^{\circ}$ C (5 K/min) in 20% O<sub>2</sub> in Ar (16 mL/min).

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#### 5.2.3. Catalytic Performance

To examine the catalytic performance of the synthesized catalysts in the conversion of synthesis gas to olefins and aromatics, experiments were performed at 1 bar and 10 bar pressure.

Catalytic performance at 1 bar. The catalytic performance was investigated at 1 bar by loading 20 mg of Fe-NP supported on zeolite (sieve fraction of 75-150 µm) diluted with 150 mg silicon carbide (sieve fraction of 212-425 µm) into a quartz reactor. After insitu reduction at 350°C (5 K/min) in a flow of 15 mL/min of hydrogen in nitrogen (2:1 v/v, resulting GHSV =  $12,500 \text{ h}^{-1}$ ) for 2 h, a carburization step was performed at 290°C (5 K/min) in a flow of 6 mL/min of synthesis gas (CO:H<sub>2</sub> = 1 v/v, resulting GHSV = 5,000 h<sup>-1</sup>) for 1 h. The reaction was carried out at 340°C (5 K/min) in a flow of 6 mL/min of synthesis gas  $(CO:H_2 = 1 \text{ v/v}, \text{ resulting GHSV} = 5,000 \text{ h}^{-1})$  for 16 h. The hydrocarbon products were analyzed with an online-gas chromatograph (Varian 430-GC) equipped with a flame ionization detector. CO conversion was calculated from the formation of hydrocarbon from synthesis gas. Selectivities were calculated as hydrocarbon distribution on carbon atom basis  $(CO_2 \text{ free})$ . A CO<sub>2</sub> selectivity of 40-45% is expected which is around the thermodynamic limit under these conditions. In this specific gas chromatograph, lower olefins and paraffins could not be separated. Therefore, the C<sub>2</sub>-C<sub>4</sub> selectivity will always be shown as a combined number of both the olefins and the paraffins. The activity was calculated as iron time yield (FTY) which is defined as moles of CO being converted per gram of iron per second.

**Catalytic performance at 10 bar.** The experiments performed at 10 bar were carried out in a 16-channel high throughput set-up (Avantium Flowrence). 15 mg of the Fe-NP supported on zeolite (sieve fraction of 75-150  $\mu$ m) was diluted with 100 mg silicon carbide (sieve fraction of 212-425  $\mu$ m) and loaded into stainless steel reactors with 2.6 mm inner diameter. After *in-situ* reduction in a flow of 30% H<sub>2</sub> in He (v/v, resulting GHSV = 6,900 h<sup>-1</sup>) at 350°C and 1 bar for 2 h, a carburization step was performed at 290°C (5 K/min) and 1 bar for 1 h in a flow of 3.75 mL/min synthesis gas (CO:H<sub>2</sub>:He = 6:12:1 v/v/v, resulting GHSV = 4,100 h<sup>-1</sup>). Reaction conditions were applied by increasing the reactor temperature to 340°C with 5 K/min and increasing the pressure to 10 bar in a flow of 3.75 mL/min synthesis gas (CO:H<sub>2</sub>:He = 4,100 h<sup>-1</sup>). The reaction products were analyzed by an online gas chromatograph (Agilent 7890A) equipped with a flame ionization detector and a thermal conductivity detector. For the CO conversion in the high-pressure experiments, the conversion towards hydrocarbons and the formation of CO<sub>2</sub> in the WGS was taken into account. Selectivities were calculated as distribution within hydrocarbon on carbon atom basis (CO<sub>2</sub> free).

# 5.3. Results and Discussion 5.3.1. Characterization of the catalysts

Iron oxide nanoparticles (Fe-NP) of 6 nm were synthesized according to a previously published method <sup>41,43</sup>. Figure 5-1-A shows a transmission electron micrograph of the colloidal particles synthesized with organic oleic acid and oleylamine ligands. The organic ligands separated the iron oxide particles by 2 nm when dried on the transmission electron microscopy (TEM) grid, which is associated with the length of one oleic acid or oleylamine ligand <sup>51,52</sup>. These Fe-NP were used in an inorganic ligand exchange step to add Na+S promoters, following a procedure mentioned in previous research <sup>45,46</sup> (FeP-NP). Notably, the particle size was unaffected after the inorganic ligand exchange, as can be observed in the histograms but particles came in close proximity to one another on the TEM grid (Figure 5-1-B). The shortening of distance was assigned to stronger particle-particle interactions originating from the charge stabilizing ligands compared to the steric stabilizing organic ligands in Fe-NP and the replacement of long oleic acid and oleylamine ligands by small Na/S ligands <sup>52</sup>.



**Figure 5-1:** Electron micrographs of the colloidal iron oxide nanoparticles with organic ligands (A) and inorganic ligands (B) dried on a TEM grid. The insets show the histogram of the size of the particles with a number-average particle size of 6 nm.

The Fe-NP in toluene and the FeP-NP in methanol were attached to an H-ZSM-5 zeolite producing Fe/Z and FeP/Z, respectively (Figure 5-2) (Sample codes and descriptions are summarized in Table D1, Appendix D). The micropore dimensions of H-ZSM-5 zeolites are 0.53x0.58 nm <sup>53</sup>, implying that the colloidal particles of 6 nm could not enter the micropores, but attached to the external surface of the zeolite crystals. The bare H-ZSM-5 material had a micro-pore surface area of  $365 \text{ m}^2/\text{g}$  and an external surface area of  $50 \text{ m}^2/\text{g}$  (obtained from T-plot) as obtained from argon physisorption, see Figure D2 in Appendix D. As the external surface area was relatively small, the particle to particle distances were small, especially compared to colloidal particles with similar weight loading on carbon nanotubes from previous literature <sup>41,43</sup>, which had an external surface area of  $230 \text{ m}^2/\text{g}$ . The particle

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size of the Fe-NP was not significantly affected by the attachment to the support, see insets in Figure 5-2. FeP/Z in Figure 5-2-B displayed chains of particles probably because of the small ligand sizes which enabled magnetic interactions of maghemite or magnetite domains. The inorganic ligand exchange of Fe/Z to obtain Fe/Z-P did not alter the particle size and distribution, as it can be seen in Figure 5-2-C.



**Figure 5-2:** Electron micrographs of the iron oxide nanoparticles attached to H-ZSM-5 with organic ligands, Fe/Z (A). Na+S ligand exchange performed before attachment of Fe to the zeolite, FeP/Z (B) and Na+S ligand exchanged after attaching, Fe/Z-P (C). Histograms of particle sizes inserted in the figures show the narrow Fe particle size distribution and average particle size of 6 nm independent of the synthesis method.

Table 5-1: Particle size, standard deviation and weight loading of all catalysts. No size change was found when
attaching the Fe-NP to the zeolite support, or when washing and calcining the catalysts. The weight loading was
determined by ICP-AES and showed all catalysts had similar iron weight loadings.

Sample name	Particle size (nm)	Fe (wt-%)	Na/Fe (at/at)	S/Fe (at/at)	Na/BAS (mol/mol)	
Fe/Z	6.0	3.3	<d.1.< td=""><td><d.1.< td=""><td>N.D.</td></d.1.<></td></d.1.<>	<d.1.< td=""><td>N.D.</td></d.1.<>	N.D.	
Fe/Z-W	6.2	3.2	<d.1.< td=""><td><d.1.< td=""><td>N.D.</td></d.1.<></td></d.1.<>	<d.1.< td=""><td>N.D.</td></d.1.<>	N.D.	
FeP/Z	6.0	2.8	0.21	0.03	0.79	
FeP/Z-W	5.9	2.7	<d.1.< td=""><td><d.1.< td=""><td>N.D.</td></d.1.<></td></d.1.<>	<d.1.< td=""><td>N.D.</td></d.1.<>	N.D.	
Fe/Z-P	6.0	3.7	0.17	0.05	0.73	
Fe/Z-P-W	6.0	3.2	0.14	0.03	0.56	
< d.l. the detection limit for sulfur was 0.07 wt% and for sodium 0.02 wt%.						

<d.l. the detection limit for sulfur was 0.07 wt% and for sodium 0.02 w N.D. = not determined. BAS = Bronsted Acid Sites

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was used to determine the weight loading of iron, sodium and sulfur on the catalysts, see Table 5-1. The iron weight loading was close to 3 wt-% in all samples, however, the sodium and sulfur content varied per catalyst. As the sulfur content was relatively low in the catalysts and close or below to the detection limit of the apparatus, the ICP values for sulfur should be considered only as indicative values.

Previous research gave an indication that for colloidal Fe-NP-based catalysts an Na/Fe ratio of 0.09-0.12 at/at would be optimal for a high CO conversion and high  $C_2$ - $C_4$  olefin selectivity <sup>44,54</sup>. Considerably higher Na/Fe ratios resulted in a decrease in activity by overpromotion of the catalyst <sup>54</sup>. The sodium to iron ratio in this study was relatively high

(Na/Fe = 0.17-0.21 at/at) on both of the promoted catalysts, most likely overpromoting both systems. In addition, there is a possibility that the excess of sodium could be located on the Brønsted acid (BAS) sites of the zeolite, blocking the acid sites, and therefore deactivating the zeolite.

#### 5.3.2. Removal of promoter excess

To remove the excess of promoters from the iron nanoparticles and zeolite, an additional washing step using ion exchange was applied with ammonium nitrate, creating the following catalysts: Fe/Z-W, FeP/Z-W and Fe/Z-P-W. TEM images of the catalysts obtained through the washing step are shown in Figure D3 (Appendix D). No significant change in particle size and hardly in iron content were observed from TEM and ICP measurements (Table 5-1). ICP indicated that due to the washing step the sodium on FeP/Z was almost entirely removed from the catalyst. In the Fe/Z-P catalyst, however, some sodium was removed but most was retained, and hence this catalyst was more comparable with active catalysts from previous research <sup>44,54</sup>.

To get an indication of whether sodium was specifically attached to the iron and/or to the Brønsted acid sites (BAS), temperature-controlled desorption NH<sub>3</sub>-TPD and pyridine IR were measured, see Figures D4-D9 in Appendix D. The NH<sub>3</sub>-TPD results could only be used as indicative values as the ammonia did not specifically bind to only the acid sites of the zeolite but also the iron (-oxide or -hydroxide) sites <sup>55</sup>. Therefore, pyridine IR was used to obtain a quantity for the BAS, see Figures D6-D9 in Appendix D. Using pyridine IR, a peak indicating the BAS can be found at 1543 cm<sup>-1</sup> while the peak indicating the Lewis acid sites (LAS) are at 1455 cm<sup>-1</sup>. The peak at 1490 cm<sup>-1</sup> originates from BAS in the vicinity of LAS <sup>50</sup>. To confirm that the pyridine did not absorb on the iron particles, measurements were performed on SiO<sub>2</sub> and Fe-NP/SiO<sub>2</sub>, see Figures D6-D7 (Appendix D). No pyridine was absorbed by the silica itself, as indicated by Figure D6 (Appendix D). The Fe-NP did absorb pyridine as a peak was found at 1450 cm<sup>-1</sup> to indicate LAS, see Figure D7 (Appendix D). However, this pyridine was weakly bound to the iron particles and desorbed before a temperature of 150°C was reached (the temperature used to calculate the number of BAS and LAS), confirming that this absorbed pyridine was of no influence on the calculations done for the acid site concentrations.

By integrating the BAS peak in Figure D8 (Appendix D) it was found that the BAS in the H-ZSM-5 zeolite was 0.14 mmol/g. From this number and the ICP values given in Table 5-1 (assuming that all sodium would have been incorporated in the zeolite) the maximum amount of blocked acid sites was calculated. It was established that if all sodium was located on the zeolite a maximum of 79% of all the BAS on the zeolite could be deactivated. However, when comparing the concentration of the BAS in Figure D9 (Appendix D), it was noticeable that all the catalysts remained relatively similar to the parent zeolite implying that the Na was mostly situated on the Fe-NP. Therefore, even though

sodium could have deactivated 79% of the BAS, pyridine IR showed that acidity remained unchanged upon addition of promoters via ligand exchange, which shows that the ligands have a strong affinity towards the iron particles.

## 5.3.3. Synthesis gas conversion

To assess the activity and selectivity towards methane, C<sub>2</sub>-C<sub>4</sub> fraction and aromatics, the catalyst performance was observed under Fischer-Tropsch to Olefins (FTO) conditions to convert synthesis gas to olefins and aromatics (Figure 5-3 and Figure 5-4). The activity is shown as iron time yield (FTY), i.e., the number of moles of CO converted per gram of iron per second. The promoted and unpromoted catalysts showed low activity, as can be observed in Figure 5-3-A, and low CO conversion as observed in Table D2 (Appendix D). To make sure this was not due to any residual organic ligands blocking the active iron sites, thermogravimetric analysis coupled with mass spectrometry (TGA-MS) was carried out, see Figure D10 (Appendix D). It was found that Fe/Z retained some of the ligands after the washing and drying steps, but these were removed during the *in situ* reduction done prior to catalysis. As discussed earlier, the promoted catalysts were likely overpromoted and did not show activity due to the high sodium content <sup>44</sup>. An equally low CO conversion was found in the washed Fe/Z-W catalyst (Figure 5-3-B), clearly indicating that without promoters no activity is found. However, when the promoted catalysts were washed with the ammonium nitrate solution to remove the excess of promoters, the activity was recovered, see Figure 5-3-B. Interestingly, FeP/Z-W retained activity after washing, although ICP indicated that sodium content was below Na/Fe = 0.03 (at/at). Most probably small fractions of sodium, undetectable for ICP, had not been removed and still acted as promoters for this catalyst. After 4 hours on stream, catalyst FeP/Z-W seemed to have reached equilibrium and was stable up to 16 hours on stream. Fe/Z-P-W however, showed activity loss during the 16 hours on stream, not reaching equilibrium within this time. As all other catalysts had relatively low activity, it was difficult to assess if these catalysts stayed stable, or merely inactive. It is well known that the active phase in Fischer-Tropsch catalysis are iron carbides. From previous literature it is apparent that using Na and S promote carbide formation and therefore activity during FT. Thus, it was assumed that the promoters in all washed catalysts facilitated the formation of iron carbides and hence a higher activity than Fe/Z-W<sup>23,24,28,41</sup>.



**Figure 5-3:** Iron time yield (FTY; defined as moles of CO being converted per gram of iron per second) at 1 bar and 340°C with H<sub>2</sub>:CO ratios of 1 plotted as a function of time on stream for as-synthesized catalysts (A) and washed catalysts (B). As can be observed in graph (A), (un)promoted as-synthesized catalysts had a low activity due to overpromotion compared to the washed catalysts (B). Adding promoters and afterward removing excess Na led to active catalysts. All catalysts were operated at CO conversions in the range of 3-5% conversion.

The methane, aromatics,  $C_2$ - $C_4$  (olefins and paraffins) and  $C_{5+}$ -aliphatics selectivities were only plotted for the FeP/Z-W and Fe/Z-P-W catalysts, as these showed CO conversions to allow reliable measurement of selectivities, see Figure 5-4. The  $C_2$ - $C_4$ selectivities are given as a sum of paraffins and olefins. A high olefins/paraffins ratio of  $\sim 10$ (mol/mol) is expected for the washed catalysts, as at low pressures relatively small amounts of olefins undergo secondary hydrogenation reactions <sup>28</sup>. The methane selectivity gives an indication of the presence of sodium and sulfur promoters on the iron particles, as these promoters significantly decrease the methane selectivity <sup>23</sup>. FeP/Z-W had a methane selectivity of 40%<sub>C</sub>, in agreement with the low Na/S content obtained from ICP further indicating that most of the Na and S had been removed. Fe/Z-P-W seemed to have retained the promoter effect, enough to lower the methane selectivity to  $15\%_{\rm C}$ . This catalyst also obtained a relatively high C2-C4 selectivity and a low selectivity towards C5+-aliphatics. The selectivities towards  $C_4$ -isomers and aromatics is shown in Table D2 (Appendix D) which are similar for both active catalysts. Both washed catalysts produced aromatics at 1 bar but as FeP/Z-W had a relatively low Na content, it showed a high selectivity towards methane and a lower selectivity towards olefins and aromatics. The methane selectivity is a good measure for Na and S depletion from the iron phase <sup>32</sup> and hence it was tracked over time (Figure D11 in Appendix D) to infer if migration of sodium or sulfur species to the ZSM-5 support occurred. At 1 bar pressure, no change with time of the methane selectivity was found, indicating no migration of sodium and sulfur species. The deactivation of FeP/Z-W is limited but that of Fe/Z-P-W is extensive which can be explained by the different particleparticle distances of the fresh catalysts (Figure 5-2-B and -C). The smaller interparticle distances of FeP/Z-W may facilitate sintering most probably already during the reduction leading to lower activity but higher stability whereas with Fe/Z-P-W the sintering during

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reduction is limited leading to high initial activity but more particle growth with concomitant deactivation during FT.

Additionally, the catalytic performance was established for all catalysts at medium pressure (10 bar) and reported in Table D3 (Appendix D). The CO conversions of the washed catalysts were similar (between 10-15%). The activity increase after washing the catalysts was also seen at medium pressure. Furthermore, Fischer-Tropsch at medium pressure led to a significant increase in methane formation and a concomitant decrease of aromatics selectivity pointing to a higher hydrogenation activity <sup>28</sup>. The FT activity of the promoted catalysts was similar to promoted colloidal particles supported on carbon nanotubes as reported in literature <sup>44</sup>.



**Figure 5-4:** Catalyst selectivity of H-ZSM-5 supported iron catalysts (FeP/Z-W in red and Fe/Z-P-W in green) under FTO conditions at 340°C, 1 bar,  $H_2/CO = 1$  (v/v), GHSV: 4,200 h<sup>-1</sup>, TOS = 15 h. The methane selectivity of FeP/Z-W was high compared to Fe/Z-P-W as, according to ICP, most of the promoted Na/S was removed during the washing step. Both catalysts produced aromatics and Fe/Z-P-W formed a relatively high amount of  $C_2$ - $C_4$  products.

#### 5.3.4. Analysis of the used catalysts

The used catalysts of the 1 bar and 10 bar experiment were analyzed using TEM (Figure 5-5 and Figure D12 and Table D3 in Appendix D). At 1 bar, notably, particles were remarkably stable in the unpromoted catalyst (Figure 5-5-A and -D), especially considering the initial small particle-particle distances. Growth was observed in the promoted catalysts, particularly FeP/Z, in line with previous studies showing that if Na and S are present, this accelerates particle growth <sup>24</sup>. A combination of factors could have caused this growth, namely a large number of promoters and altered particle-support interaction as well as a less homogeneous distribution of particles in the fresh catalyst due to the short ligands. This resulted in particle growth to at least twice the initial diameter, as can be observed in Figure 5-5-B. Scanning-Transmission electron microscopy (STEM) images were made for this

catalyst to better observe the contrast between the large iron particles and the zeolite. Moreover, when applying high-pressure conditions, the growth of FeP/Z became even more evident (Figure D12-E, Appendix D).

At 10 bar, Fe/Z-P (Figure D12-C, Appendix D) grew into a bimodal size distribution at showing that the promoters have a large influence on the catalyst stability, which is in agreement with previous work on carbon nanofibers <sup>24</sup>. In this previous research on colloidal particles attached to carbon performed at 10 bar, a bimodal particle size distribution was seen as well. The increased growth rate was therefore attributed to the higher pressure used in catalysis.<sup>44</sup> This is supported by Figure D1 (Appendix D), where 10 bar catalysis did yield particle sizes comparable with the previously discussed colloidal particles on carbon.

Furthermore, in Figure 5-5-E and Figure D13 (Appendix D) it is observed that the particle size distribution in FeP/Z-W ranged from particles smaller than the fresh catalyst' size (< 5 nm) to larger (> 10 nm) particles. This strongly indicates that the growth mechanism is dominated by the Ostwald ripening process <sup>56</sup>. In previous studies, DFT calculations found that elevated temperatures and the presence of CO can induce subcarbonyl species with high mobility, making Fischer-Tropsch catalysts prone to Ostwald ripening <sup>57–59</sup>. To our knowledge, no similar results have been reported with evidence of particle shrinking after catalysis for iron FT catalysis. These data indicate that sintering of the colloidal particles goes through the Ostwald ripening process where Fe subcarbonyls most likely play an important role. Furthermore, as pointed out in previous research, sulfur might accelerate the production of iron pentacarbonyl species which indicates that the S promoters enhance the growth rather than suppress it <sup>60</sup>.

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**Figure 5-5:** TEM images of all 1 bar used catalysts. A-C) Fe/Z (A), FeP/Z (B) and Fe/Z-P (C). D-F) Fe/Z (D), FeP/Z (E) and Fe/Z-P (F). The unpromoted catalysts (Fe/Z and Fe/Z-W) showed little particle growth. Catalysts that had been promoted after attachment (Fe/Z-P and Fe/Z-P-W) showed particle growth up to 20 nm. Spent FeP/Z and FeP/Z-W catalysts showed next to larger particles also smaller particles (see arrows) compared to the fresh catalyst with a distribution that is skewed to larger sizes, as can be seen from the inset histograms. A large fraction of the original 6 nm particles had shrunk to < 5 nm particles or grown to particles > 10 nm.

#### 5.4. Summary and Conclusions

In summary, using colloidal particles attached to an H-ZSM-5 support resulted in a uniform metal particle distribution on the external surfaces of the zeolite crystals (Fe/Z) even if these particles were promoted afterward with Na and S (Fe/Z-P) while at the same time displaying a narrow particle size distribution when organic ligands were used. When inorganic ligands were present before attaching the particles to the zeolite surface (FeP/Z), particles were less uniformly distributed due to their small ligand sizes but still showed a narrow particle size distribution. The large amount of Na and S in both Fe/Z-P and FeP/Z resulted in low catalyst activity, as both catalysts were overpromoted. The promoter amount was lowered with an additional washing step using ammonium nitrate enhancing the activity for both catalysts. However, washing the FeP/Z catalyst caused the amount of promoters to drop below the detection limit of ICP, thus losing promotion effect and therefore obtaining a high methane selectivity. After washing Fe/Z-P showed a low selectivity towards methane and the formation of aromatics. Pyridine IR showed that the zeolite retained acidity using the colloidal ligand exchange method even though the zeolite was in direct contact with the

promoter solution. Clearly, this ligand exchange is a promising method to obtain active and selective iron on zeolite catalysts because it enables the steering of promoters to the iron particles instead of on the zeolite acid sites.

Additionally, it was confirmed again that adding Na and S promoters accelerated particle growth during catalysis. During the analysis of the FeP/Z-W used catalyst, it was found that the particle size had both increased and decreased, suggesting an Ostwald ripening process accelerated by the added promoters. Therefore, this research additionally shows that due to the advantageous narrow particle size distribution, colloids can be used to investigate particle growth and that using ligand exchange directs the promoters specifically towards the iron particles instead of reducing zeolite acidity.

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# 6

# Conversion of synthesis gas to aromaticsrich gasoline at medium temperature with a Fischer-Tropsch and ZSM-5 dual catalyst bed

The production of fuels and base chemicals such as gasoline, olefins and aromatics from synthesis gas is of great interest from both an academic and an industrial point of view. We prepared a bulk iron Fischer Tropsch catalyst promoted with potassium capable of converting synthesis gas to olefins and combined it with an H-ZSM-5 zeolite to convert the formed olefins to aromatics on the zeolite acid sites. All experiments were performed in stacked bed mode to avoid migration of potassium promoters from the iron catalyst to the zeolite, which can deactivate acid sites in the zeolite. Operating at a pressure of 20 bar and temperatures between 250°C and 300°C instead of high temperatures of 300°C-350°C led to a methane selectivity of only 7-14% c. Olefins in the range of C<sub>4</sub>-C<sub>8</sub> were converted to aromatics in the initial section of the zeolite bed, while further into the zeolite bed  $C_2$ - $C_3$ olefins oligomerized to longer olefins and alkylated light aromatics subsequently forming heavier aromatic hydrocarbons. Investigation of the influence of CO conversion on the aromatization of olefins showed a maximum in aromatic selectivity (excluding  $CO_2$ ) of  $18\%_C$ at medium CO conversion ( $X_{CO} = 26-47\%$ ). The resulting product fraction in the gasoline range ( $C_5$ - $C_{11}$ ) showed octane numbers as high as 91 and selectivities of up to 55%<sub>C</sub>. This work provides detailed insight into the chemical events that occur in bifunctional catalyst beds and can contribute to the development of an industrial process to convert synthesis gas to aromatics-containing gasoline in a single reactor.

Weber, J. L., Martínez del Monte, D., Beerthuis, R., Dufour, J., Martos, C., de Jong, K. P., & de Jongh, P. E. Conversion of Synthesis Gas to Aromatics at Medium Temperature with a Fischer Tropsch and ZSM-5 Dual Catalyst Bed *Catalysis Today* **369**, 175–83 (2021).

#### 6.1. Introduction

To reduce the carbon footprint of chemical processes and the worldwide carbon dioxide emissions, new pathways for the production of chemicals and fuels need to be developed <sup>1,2</sup>. The conversion of synthesis gas to chemicals has received significant attention in the past years, since it opens a route for the production of platform chemicals for the chemical industry that is independent of crude oil. Synthesis gas is a mixture of carbon monoxide and hydrogen and can be derived from carbon-containing sources such as methane, coal, biomass, or from  $CO_2$  capture with renewable hydrogen <sup>3–6</sup>.

Gasoline contains mostly  $C_5$ - $C_{11}$  hydrocarbons <sup>7</sup>. The specifications for gasoline are among others a research octane number (RON, classification number for spark-ignition characteristics) between 91 and 102. The octane number of gasoline increases with increasing content of branching of molecules, olefins, and especially aromatics <sup>8–11</sup>.

Recent publications have mostly focused on the synthesis of short olefins (C<sub>2</sub>-C<sub>4</sub>)  $^{12-17}$ . Synthesis gas can be converted directly using the Fischer-Tropsch to olefins (FTO) process, which allows to form C<sub>2</sub>-C<sub>4</sub> olefins with 65%<sub>C</sub> selectivity within the hydrocarbons (excluding CO<sub>2</sub>)  $^{12,13}$ . Typically, the product distribution of the Fischer-Tropsch synthesis is described with the Anderson-Schulz-Flory (ASF) distribution, which means that the preferential formation of short olefins implies an undesirably high methane fraction  $^{18}$ . The presence of sodium and sulfur promoters in iron (carbide) based FTO catalysts, however, can lead to a deviation from the Anderson-Schulz-Flory distribution with less methane and an increased olefin to paraffin ratio  $^{19-21}$ .

Alternatively, a bifunctional catalyst system can be used to convert synthesis gas in a single reactor to reactive oxygenate intermediates such as methanol <sup>22</sup>, dimethyl ether <sup>23</sup>, or ketene <sup>15,24</sup> on a metal oxide catalyst and subsequently to short olefins using solid acids such as zeolites. The product distribution of these bifunctional catalyst systems is determined by the pore confinement of the zeolite and can be controlled by the pore structure and acid strength. Using a SAPO-34 zeolite with 8-membered rings led to the formation of a mixture of C<sub>2</sub>-C<sub>4</sub> olefins with a total selectivity of 80% c <sup>15,25</sup>, whereas a zeolite with mordenite structure and selectively blocked 12-membered ring sites formed ethylene in the 8-membered ring side pockets with 73% c selectivity <sup>24</sup>. Larger pore diameters of the H-ZSM-5 zeolite consisting of a 10-membered ring pore system allowed the formation of aromatic hydrocarbons from oxygenate intermediates with selectivities as high as 80% c <sup>22,26–28</sup>.

To convert synthesis gas into aromatics via olefinic intermediates instead of oxygenates, an iron (carbide) based Fischer-Tropsch catalyst can be combined with an H-ZSM-5 zeolite <sup>29–35</sup>. Combining a sodium and sulfur promoted iron (carbide) FTO catalyst with the acid properties of a H-ZSM-5 zeolite in a high temperature and low pressure process (400°C, 1 bar) resulted in the formation of C<sub>6</sub>-C<sub>8</sub> aromatics with reasonable selectivity of up to 27%<sub>C</sub>, while C<sub>2</sub>-C<sub>4</sub> olefins are preserved with 41%<sub>C</sub> selectivity <sup>36</sup>. We found that the pathway for aromatization of olefins in this high temperature process followed dehydro-

aromatization rather than hydrogen transfer, resulting in a  $C_2$ - $C_4$  paraffin selectivity of only 4-10%<sub>C</sub> and decreased hydrogen to carbon ratio in the overall hydrocarbon products compared to the FTO catalyst without zeolite. Furthermore, the activity of the FTO function was enhanced by close proximity of the zeolite, due to enhanced formation of iron carbides.

However, the close proximity also led to the migration of sodium ions from the FTO catalyst to the acid sites of the zeolite, resulting in decreased acidity of the zeolite and loss of promotion effect of the sodium and sulfur and therefore increased methane selectivity <sup>37,38</sup>. This migration of sodium ions can be mitigated by increasing the distance between the FTO catalyst and the zeolite for instance by operating in stacked bed mode with the zeolite downstream of the FTO catalyst <sup>39–41</sup>.

Typically, the low temperature Fischer-Tropsch (LT-FT) process is operated at temperatures between 200°C and 240°C and pressures of 25-45 bar, whereas the high temperature Fischer-Tropsch (HT-FT) process takes place between 300°C and 350°C and 20-40 bar <sup>42</sup>. In previous publications <sup>36,37</sup>, we discussed fundamental insights for reaction conditions (400°C and 1 bar) that are not applied in industrial processes. These harsh conditions caused rapid deactivation of the bifunctional catalysts.

In this work, we use a bulk iron catalyst promoted with potassium to convert synthesis gas to olefins at 250-300°C and 20 bar, avoiding rapid deactivation and combining it with an H-ZSM-5 zeolite in stacked bed mode to convert the olefins to aromatics in a single reactor.

Operating at lower temperatures shifts the Anderson-Schulz-Flory distribution to higher alpha values, resulting in low methane selectivity and heavier olefin intermediates, which removes the need for oligomerization of short olefins to form aromatics. Additionally, the lower operation temperature increases the selectivity to hydrocarbon products in the gasoline range (C<sub>5</sub>-C<sub>11</sub>) compared to the HT-FT process. We show that only long olefins are converted in the initial section of the zeolite bed followed by oligomerization of short olefins and further aromatization in the consecutive sections of the zeolite bed. The yield of aromatics decreases with increasing CO conversion. The resulting products in the range of  $C_5$ - $C_{11}$  (olefins, paraffins, isomers and aromatics) show an estimated octane number of up to 91, which enables the use of this fraction as gasoline.

# 6.2. Experimental 6.2.1. Catalyst Preparation

We prepared iron oxide by precipitation from an iron nitrate nonahydrate solution followed by decomposition of the precursor. 20.32 g Fe(NO<sub>3</sub>)<sub>3</sub> 9 H<sub>2</sub>O (Acros Organics) was dissolved in 500 mL demineralized water (0.1 mol/L, initial pH 1.67). The pH was increased to 10 by adding an ammonia solution (Merck, 28-30 wt-%) under vigorous stirring at 25°C. One hour after pH 10 was reached, the stirring was turned off and the precipitate was let to sediment for 16 h at 25°C. After sedimentation, the supernatant was decanted and the

precipitate was centrifuged at 3000 rpm for 5 min. Subsequently, the remaining supernatant was decanted and the precipitate was re-dispersed in demineralized water, centrifuged for 10 min at 3000 rpm and the supernatant was decanted. This washing step was performed in total three times. The resulting gel was dried in an oven in static air at 120°C for 16 h and treated at 350°C (5 K/min) for 2 h in a flow of nitrogen. The resulting catalyst was denoted as "Fe".

The potassium promoter was introduced by incipient wetness impregnation of the calcined iron oxide powder with a solution containing potassium nitrate (Sigma Aldrich, 217.0 mg/mL in demineralized water), resulting in 1.95 wt-% K/Fe<sub>2</sub>O<sub>3</sub> and a molar ratio of K:Fe=0.043 at/at. After impregnation the material was dried and heat-treated under nitrogen flow at 120°C (5 K/min) for 2 h and 350°C (5 K/min) for 1 h. The heat-treated sample was pelletized, ground and sieved to a sieve fraction between 150-212  $\mu$ m. The resulting potassium-promoted iron catalyst was denoted as "FeK".

To convert the ZSM-5 zeolite (Zeolyst, Si:Al=15 at/at) from the ammonium form to the proton form, calcination was carried out at 550°C for 4 h in static air. Afterwards, the calcined zeolite was pelletized, ground and sieved to a sieve fraction of 150-212  $\mu$ m.

## 6.2.2. Characterization

The dried precipitate was heated in a nitrogen flow in a TA Instruments Q50 thermal gravimetric analyzer (TGA) to determine the optimum temperature for calcination.

To gain information about the crystal phase and crystal size of the dried and calcined precipitate, X-ray diffractograms (XRD) were recorded on a Bruker D2 Phaser, equipped with a Co source operating at  $\lambda$ =1.789 Å between 2 $\Theta$ =10-80° with an increment of 0.07° per step and 1 s exposure time.

 $N_2$ -physisorption and Ar-physisorption at -196°C were carried out on a Micromeritics TriStar 3000 to determine the specific surface area and mesopore volume of the calcined and promoted bulk iron catalyst as well as the zeolite. Prior to measurement, the materials were dried in nitrogen flow at 250°C for 16 h. The total pore volume was determined from single point adsorption at p/p<sub>0</sub>=0.995. The isotherms of the promoted and calcined iron catalyst can be found in Figure E1 in Appendix E.

Inductively coupled plasma optical emission spectroscopy (ICP-OES) was carried out on a Spectro Arcos after digestion of the promoted and calcined bulk iron catalyst in *aqua regia*.

Bright-field transmission electron microscopy and scanning transmission electron microscopy in combination with energy dispersive X-ray spectroscopy (STEM-EDX) in high annular angle dark field mode (HAADF) were performed using a FEI Talos F200X, equipped with a high brightness field emission gun and a Super-X G2 EDX detector and operating at 200 kV. Scanning electron microscopy was performed on a Helios NanoLab G3 in immersion mode and using 5 kV acceleration.
#### 6.2.3. Catalytic Performance

To investigate the performance of the promoted bulk iron catalyst in combination with the H-ZSM-5 zeolite in the conversion of synthesis gas to olefins and aromatics, experiments were carried out in a 16 channel parallel reactor setup (Avantium Flowrence). The calcined and sieved catalysts were loaded into stainless steel reactor tubes with 2.6 mm inner diameter in a stacked bed configuration with the zeolite downstream of the iron. The iron catalyst had beforehand been diluted with a 5-fold mass of silicon carbide to avoid clogging and channeling in the iron catalyst bed. An illustration of insufficient dilution of the iron catalyst with silicon carbide can be found in Appendix E (Figure E2).

To study the influence of zeolite bed height on the aromatization, between 5 mg and 40 mg H-ZSM-5 was loaded into the reactors, resulting in zeolite bed heights of 2-17 mm. After placing a ~1 mm layer of silicon carbide on top of the zeolite bed, the iron catalyst was loaded into the reactor. To operate at similar CO conversion levels and therefore achieve a better comparison of the resulting selectivities, more catalyst was loaded into the reactor when operating at lower reaction temperatures. For the experiments at 250°C, 40 mg iron catalyst was loaded. At 275°C and 300°C the amount was reduced to 20 mg and 10 mg, respectively.

Furthermore, experiments were conducted to investigate the influence of CO conversion on the aromatization, using a zeolite bed with fixed height. 20 mg of H-ZSM-5 was loaded into the lower part of the reactor, giving a zeolite bed height of 9 mm. After placing a  $\sim$ 1 mm silicon carbide layer on top of the zeolite bed, 5-50 mg iron catalyst was loaded into the reactor.

After the reactors were placed in the test unit, the iron catalysts were reduced *in-situ* by heating to 350°C with 5 K/min in 6.25 mL/min 30% H<sub>2</sub> in N<sub>2</sub> v/v at 1 bar pressure and holding these conditions for 2 h. Afterwards, the reactors were cooled down to reaction temperature between 250°C and 300°C with 5 K/min. After switching to synthesis gas with 7.5 mL/min and CO:H<sub>2</sub>:He = 9:9:1 v/v/v, the pressure in the reactors was increased to 20 bar. The gas flowing through the reactors was diluted with 25 mL/min N<sub>2</sub> at the end of every individual reactor to avoid product condensation. The products were analyzed with an online gas-chromatograph Agilent 7890-B, equipped with two flame ionization detectors and a thermal conductivity detector. The iron (-carbide) based catalysts showed high water-gasshift activity (CO+H<sub>2</sub>O $\leftrightarrow$ CO<sub>2</sub>+H<sub>2</sub>), resulting in CO<sub>2</sub> selectivity of ~50% c. Reported product selectivities are given as hydrocarbon distribution excluding CO<sub>2</sub>. The octane number of the  $C_5$ - $C_{11}$  products was estimated by using the blending research octane number (BRON) of the single components. The BRON can describe the effect of a single component being blended into a base gasoline, whereas the pure research octane number (RON) of a component is measured as pure compound <sup>10</sup>. The BRON of the C<sub>5</sub>-C<sub>11</sub> paraffins, iso-paraffins, olefins, isoolefins and aromatics were either found in literature <sup>8-10</sup> or estimated by extrapolation (Appendix A, Figure A1-A5 and Table A1-A3).

After the reaction finished, the hydrocarbon products were stripped from the catalysts by flowing 50%  $H_2$  in  $N_2$  v/v with 12.5 mL/min at 350°C and 10 bar for 4 h, followed by stripping at 300°C and 1 bar for 5 h with the same flow conditions. The spent catalysts were characterized after hydrogen stripping.

## 6.3. Results and Discussion6.3.1. Characterization of the catalysts

To determine an appropriate temperature for heat treatment, the weight loss of the dried precipitate was measured while heating in nitrogen flow. The weight loss roughly between 200°C and 400°C (Figure 6-1) of about 8 wt% corresponds to that expected from the dehydration of FeOOH to  $Fe_2O_3$  (10 wt-%). The conversion of FeOOH to  $Fe_2O_3$  was complete at 350°C, which was hence chosen as the decomposition temperature for the dried precipitate.



Figure 6-1: Weight and weight change during thermogravimetric analysis in nitrogen flow as function of temperature of the iron precipitate after drying. Heating rate: 15 K/min.

XRD (Figure 6-2) of the precipitate after drying at 120°C in air showed the presence of crystalline goethite ( $\alpha$ -FeOOH) and hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>). After further heat treatment at 350°C in a nitrogen flow only crystalline hematite was observed, showing that heating to 350°C was sufficient to convert the dried precipitate into iron oxide.



**Figure 6-2:** X-ray diffractogram of the precipitate after drying and after subsequent heat treatment at 350°C in nitrogen flow for 2 h. Stars: XRD pattern of  $Fe_2O_3$ , circles: FeOOH.

A transmission electron micrograph and scanning electron micrograph of the ironpotassium catalyst after heat treatment can be found in Figure 6-3. The sample exhibited a needle-like structure. This is as expected as goethite ( $\alpha$ -FeOOH) is known to form a needlelike structure when formed via precipitation from an iron nitrate solution <sup>43</sup>. This structure was maintained during the heat treatment at 350°C in nitrogen flow. ICP-OES showed an iron content of 65.4 wt% and 1.95 wt% potassium in the promoted and calcined iron catalyst. This resulted in a ratio of K:Fe = 0.043 at/at, which is in good agreement with the values we expected (nominal composition: 68.0 wt.-% Fe, 1.95 wt.-% K, balance oxygen).



Figure 6-3: A: High annular angle dark field scanning transmission electron microscopy (HAADF-STEM) image of calcined FeK and B: scanning electron microscopy image of calcined FeK.

#### 6.3.2. Catalytic performance

In this section, we discuss the performance of the iron catalysts at temperatures between  $250^{\circ}$ C and  $300^{\circ}$ C, and 20 bar pressure in terms of activity and selectivity with and without zeolite present. Also, we investigated the influence of the zeolite bed height, and hence the residence time of olefins formed on the iron catalyst in the zeolite bed, in stacked bed. Placing various amounts of zeolite downstream of the iron catalyst allowed us to follow aromatization, cracking, isomerization, and the corresponding octane number of the C<sub>5</sub>-C<sub>11</sub> fraction at different positions in the zeolite bed. Finally, the influence of CO conversion on the aromatization in a zeolite bed with fixed height is discussed.

**Influence of reaction temperature on the performance of the iron catalyst.** The experiments to evaluate the performance of the potassium promoted iron catalyst were conducted with CO conversions of 15-20%, allowing a direct comparison of the selectivities at similar conversion. This was achieved by decreasing the amount of iron catalyst placed inside the reactor with increasing reaction temperature, while keeping the flow constant for all experiments.

At 250°C and a GHSV of 10,000 h<sup>-1</sup>, FeK showed a CO conversion of 17% in the initial phase of the reaction. However, the CO conversion decreased upon the first 15 h on stream and stabilized at 6-7% after ~20 h (Figure 6-4-A). Increasing the reaction temperature to 275°C and the GHSV to 20,000 h<sup>-1</sup>, led to a CO conversion between 13% and 16%. The experiment conducted at a reaction temperature of 300°C and GHSV of 40,000 h<sup>-1</sup> showed 19% CO conversion in the initial phase of the reaction, gradually decreasing to 13% conversion.

The activity normalized to the mass of iron (iron time yield, FTY) decreased from  $0.8 \times 10^{-5} \text{ mol}_{\text{CO}} \text{ g}_{\text{Fe}^{-1}} \text{ s}^{-1}$  to  $0.3 \times 10^{-5} \text{ mol}_{\text{CO}} \text{ g}_{\text{Fe}^{-1}} \text{ s}^{-1}$  for the experiments performed at 250°C (Figure 6-4-B). At 275°C the FTY was higher, 1.2-1.4 × 10<sup>-5</sup> mol<sub>CO</sub> g<sub>Fe</sub><sup>-1</sup> s<sup>-1</sup>, due to the increased reaction temperature. The FTY decreased from  $3.4 \times 10^{-5} \text{ mol}_{\text{CO}} \text{ g}_{\text{Fe}^{-1}} \text{ s}^{-1}$  to  $2.3 \times 10^{-5} \text{ mol}_{\text{CO}} \text{ g}_{\text{Fe}^{-1}} \text{ s}^{-1}$  within the first 40 h on stream, when operated at 300°C.

In general, the iron mass normalized activity increased with increasing reaction temperature, as expected. The deactivation was more severe at 250°C than at 275°C and 300°C, respectively. We ascribe this decrease in activity to hydrocarbon deposition on the surface of the catalyst. These hydrocarbons are less likely to be removed at low operating temperatures.



**Figure 6-4:** Activity of FeK as function of time at 250°C, 275°C and 300°C. **A:** CO conversion as function of time on stream. **B:** FTY (iron time yield, moles of CO converted per gram of iron and second) as function of time on stream. Reaction conditions: 250-300°C, 20 bar, CO:H<sub>2</sub>=1 v/v. FeK was tested at 250°C with an FeK based GHSV of 10,000 h<sup>-1</sup>, at 275°C with GHSV of 20,000 h<sup>-1</sup> and 300°C with GHSV of 40,000 h<sup>-1</sup> to reach same conversion levels (15-20%) in the initial phase of the reaction. Error bars indicate standard deviation from four experiments at 250-275°C and seven experiments at 300°C.

FeK produced 8% methane at 250°C, whereas the selectivity to methane increased to  $14\%_{\rm C}$  at 275°C and 300°C (Figure 6-5). These methane selectivities are similar to the selectivities achieved with a supported FTO catalyst promoted with sodium and sulfur and operated at high temperatures (340-350°C) and low pressure <sup>36</sup>.

The C<sub>2</sub>-C<sub>4</sub> fraction (sum of olefins and paraffins) in the hydrocarbon products was 29-31%<sub>C</sub>, independent of the temperature. However, the contribution of olefins to the C<sub>2</sub>-C<sub>4</sub> fraction increased with reaction temperature from 69%<sub>C</sub> at 250°C and 71%<sub>C</sub> at 275°C to 80%<sub>C</sub> at 300°C <sup>44</sup>. This shows that chain termination via  $\beta$ -hydride abstraction is enhanced with

increasing reaction temperature, and/or  $\alpha$ -hydrogenation is reduced (Figure E3, Appendix E). The selectivity to aliphatic C<sub>5+</sub> products decreased from 63%<sub>C</sub> at 250°C to 54%<sub>C</sub> and 56%<sub>C</sub> at 275°C and 300°C, respectively.

These relatively low methane selectivities as well as the high  $C_{5+}$  selectivities correspond to  $\alpha$ -values between 0.70 and 0.75 for the ASF distribution for all temperatures tested. An  $\alpha$ -value in this range can be beneficial for the aromatization of olefin intermediates, because this gives the highest selectivity to the  $C_6$ - $C_{10}$  fraction according to the ASF distribution (Figure E4, Appendix E) for which no oligomerization is needed to form  $C_6$ - $C_{10}$  aromatics. Additionally, the olefin/paraffin ratio of the products increased with reaction temperature, resulting in higher selectivity to reactive olefinic intermediates at higher temperatures.



**Figure 6-5:** Hydrocarbon product distribution based on carbon atom selectivity (CO<sub>2</sub> free) of FeK tested at 250°C, 275°C and 300°C and CO conversion between 15-20%. Reaction conditions: 250-300°C, 20 bar, CO:H<sub>2</sub>=1 v/v. FeK was tested at 250°C with FeK based GHSV of 10,000 h<sup>-1</sup>, at 275°C with GHSV of 20,000 h<sup>-1</sup> and 300°C with GHSV of 40,000 h<sup>-1</sup> to reach same conversion levels in the initial phase of the reaction of 15-20%.

**Influence of zeolite bed height on aromatization.** To convert the olefins formed on the iron catalyst to aromatics, H-ZSM-5 zeolite beds with different heights were placed downstream of the FeK bed in stacked mode. Figure 6-6-A-C shows an overview of the resulting selectivities, obtained at temperatures between 250°C and 300°C. Indeed the selectivity to methane did not change significantly upon the addition of H-ZSM-5 zeolite downstream of FeK, confirming that the potassium promoter did not migrate from the iron catalyst to the zeolite resulting in catalyst deactivation, as reported earlier <sup>37</sup>.

The selectivity to C<sub>2</sub>-C<sub>4</sub> olefins increased upon placing a zeolite bed downstream of FeK at 250°C and 275°C from 20%<sub>C</sub> to 28%<sub>C</sub> and 22%<sub>C</sub> to 33%<sub>C</sub>, respectively (Figure 6-6-A and -B). Simultaneously, the selectivity to C<sub>5+</sub> aliphatics decreased in these experiments from 63%<sub>C</sub> to 50%<sub>C</sub> and from 54%<sub>C</sub> to 41%<sub>C</sub>, suggesting that the increase in C<sub>2</sub>-C<sub>4</sub> olefins

was caused by partial cracking of the  $C_{5+}$  fraction.  $C_2-C_4$  paraffins were not affected and remained between 9%<sub>C</sub> and 11%<sub>C</sub> for the experiments conducted at 250°C and 275°C. Furthermore,  $C_6-C_{10}$  aromatics were formed with only 2-3%<sub>C</sub> selectivity at these temperatures.

Results at 300 °C were markedly different (Figure 6-6-C). With a zeolite bed of 4 mm the selectivity to  $C_2$ - $C_4$  olefins increased from 24%<sub>C</sub> to 35%<sub>C</sub>, whereas the  $C_{5+}$  selectivity decreased from 56%<sub>C</sub> to 43%<sub>C</sub> and  $C_6$ - $C_{10}$  aromatics were formed with 2%<sub>C</sub> selectivity. With increasing zeolite bed height to 13 mm, the selectivity to  $C_2$ - $C_4$  olefins decreased to 12%<sub>C</sub>, whereas  $C_2$ - $C_4$  paraffins increased from 6%<sub>C</sub> to 21%<sub>C</sub> and  $C_6$ - $C_{10}$  aromatics increased to 13%<sub>C</sub>.

The simultaneous decrease in C<sub>2</sub>-C<sub>4</sub> olefin selectivity and increase in C<sub>2</sub>-C<sub>4</sub> paraffin and C<sub>6</sub>-C<sub>10</sub> aromatic selectivity indicates that the aromatization of olefins followed hydrogen transfer. Here, hydrogen is transferred from olefins molecules to other olefin molecules forming paraffins and dienes, after which the dienes undergo cyclization and aromatization <sup>45,46</sup>. As at 300°C C<sub>6</sub>-C<sub>10</sub> aromatics were formed with up to 13%<sub>C</sub> selectivity with a 13 mm zeolite bed, we will discuss the aromatization at 300°C more in detail in the following section.

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**Figure 6-6:** Hydrocarbon distribution based on carbon atom selectivity (CO<sub>2</sub> free) of FeK and H-ZSM-5 in stacked bed mode with zeolite bed height between 4 mm and 13 mm tested at **A:** 250°C, **B:** 275°C and **C:** 300°C and CO conversion between 15-20%. Reaction conditions: 250-300°C, 20 bar, CO:H<sub>2</sub>=1 v/v. FeK was tested at 250°C with FeK based GHSV of 10,000 h<sup>-1</sup>, at 275°C with GHSV of 20,000 h<sup>-1</sup> and 300°C with GHSV of 40,000 h<sup>-1</sup> to reach same conversion levels in the initial phase of the reaction of 15-20%.

The selectivities to  $C_2$ - $C_3$  olefins,  $C_4$ - $C_8$  olefins and  $C_6$ - $C_{10}$  aromatics as function of zeolite bed height at 300°C are shown in Figure 6-7-A. The iron catalyst showed at 300°C a

selectivity to  $C_2$ - $C_3$  olefins of 23%<sub>C</sub> and  $C_4$ - $C_8$  olefins of 32%<sub>C</sub>, whereas no aromatics were formed under these conditions. Placing H-ZSM-5 zeolite downstream of FeK with a bed height of 2-4 mm did not change the selectivity to  $C_2$ - $C_3$  olefins, but led to a sharp decrease of in C<sub>4</sub>-C<sub>8</sub> olefins of 19%<sub>C</sub> with a zeolite bed of 2 mm. At the same time C<sub>6</sub>-C<sub>10</sub> aromatics were formed with low selectivity of 2-3%<sub>C</sub> at zeolite bed heights of 2-4 mm.

Higher zeolite beds led to a gradual decrease of the  $C_2$ - $C_3$  olefin selectivity from 10%<sub>C</sub> at 7 mm zeolite bed height to 2%<sub>C</sub> at 17 mm, whereas the selectivity of  $C_4$ - $C_8$  olefins increased to 23-24%<sub>C</sub>. at 7 mm, followed by a gradual decrease to 4%<sub>C</sub> C<sub>4</sub>- $C_8$  olefins at a zeolite bed height of 17 mm. With increasing amount of zeolite downstream of FeK the selectivity to C<sub>6</sub>-C<sub>10</sub> aromatics increased gradually to 18%<sub>C</sub> at 17 mm zeolite bed height.

In the initial section of the zeolite bed,  $C_4$ - $C_8$  olefins were exclusively converted to aromatics with low selectivity, whereas the  $C_2$ - $C_3$  olefins remained untouched. In the further course of the zeolite bed (4 mm to 7 mm),  $C_2$ - $C_3$  olefins underwent oligomerization forming  $C_4$ - $C_8$  olefins. These  $C_4$ - $C_8$  olefins were consecutively converted into aromatics.

Figure 6-7-B shows the distribution and the average carbon number within the  $C_{6}$ - $C_{10}$  aromatics fraction as function of zeolite bed height. With increasing height of the zeolite bed, the average carbon number of the  $C_{6}$ - $C_{10}$  aromatics increased from 7.9 at 2 mm zeolite bed height to 8.3 at 13 mm. Furthermore, ethylmethylbenzene was identified as main aromatic product for a zeolite bed height of 7 mm and higher (a detailed distribution of the aromatic products can be found in Figure E5, Appendix E). Therefore, we hypothesize that the  $C_2$ - $C_3$  olefins and especially ethylene not only contribute to the oligomerization to form longer olefins, but also in the alkylation of light aromatics, forming heavier aromatic products.

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**Figure 6-7: A:** Selectivity of  $C_2$ - $C_3$  olefins,  $C_4$ - $C_8$  olefins and  $C_6$ - $C_{10}$  aromatics as function of zeolite bed height for stacked bed experiments with FeK and H-ZSM-5 zeolite at 300°C, and **B:** Distribution of  $C_6$ - $C_{10}$  aromatics fraction (mol/mol) and average carbon number of the aromatics fraction as function zeolite bed height for stacked bed experiments with FeK and H-ZSM-5 zeolite at 300°C. Reaction conditions: 300°C, 20 bar, CO:H<sub>2</sub>=1 v/v, GHSV of 40,000 h<sup>-1</sup> CO conversion of 15-20%. The volume of the zeolite bed was varied to achieve zeolite based GHSV between 4,500 h<sup>-1</sup> and 40,000 h<sup>-1</sup>. The corresponding graphs for 250°C and 275°C can be found in Figure E6, Appendix E.

It is clear that longer olefins in the range of  $C_3$ - $C_8$  are converted to aromatics already in the initial section of the zeolite bed, whereas short olefins ( $C_2$ - $C_3$ ) undergo oligomerization and alkylation of aromatics in the consecutive section of the zeolite bed. Further details of the influence of the zeolite bed height on the cracking and isomerization behavior are discussed in the following paragraphs.

Influence of zeolite bed height on cracking. The Anderson-Schulz-Flory distributions of the aliphatics (sum of linear and branched olefins and paraffins) for the stacked bed experiments performed at 250°C, 275°C and 300°C zeolite bed height are shown in Figure 6-8. The  $\alpha$ -value for FeK without zeolite was between 0.70 and 0.72, which is in good agreement with the catalytic performance data shown in the main text. This shows that

the chain growth probability of FeK was not significantly affected by the reaction temperature.

At 250°C, the ASF distribution did not change significantly with placing the zeolite downstream of FeK and increasing zeolite bed height (Figure 6-8-A). At 275°C, a uniform but minor deviation for the ASF distribution of FeK without zeolite (black dotted line) was observed for larger amounts of zeolite placed downstream of FeK (Figure 6-8-B). Hence the H-ZSM-5 zeolite was not significantly active in cracking at 250°C, and only slightly active at 275°C.

The ASF distribution of the experiments conducted at 300°C showed a clear deviation from FeK without zeolite starting from a zeolite bed height of 4 mm (Figure 6-8-C). Here, with respect to the original ASF distribution the products with carbon number greater than 9 are less present than expected, which can be assigned to either aromatization of  $C_{9+}$  olefins or cracking. Furthermore, the  $C_2$ - $C_4$  fraction is lower than in the original ASF distribution, whereas the C<sub>4</sub>-C<sub>5</sub> fraction is higher with zeolite bed heights of 7 mm and greater. This strongly indicates oligomerization of the  $C_2$ - $C_3$  olefins forming C<sub>4</sub>- $C_5$  olefins or alkylation of light aromatics forming heavier aromatics. Cracking of heavier hydrocarbons can also contribute to the surplus of C<sub>4</sub>- $C_5$  products.



**Figure 6-8:** Anderson-Schulz-Flory distribution of aliphatics (all isomers of olefins and paraffins) for different zeolite bed heights for stacked bed experiments of FeK and H-ZSM-5 zeolite performed at **A:** 250°C, **B:** 275°C and **C:** 300°C. The black dotted lines indicate the ASF distribution of FeK without zeolite of the corresponding reaction temperatures. Reaction conditions: 250-300°C, 20 bar, CO:H<sub>2</sub>=1 v/v. The stacked bed experiments of FeK and zeolite were tested at 250°C with FeK based GHSV of 10,000 h<sup>-1</sup>, at 275°C with GHSV of 20,000 h<sup>-1</sup> and at 300°C with GHSV of 40,000 h<sup>-1</sup> to reach same conversion levels in the initial phase of the reaction of 15-20%. The volume of the zeolite bed was varied to achieve zeolite based GHSV between 4,500 h<sup>-1</sup> and 40,000 h<sup>-1</sup>.

Influence of zeolite bed height on isomerization. FeK without zeolite showed 14-17%<sub>C</sub> branched isomers in the C<sub>5</sub>-C<sub>8</sub> fraction at temperatures between 250°C and 300°C (Figure 6-9). With zeolite downstream of FeK at 250°C and 275°C the fraction of branched isomers increased to 63-70%<sub>C</sub> for a zeolite bed height between 4 mm and 13 mm. At 300°C reaction temperature, a higher fraction of branched isomers was observed. After 2 mm into the zeolite bed,  $73\%_C$  of the C<sub>5</sub>-C<sub>8</sub> fraction were found as branched isomers, whereas the branching increased further to  $83\%_C$  after 4 mm. With increasing length of the zeolite bed, the branching decreased gradually to 70%C at 17 mm.

This shows that the zeolite is active in the isomerization of hydrocarbons even at temperatures as low as 250°C or 275°C, which seem too low for aromatization and cracking. The decrease of branched isomer fraction with increasing zeolite bed height of the experiments operated at 300°C could be caused by dealkylation of highly alkylated aromatics. However, we did not observe an increase in C<sub>2</sub>-C<sub>3</sub> olefins or C<sub>4</sub>-C<sub>8</sub> olefins, accordingly. Another explanation could be the oligomerization of C<sub>2</sub>-C<sub>3</sub> olefins forming linear oligomers in the range of C<sub>5</sub>-C<sub>8</sub> alighted.



**Figure 6-9:** The fraction of isomers within the aliphatic  $C_5$ - $C_8$  products (olefins and paraffins) as function of zeolite bed height for stacked bed experiments of FeK and H-ZSM-5 zeolite performed at 250-300°C. Reaction conditions: 250-300°C, 20 bar, CO:H<sub>2</sub>=1 v/v. The stacked bed experiments of FeK and zeolite were tested at 250°C with FeK based GHSV of 10,000 h<sup>-1</sup>, at 275°C with GHSV of 20,000 h<sup>-1</sup> and at 300°C with GHSV of 40,000 h<sup>-1</sup> to reach same conversion levels in the initial phase of the reaction of 15-20%. The volume of the zeolite bed was varied to achieve zeolite based GHSV between 4,500 h<sup>-1</sup> and 40,000 h<sup>-1</sup>.

Influence of aromatization, cracking, and isomerization on gasoline selectivity and octane number. Without zeolite the  $C_5$ - $C_{11}$  (paraffins, olefins and aromatics) selectivity is 37% (Figure 6-10) which is below the value predicted by the ASF distribution of 48% ( $^{47}$ ). With increasing zeolite bed height, the  $C_5$ - $C_{11}$  selectivity shows an increase up to 51%-55% at 7 mm-17 mm zeolite bed height. This is predominantly the result of cracking of long hydrocarbons and oligomerization of shorter olefins. Isomerization did not contribute to the increased  $C_5$ - $C_{11}$  selectivity. Aromatization of olefins only had a minor effect on the selectivity increase since aromatics were formed from longer olefins. However, alkylation of light aromatics with short olefins added to the  $C_5$ - $C_{11}$  products.

The octane number of the  $C_5$ - $C_{11}$  products showed a steady increase with increasing zeolite bed height from 58 (without zeolite) to 91 at 17 mm zeolite bed height. The relatively high octane number of the products in the gasoline range produced without zeolite present can be explained by the high fraction of olefins present in the products. Isomerization of aliphatics in the initial zeolite bed caused an increasing octane number of the corresponding products at zeolite bed heights between 2 mm and 4 mm. In the further course of zeolite bed, the fraction of isomers of the aliphatics decreased, whereas aromatization increased. Therefore, we conclude that aromatization is the main contribution to the octane number increase for larger zeolite bed heights.



**Figure 6-10:** The selectivity to  $C_5-C_{11}$  hydrocarbons and corresponding octane number of this fraction as function of zeolite bed height for stacked bed experiments of FeK and H-ZSM-5 zeolite. Reaction conditions: 300°C, 20 bar, CO:H<sub>2</sub>=1 v/v and GHSV of 40,000 h<sup>-1</sup>.

**Influence of CO conversion on aromatization.** To investigate the influence of CO conversion on the aromatization through an H-ZSM-5 zeolite bed, the amount of FeK upstream of the zeolite bed was varied to achieve FeK based GHSV between 8,000  $h^{-1}$  and 75,000  $h^{-1}$ , whereas the height of the zeolite bed was kept at 9 mm.

Operating at a low GHSV of 8,000 h<sup>-1</sup> at a temperature of 300°C in 20 bar synthesis gas (CO:H<sub>2</sub>=1 v/v) resulted in a high CO conversion (71%) while by increasing the GHSV, the CO conversion was reduced to 3.5% at a GHSV of 75,000 h<sup>-1</sup> (Figure 6-11-A). The selectivity to C<sub>6</sub>-C<sub>10</sub> aromatics was 2.1%<sub>C</sub> at 71% CO conversion and gradually increased to 3.0%<sub>C</sub> at 41% CO conversion. Operating at a medium GHSV of 37,000 h<sup>-1</sup> led to a drastic increase in C<sub>6</sub>-C<sub>10</sub> aromatics selectivity to 10%<sub>C</sub> with 29% CO conversion.

At low CO conversion of 3.5% a very low yield of  $0.1\%_{\rm C}$  to  $C_6-C_{10}$  aromatics was observed, whereas, with increasing CO conversion to 26-47% also the yield to  $C_6-C_{10}$ aromatics increased to 2.8-3.2%<sub>C</sub> (Figure 6-11-B). However, the yield decreased to 1.9-2.0%<sub>C</sub> at high CO conversion between 53% and 76%. This also resulted in lowered yield to  $C_6-C_{10}$  aromatics, as the yield of olefins increases with higher conversion, whereas the zeolite bed height remained constant, which is analogue to having a short zeolite bed at lower CO conversion. At medium CO conversion the optimum balance between selectivity and CO conversion led to a maximum yield to  $C_6-C_{10}$  aromatics.



**Figure 6-11: A:** CO conversion and selectivity to  $C_6$ - $C_{10}$  aromatics (CO<sub>2</sub> free) as function of FeK based GHSV and **B:** Yield to  $C_6$ - $C_{10}$  aromatics as function of CO conversion for stacked bed experiments of FeK and zeolite operated at 300°C. Reaction conditions: 300°C, 20 bar, CO:H<sub>2</sub>=1 v/v, FeK based GHSV 8,000-75,000 h<sup>-1</sup> and zeolite bed height of 9 mm. Measurement point with CO conversion below 5% were not considered for selectivity, due to the large error.

#### 6.3.3. Spent catalyst analysis

The pore volume as well as the specific surface area of the fresh FeK were measured using nitrogen physisorption and can be found in Table 6-1 next to argon physisorption data obtained for the fresh and spent H-ZSM-5 zeolite.

Fresh FeK showed a specific surface area of  $32 \text{ m}^2/\text{g}$  and 0.23 mL/g pore volume with mostly mesopores. The surface area and pore volume of the spent FeK were too low to be determined by physisorption. The fresh H-ZSM-5 zeolite had a specific surface area of  $430 \text{ m}^2/\text{g}$  and 0.22 mL/g pore volume, mostly micropores. The spent zeolite (after 50 h,  $300^{\circ}$ C, 20 bar, CO:H<sub>2</sub>=1 v/v, FeK based GHSV of 40,000 h<sup>-1</sup> and zeolite bed height of 9 mm) showed a specific surface area of  $260 \text{ m}^2/\text{g}$  and reduced pore volume of 0.11 mL/g. The decrease in pore volume was mostly caused by the decrease in micropore volume. Porosity analysis of the spent FeK was not possible, due to hydrocarbon products being present on the surface of the catalyst. The decrease in specific surface area and pore volume of the spent zeolite was assigned to coke formation inside the micropores upon aromatization of olefins.

**Table 6-1:** Surface area and pore volume of fresh FeK determined with nitrogen physisorption and fresh and spent

 H-ZSM-5 determined with argon physisorption.

	• • •	-		
Sample	Surface area	$\mathbf{V}_{\text{total}}$	$\mathbf{V}_{\mathbf{micro}}$	V <sub>meso</sub>
	$m^2/g$	mL/g	mL/g	mL/g
FeK	32	0.23	0.005	0.22
H-ZSM-5	430	0.22	0.15	0.07
spent H-ZSM-51)	260	0.11	0.05	0.05

<sup>1)</sup> reaction conditions: 300°C, 20 bar, CO:H2=1 v/v, FeK based GHSV of 40,000 h<sup>-1</sup>, zeolite bed height of 9 mm, after 50 h.

Figure 6-12 shows EM images of FeK after reduction and after 50 h on stream. The initial needle structure was partially maintained upon reduction at 350°C for 2 h in 30% H<sub>2</sub> in N<sub>2</sub> (v/v) at 1 bar. After applying Fischer-Tropsch conditions of 300°C, 20 bar and CO:H<sub>2</sub>=1 v/v, the iron catalyst showed fragmentation of the needles (Figure 6-12-B and -D, TEM and SEM images for spent catalysts operated at 250°C and 275°C can be found in Figure E7, Appendix E). In bright-field TEM and SEM, we also found that the spent iron catalyst was embedded in hydrocarbon products. This is in agreement with the observation of the activity decreasing in the first 10 h of the experiments. In the initial phase of the reaction a product layer is formed around the iron (-carbide) based catalysts. This layer hindered the diffusion of synthesis gas to the active sites of the iron (-carbide) based catalyst.



**Figure 6-12:** High annular angle dark field scanning transmission electron microscopy (HAADF-STEM) images of **A**: reduced FeK at 350°C for 2 h in 30% H<sub>2</sub> in N<sub>2</sub>, Bright-field TEM images of **B**: spent FeK at 300°C and scanning electron microscopy (SEM) images of **C**: reduced FeK at 350°C for 2 h in 30% H<sub>2</sub> in N<sub>2</sub>, **D**: spent FeK at 300°C. Reaction conditions for spent samples: 300°C at GHSV=40,000 h<sup>-1</sup>, 20 bar, CO:H<sub>2</sub>=1 v/v, TOS=50 h.

The thermogravimetric analysis of the spent catalysts showed that the amount of carbon species on the iron (-carbide) based catalyst increased with increasing reaction temperature. The zeolite, on the other hand, showed less carbon deposits with increasing temperature. At 300°C the amount of coke formed on the zeolite shows the same increasing trend as the selectivity to aromatics in the corresponding experiments, since aromatics act as coke precursors. A detailed TGA study can be found in Appendix E (Figure E10-E12 and Table E1).

#### 6.4. Conclusions

We combined a bulk iron catalyst promoted with potassium with an H-ZSM-5 zeolite in stacked bed mode to convert synthesis gas to aromatics-containing gasoline at medium temperatures between 250°C and 300°C and 20 bar pressure.

Placing a bed of H-ZSM-5 downstream of the iron catalyst and operating at 300°C up to 18  $%_{\rm C}$  C<sub>6</sub>-C<sub>10</sub> aromatics were formed. Olefins in the range of C<sub>4</sub>-C<sub>8</sub> exclusively were converted to aromatics in the initial section of the zeolite bed, whereas C<sub>2</sub>-C<sub>3</sub> olefins remained untouched. In the further course of the zeolite bed, C<sub>2</sub>-C<sub>3</sub> olefins underwent oligomerization,

resulting in an increase in C<sub>4</sub>-C<sub>8</sub> olefin selectivity, followed by further aromatization of long olefins. Furthermore, C<sub>2</sub>-C<sub>3</sub> olefins contributed to alkylation of light aromatics forming ethylmethylbenzene as main product within the aromatics with a  $73\%_{\rm C}$  share in the C<sub>9</sub> aromatics fraction and  $26\%_{\rm C}$  in the total aromatics. Branched isomers made up to 83% of the aliphatic hydrocarbon products in the C<sub>5</sub>-C<sub>8</sub> fraction and also cracking of heavier hydrocarbons played an important role at 300°C. Utilizing aromatization, cracking, and isomerization of the FT products allowed us to produce gasoline directly from synthesis gas with 55%<sub>C</sub> selectivity and an octane number of 91.

These findings can greatly contribute to designing a process to convert synthesis gas to aromatics-containing gasoline with high octane numbers. Additionally, we unraveled the role of short and long olefins in the aromatization of Fischer-Tropsch products.

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# 7a

### Summary, Conclusion, and Outlook

#### Summary and conclusion

The world population is increasing and the demand for chemicals and fuels is higher than ever. The use of fossil feedstocks to serve these needs adds to the concentration of greenhouse gases in the atmosphere and drives unwanted climate change. Hence, new pathways for the production of chemicals and fuels are investigated and implemented. Synthesis gas (a mixture of  $H_2$  and CO) is an alternative to crude oil as it can be obtained from renewable sources such as municipal waste or biomass or from CO<sub>2</sub> combined with  $H_2$ obtained by electrolysis of water.

Iron-carbide based Fischer-Tropsch (FT) catalysts allow to convert synthesis gas to hydrocarbon products. The promotion of these FT catalysts with sodium and sulfur reduces the formation of undesired methane and increases the olefin content in the products as well as the activity in synthesis gas conversion. These types of catalysts are called Fischer-Tropsch to Olefins (FTO) catalysts. By the addition of a suitable zeolite to the FTO catalysts (forming a bifunctional catalyst) the formed olefins can (partially) be converted into aromatics. However, in close proximity between the FTO catalysts and zeolites alkaline promoters, such as sodium, can migrate from the FTO catalyst to the zeolite causing decreased activity of both catalysts. Colloidal iron nano particles attached to zeolites show promising application as model catalysts. The method of introducing sodium and sulfur promoters to these bifunctional catalysts has a large influence on the activity and stability in synthesis gas conversion to form olefins and aromatics. Bulk iron catalysts (promoted with alkaline metals) are widely applied in the high temperature Fischer-Tropsch synthesis to produce olefin rich hydrocarbons. Operating a potassium promoted bulk iron catalyst at medium temperature (250°C-300°C) causes a shift towards heavier products compared to high temperature applications. Placing a zeolite catalyst bed downstream of the bulk iron catalyst allows to convert higher olefins to aromatics and crack long hydrocarbons into C<sub>5</sub>-C<sub>11</sub> products. Additionally, isomerization of hydrocarbons is promoted. The resulting hydrocarbons mixture complies with requirements for gasoline fuel, such as a high octane number.

The aim of the research was to gain insight into bifunctional catalysts consisting of iron based FT catalysts and zeolites to convert synthesis gas to chemicals, namely olefins and aromatics, as well as gasoline. Chapters 3 and 4 describe a study of the processes of aromatization and deactivation by promoter migration for sodium- and sulfur-containing FTO catalysts. Colloidal iron nano particles attached to a zeolite catalyst were applied as model catalysts in chapter 5 to investigate the influence of promotion on the growth of the iron nano particles. Chapter 6 describes the use of bulk iron catalysts in combination with zeolites at medium temperatures (250°C-300°C) to understand aromatization, isomerization and cracking during the direct conversion of synthesis gas to gasoline. In the following paragraphs the results of the individual chapters are described.

A detailed analysis of the recent literature on bifunctional catalysis to convert synthesis gas to chemicals and fuels is presented in **Chapter 2**. We focused on dimethyl ether (DME),  $C_2$ - $C_4$  olefins, aromatics, and gasoline. Beside displaying the recent advances in the

fields, the performances of the bifunctional catalyst systems is compared to the combination of two monofunctional catalysts. The direct DME synthesis is attractive, especially when it is used together with *in-situ* water removal, which is able to achieve 98%c selectivity to DME. A novel bifunctional catalyst system consisting of metal oxides and zeolite (called OX-ZEO) can form  $C_2$ - $C_4$  olefins with 42% c selectivity, due to a large fraction of olefins in the hydrocarbon products and high water-gas-shift (WGS) activity that gives rise to formation of  $CO_2$ . FTO catalysts showed lower selectivity of around 20% to lower olefins. However, a reduced WGS activity of FTO catalysts can boost the overall selectivity towards olefins into the range of the OX-ZEO process. Furthermore, we showed that aromatics can be produced using bifunctional catalysts such as OX-ZEO with suitable zeolites or a combination of FT catalysts and zeolites. The OX-ZEO process showed high efficiency  $(38\%_{\rm C} \text{ selectivity to aromatics})$ , which could be boosted up to  $76\%_{\rm C}$  aromatics by reducing the WGS activity. For the direct production of gasoline from synthesis gas many pathways are possible. We analyzed the combination of cobalt-based and iron-based FT catalysts with zeolites (denoted as Co+Z and Fe+Z, respectively) as well as bifunctional OX-ZEO catalysts in detail. Co+Z demonstrated the highest selectivity to  $C_5$ - $C_{11}$  hydrocarbons but only low octane numbers (mainly between 20 and 50). Fe+Z on the other hand displayed lower selectivities of  $\sim 20\%$  but the octane numbers of the corresponding products were higher (65-91). The OX-ZEO catalysts produced high octane product mixtures (octane numbers between 73 and 89) with medium selectivity ( $\sim$ 39%<sub>C</sub>).

In **Chapter 3** we describe iron-carbide based FTO catalysts, promoted with sodium and sulfur, and combined with H-ZSM-5 zeolites to convert synthesis gas directly to olefins and aromatics in a single catalyst bed. The bifunctional catalyst showed higher activity compared to the FTO catalyst alone. Mößbauer spectroscopy revealed enhanced iron carbide formation on the FTO catalyst in the presence of a zeolite. Aromatization of olefins usually follows the hydrogen transfer mechanism, where formally hydrogen is transferred from a cycloalkane molecule to one or more olefins, leading to the formation of paraffins as a side product. However, we found that the aromatization of olefins under the applied reaction conditions (400°C, atmospheric pressure) followed a dehydrogenation route rather than hydrogen transfer. This allowed to convert synthesis gas to chemicals consisting of 27%c aromatics next to 41% C<sub>2</sub>-C<sub>4</sub> olefins with only 9.7% C<sub>2</sub>-C<sub>4</sub> paraffins (remaining was CO<sub>2</sub>).

The influence of proximity between sodium and sulfur promoted FTO catalysts and zeolites on the activity and stability is described in **Chapter 4**. The presence of both sodium and sulfur promoters on the FTO catalyst led to decreased methane selectivity. The bifunctional catalyst was used in a single reactor with various proximities ranging from cm-scale (in a stacked bed) to  $\mu$ m-scale (as composite mixture). Experiments with  $\alpha$ -alumina supported FTO catalysts showed high methane selectivities when they were mixed with an H-ZSM-5 zeolite in  $\mu$ m-scale. At medium proximity (mixed bed with small grain sizes of ~100  $\mu$ m) the methane selectivity gradually increased over time. Using larger grain sizes of ~500  $\mu$ m in a mixed bed configuration led to a low and stable methane selectivity. Moreover,

aromatics formation increased with increasing distance between the two catalytic functions, while methane formation decreased. X-ray photoelectron spectroscopy revealed a shift on the Na 1s signal to higher binding energies for the spent bifunctional catalysts in close proximity. This signal was assigned to sodium contained in the zeolite. From this it was concluded that sodium promoters migrated from the FTO catalyst to the zeolite, causing loss of sodium promotion effect on the FTO catalysts and deactivation of acid sites in the zeolite. An FTO catalyst carried on carbon nanotubes (CNT) showed no evidence of sodium migration even as a composite mixture with high proximity. This may be due to limited diffusion of sodium ions across the surface of the CNTs.

Colloidal iron nano particles attached to zeolites are described as model catalysts in **Chapter 5**. The colloids were prepared using organic ligands and showed a narrow size distribution around 6 nm. Inorganic ligand exchange was performed as a method to introduce sodium and sulfur as promoters for the iron nano particles. This ligand exchange was executed either before or after the attachment of iron nano particles to the zeolites. Experiments at 340°C and atmospheric pressure showed that the bifunctional catalysts with the promoters being introduced after attachment to the zeolites performed with higher activity and selectivity to aromatics and less methane formation. Also, these bifunctional catalysts were less prone for particle growth. However, the presence of promoters on the iron nano particles (independent of the introduction method) caused more intense particle growth compared to unpromoted nano particles. The analysis of the particle size of the spent catalyst in which the promoters were introduced before attachment also showed that the iron nano particle size had both decreased and increased, indicating an Ostwald ripening process.

**Chapter 6** describes potassium-promoted bulk iron catalysts combined with H-ZSM-5 zeolites to convert synthesis gas directly into aromatics-containing gasoline. The experiments were conducted in a stacked bed mode (iron catalyst upstream of zeolite) at 20 bar and between 250°C and 300°C. By varying the zeolite bed height downstream of the iron catalyst, processes taking place in zeolite bed could be monitored. At reaction temperature of 250°C and 275°C only little cracking and aromatization of the Fischer-Tropsch products in the zeolite bed were observed. At 300°C, heavier Fischer-Tropsch products were cracked, and aromatics were formed up to  $18\%_{\rm C}$ . These aromatics were formed directly from C<sub>4</sub>-C<sub>8</sub> olefins, and additionally indirectly from C<sub>2</sub>-C<sub>3</sub> olefins by oligomerization to longer olefins, while light aromatics were also alkylated. Additionally, branched isomers were extending to  $83\%_{\rm C}$  in the C<sub>5</sub>-C<sub>8</sub> aliphatic fraction. The gasoline fraction (C<sub>5</sub>-C<sub>11</sub>) was formed with up to  $55\%_{\rm C}$  selectivity and displayed an octane number as high as 91, which makes this fraction suitable as gasoline fuel.

The research described in this thesis focused on understanding the interaction between iron-based Fischer-Tropsch catalysts and zeolites for the conversion of synthesis gas into chemicals and fuels and the associated mechanisms that determine catalytic performance. The reported results demonstrate the versatility of these bifunctional catalysts and aid in the development of new catalyst systems.

#### Outlook

The insights gained in this thesis contribute to the design of a bifunctional catalyst system to convert synthesis gas to chemicals and fuels. This does require that higher conversions of Fischer-Tropsch olefins to aromatics be achieved without much formation of paraffins.

In this work sodium and sulfur promoters have been placed on the surface of iron nano particles and consecutively attached to zeolites. It is not known exactly where the promoters are located after activation and during catalysis, whether they are on the iron particles, at the interface with the carrier material or scattered on the surface of the carrier. The ability to localize the promoters in-situ during catalysis could greatly contribute to the design of a bifunctional catalyst that is less susceptible to deactivation by promoter migration.

The most recent literature shows interest in the conversion of  $CO_2$  with hydrogen into chemicals and fuels. A bifunctional catalyst consisting of an iron-based Fischer-Tropsch catalyst and zeolite may contribute to this.

#### **Nederlandse Samenvatting**

De wereldbevolking neemt toe en de vraag naar chemicaliën en brandstoffen is groter dan ooit. Het gebruik van fossiele grondstoffen om aan deze vraag te voldoen draagt bij aan de concentratie van broeikasgassen in de atmosfeer, en draaft bij aan ongewenste klimaatverandering. Daarom worden nieuwe routes voor de productie van chemicaliën en brandstoffen onderzocht en geïmplementeerd. Synthesegas, een mengsel van H<sub>2</sub> en CO, is een alternatief voor ruwe olie dat kan worden verkregen uit hernieuwbare bronnen zoals huishoudelijk afval of biomassa of uit CO<sub>2</sub> in combinatie met H<sub>2</sub> verkregen door elektrolyse van water.

Fischer-Tropsch (FT) katalysatoren op basis van ijzercarbide maken het mogelijk om synthesegas om te zetten in koolwaterstoffen. De modificatie van deze FT-katalvsatoren met natrium en zwavel als promotoren vermindert de vorming van ongewenst methaan en verhoogt het alkeengehalte in de producten en de activiteit bij conversie van synthesegas. Dit soort katalysatoren worden "Fischer-Tropsch to Olefins" (FTO)-katalysatoren genoemd. Door toevoeging van een geschikte zeoliet aan de FTO-katalysatoren (waardoor een bifunctionele katalysator wordt gevormd) kunnen de gevormde olefinen (gedeeltelijk) worden omgezet in aromaten. Echter, in de nabijheid van de FTO-katalysatoren en zeolieten kunnen alkalische promotoren, zoals natrium, migreren van de FTO-katalysator naar de zeoliet, waardoor beide katalysatoren minder actief worden. Colloïdale ijzernanodeeltjes gehecht aan zeolieten zijn veelbelovend als modelkatalysator. De methode om natrium- en zwavelpromotoren toe te voegen aan deze bifunctionele katalysatoren heeft een grote invloed op de activiteit en stabiliteit bij de omzetting van synthesegas naar olefinen en aromaten. Ongedragen ('bulk') ijzerkatalysatoren (met alkalimetalen) worden op grote schaal toegepast in de hoge temperatuur Fischer-Tropsch synthese om alkeenrijke koolwaterstoffen te produceren. Het werken met een met kalium gemodificeerde bulk-ijzerkatalysator bij middelhoge temperatuur (250°C-300°C) veroorzaakt een verschuiving naar zwaardere producten in vergelijking met omzettingen bij hogere temperaturen. Door een zeoliet kataysator na de ijzerkatalysator te plaatsen, kunnen hogere olefinen worden omgezet in aromaten, en kunnen lange koolwaterstoffen worden gekraakt in  $C_5$ - $C_{11}$ -producten. Bovendien wordt de isomerisatie van koolwaterstoffen bevorderd. Het resulterende koolwaterstofmengsel voldoet aan eisen voor benzine, zoals een hoog octaangetal.

Het doel van dit onderzoek was om inzicht te krijgen in bifunctionele katalysatoren bestaande uit FT-katalysatoren op basis van ijzer en zeolieten om synthesegas om te zetten in chemicaliën en componenten van brandstoffen, namelijk olefinen en aromaten. In hoofdstuk 3 en 4 wordt een studie van de processen van aromatisering en deactivering door promotormigratie beschreven voor natrium- en zwavel houdende FTO-katalysatoren. Colloïdale ijzernanodeeltjes gehecht aan een zeolietkatalysator werden toegepast als modelkatalysatoren (hoofdstuk 5) om de invloed van promotie op de groei van de ijzernanodeeltjes te onderzoeken. Hoofdstuk 6 beschrijft het gebruik van bulkijzerkatalysatoren in combinatie met zeolieten bij middelhoge temperaturen (250°C-300°C) om inzicht te krijgen in aromatisering, isomerisatie en kraken tijdens de directe omzetting van synthesegas naar benzine. In de volgende paragrafen worden de resultaten van de afzonderlijke hoofdstukken verder besproken.

Een gedetailleerde analyse van de recente literatuur over bifunctionele katalysatoren om synthesegas om te zetten in chemicaliën en brandstoffen wordt gepresenteerd in **hoofdstuk 2**. We concentreerden ons op dimethylether (DME), C<sub>2</sub>-C<sub>4</sub> olefinen, aromaten en benzine. Naast het weergeven van de recente vooruitgang op dit gebied, worden de prestaties van de bifunctionele katalysatorsystemen vergeleken met de combinatie van twee monofunctionele katalysatoren. De directe DME-synthese is aantrekkelijk, vooral wanneer deze wordt gebruikt in combinatie met in-situ waterverwijdering, waarmee een selectiviteit van 98% naar DME kan worden bereikt. Een nieuw bifunctioneel katalysatorsysteem bestaande uit metaaloxiden en zeoliet (OX-ZEO genoemd) kan C2-C4-olefinen vormen met een selectiviteit van 42%c, dankzij een grote fractie olefinen in de koolwaterstofproducten en een hoge "water-gas-shift" (WGS)-activiteit die aanleiding geeft tot de vorming van CO<sub>2</sub>. FTO-katalysatoren vertonen een lagere selectiviteit van ongeveer 20% voor korte olefinemolekulen. Onderdrukken van de WGS-activiteit van FTO-katalysatoren kan de selectiviteit naar olefinen verhogen tot in het bereik van het OX-ZEO-proces. Aromaten kunnen worden geproduceerd met behulp van bifunctionele katalysatoren zoals OX-ZEO met geschikte zeolieten of een combinatie van FT-katalysatoren en zeolieten. Het OX-ZEO proces heeft een hoge efficiëntie (38% c selectiviteit naar aromaten), die kan worden verhoogd tot 76% aromaten door de WGS activiteit te verminderen. Voor de directe productie van benzine uit synthesegas zijn vele routes mogelijk. We hebben de combinatie van FT-katalysatoren op basis van kobalt en ijzer met zeolieten (respectievelijk Co+Z en Fe+Z genoemd) en bifunctionele OX-ZEO-katalysatoren in detail geanalyseerd. Co+Z toonde de hoogste selectiviteit voor  $C_5$ - $C_{11}$  koolwaterstoffen maar lage octaangetallen (tussen 20 en 50). Fe+Z daarentegen vertoont een lagere selectiviteit ( $\sim 20\%_{\rm C}$ ) maar hogere octaangetallen (65-91). De OX-ZEO-katalysatoren produceerden mengsels met hoge octaangetallen (tussen 73 en 89) met een gemiddelde selectiviteit (~39%<sub>C</sub>).

In hoofdstuk 3 beschrijven we FTO-katalysatoren op basis van ijzercarbide, gepromoteerd met natrium en zwavel, en gecombineerd met H-ZSM-5 zeolieten om synthesegas rechtstreeks om te zetten in olefinen en aromaten in een enkel katalysatorbed. De bifunctionele katalysator was actiever dan de FTO-katalysator alleen. Mößbauer spectroscopie onthulde verbeterde ijzercarbidevorming in de FTO-katalysator in aanwezigheid van een zeoliet. Aromatisering van olefinen volgt gewoonlijk het mechanisme waterstofoverdracht. waarbii waterstof wordt overgedragen van van een cycloalkaanmolecuul naar een of meer olefinen, wat leidt tot de vorming van paraffinen als bijproduct. We ontdekten echter dat de aromatisering van olefinen onder de toegepaste reactieomstandigheden (400°C, atmosferische druk) een dehydrogenatieroute volgde in plaats van via waterstofoverdracht te verlopen. Hierdoor kon synthesegas worden omgezet in chemicaliën bestaande uit  $27\%_{C}$  aromaten naast  $41\%_{C}$  C<sub>2</sub>-C<sub>4</sub> olefinen met slechts  $9,7\%_{C}$  C<sub>2</sub>-C<sub>4</sub> paraffinen (de rest was CO<sub>2</sub>).

De invloed van de nabijheid tussen natrium- en zwavelgepromote FTOkatalysatoren en zeolieten op de activiteit en stabiliteit is beschreven in hoofdstuk 4. De aanwezigheid van zowel natrium- als zwavelpromotoren op de FTO-katalysator leidde tot een lagere methaanselectiviteit. De bifunctionele katalysatoren werden gebruikt in een enkel katalysatorbed met verschillende afstanden tussen de twee katalytische componenten, variërend van cm-schaal (in een gestapeld bed) tot  $\mu$ m-schaal (als samengesteld mengsel).  $\alpha$ aluminiumoxide gedragen FTO-katalysatoren toonden hoge methaanselectiviteit wanneer ze op µm-schaal werden gemengd met een H-ZSM-5 zeoliet. Bij een middelgrote nabijheid (gemengd bed met kleine korrelgroottes van ~100 µm) nam de methaanselectiviteit geleidelijk toe in de tijd. Het gebruik van grotere korrelgroottes van ~500 µm in een gemengd katalysatorbed leidde tot een lage en stabiele methaanselectiviteit. Bovendien nam de vorming van aromaten toe met toenemende afstand tussen de twee katalytische functies, terwijl de methaanvorming juist afnam. Röntgenfotoelektronenspectroscopie onthulde een verschuiving van het Na 1s-signaal naar hogere bindingsenergieën voor de gebruikte bifunctionele katalysatoren in directe nabijheid. Dit signaal werd toegekend aan natrium dat zich in de zeoliet bevond. Hieruit werd geconcludeerd dat natriumpromotoren migreerden van de FTO-katalysator naar de zeoliet, waardoor het natriumpromotie-effect op de FTOkatalysatoren verloren ging en de zure sites in de zeoliet werden gedeactiveerd. Een FTO katalysator gedragen op koolstof nanobuizen (CNT) toonde geen bewijs van natriummigratie, zelfs niet als een composiet mengsel met een directe nabijheid. Dit is mogelijk te wijten aan beperkte diffusie van natriumionen over het oppervlak van de CNTs.

Colloïdale ijzernanodeeltjes gehecht aan zeolieten als modelkatalysatoren worden beschreven in **hoofdstuk 5**. De colloïden werden bereid met organische liganden en vertoonden een smalle grootteverdeling, rond 6 nm gemiddelde deeltjesgrootte. Uitwisseling met anorganische liganden werd gebruikt om natrium en zwavel te introduceren als promotoren voor de ijzernanodeeltjes. Deze liganduitwisseling werd uitgevoerd voor of na de aanhechting van ijzernanodeeltjes aan de zeolieten. Experimenten bij 340°C en atmosferische druk toonden aan dat de bifunctionele katalysatoren waarbij de promotoren na de aanhechting aan de zeolieten werden ingebracht, een hogere activiteit en selectiviteit voor aromaten hadden en minder methaan vormden. Deze bifunctionele katalysatoren waren ook minder gevoelig voor deeltjesgroei. De aanwezigheid van promotoren op de ijzeren nanodeeltjes (onafhankelijk van de introductiemethode) veroorzaakte echter een sterkere deeltjesgroei in vergelijking met nanodeeltjes zonder promotoren. Analyse van de katalysator met promotoren geïntroduceerd voor aanhechting, toonde dat na gebruik de grootte van sommige ijzernanodeeltjes was afgenomen, maar van andere juist was toegenomen, wat duidt op een proces van "Ostwald ripening".

**Hoofdstuk 6** beschrijft kaliumgepromoteerde bulk-ijzerkatalysatoren in combinatie met H-ZSM-5 zeolieten om synthesegas rechtstreeks om te zetten in aromaathoudende

benzine. De experimenten werden uitgevoerd in een gestapeld katalysatorbed (ijzerkatalysator stroomopwaarts van zeoliet) bij 20 bar en tussen  $250^{\circ}$ C en  $300^{\circ}$ C. Door de zeolietbedhoogte stroomafwaarts van de ijzerkatalysator te variëren, konden de processen die in het zeolietbed plaatsvinden worden gevolgd. Bij reactietemperaturen van  $250^{\circ}$ C en  $275^{\circ}$ C werd slechts weinig kraken en aromatisering van de Fischer-Tropsch-producten in het zeolietbed waargenomen. Bij  $300^{\circ}$ C werden zwaardere Fischer-Tropsch-producten gekraakt waardoor tot  $18\%_{C}$  aromaten gevormd werd. Deze aromaten werden direct gevormd uit C<sub>4</sub>-C<sub>8</sub>-olefinen, en daarnaast indirect uit C<sub>2</sub>-C<sub>3</sub>-olefinen door oligomerisatie tot langere olefinen, terwijl ook lichte aromated gealkyleerd werden. De fractie vertakte isomeren was  $83\%_{C}$  in de C<sub>5</sub>-C<sub>8</sub> alifatische fractie. De benzinefractie (C<sub>5</sub>-C<sub>11</sub>) werd gevormd met een selectiviteit tot  $55\%_{C}$  en vertoonde een octaangetal tot 91, waardoor deze geschikt is als benzine.

Het onderzoek beschreven in dit proefschrift was gericht op het begrijpen van de wisselwerking tussen ijzergebaseerde Fischer-Tropsch katalysatoren en zeolieten voor de omzetting van synthesegas in chemicaliën en brandstoffen en de bijbehorende mechanismen die de katalytische prestaties bepalen. De gerapporteerde resultaten tonen de veelzijdigheid van deze bifunctionele katalysatoren en helpen bij de ontwikkeling van nieuwe katalysatorsystemen.

#### Vooruitblik

De inzichten die zijn opgedaan in dit proefschrift dragen bij aan het ontwerp van een bifunctioneel katalysatorsysteem om synthesegas om te zetten in chemicaliën en brandstoffen. Daarvoor is het wel nodig dat hogere conversies van Fischer-Tropsch olefinen naar aromaten bereikt worden zonder veel vorming van paraffinen.

In dit werk zijn natrium- en zwavelpromotoren op het oppervlak van ijzernanodeeltjes geplaatst en vervolgens zijn deze gepromoteerd ijzerdeeltjes op zeolieten afgezet. Het is niet bekend waar de promotoren zich precies bevinden na activering en tijdens katalyse, of ze zich op de ijzerdeeltjes bevinden, op het grensvlak met het dragermateriaal of verspreid over het oppervlak van de drager. De mogelijkheid om de promotoren in-situ te lokaliseren tijdens de katalyse kan een grote bijdrage leveren aan het ontwerp van een bifunctionele katalysator die minder gevoelig is voor deactivatie door promotormigratie.

De meest recente literatuur toont interesse in de omzetting van  $CO_2$  met waterstof in chemicaliën en brandstoffen. Een bifunctionele katalysator bestaande uit een ijzergebaseerde Fischer-Tropsch katalysator en zeoliet kan hieraan bijdragen. Recent advances in bifunctional synthesis gas conversion to chemicals and fuels with a comparison to monofunctional processes

#### Appendix A

#### **Supporting information Chapter 2**

Recent advances in bifunctional synthesis gas conversion to chemicals and fuels with a comparison to monofunctional processes

A detailed analysis of published data on the conversion of synthesis gas to DME, olefins, aromatics, and gasoline can be found in the supplementary information of the publication "Recent advances in bifunctional synthesis gas conversion to chemicals and fuels with a comparison to monofunctional processes" *Catal. Sci. Technol.* **14**, 4799-4842 (2024)<sup>1</sup>.

#### Determination of the octane number

The octane number of the  $C_5$ - $C_{11}$  products was estimated by using the blending research octane number (BRON) of the single components. The BRON can describe the effect of a single component being blended into a base gasoline fuel, whereas the pure research octane number (RON) of a component is measured as pure compound <sup>2</sup>. The BRON of the  $C_5$ - $C_{11}$  paraffins, iso-paraffins, olefins, iso-olefins and aromatics were either found in literature <sup>2–4</sup> or estimated by extrapolation.

The average  $C_5$ - $C_{11}$  paraffins BRON can be found in Table A1 and Figure A1. The individual BRON of all isomers were averaged for every carbon number with the same number of branches. Analog, the average BRON for olefins were determined (Table A2 and Figure A2). However, the olefins were not further divided by the position of the double bond, despite the effect of the double bond position on the BRON (Figure A3). The BRON of  $C_{6^-}$   $C_{11}$  aromatics was averaged over the corresponding carbon numbers (Table A3, Figure A4 and Figure A5).

	number of branches						
	0	1	2	3	4	5	
<b>C</b> 5	62	99	100				
<b>C</b> <sub>6</sub>	19	85	93				
<b>C</b> <sub>7</sub>	0	54	84	113			
<b>C</b> 8	-19	31	69	101	120		
C9	-30	$20^{1}$	56 <sup>1</sup>	92	121		
C <sub>10</sub>	-41	2	34	$70^{1}$	111		
C11	-48 <sup>1</sup>	-121	18 <sup>1</sup>	55 <sup>1</sup>	<b>98</b> <sup>1</sup>	130 <sup>1</sup>	

Table A1: average blending research octane numbers of C5-C11 paraffins divided into number of branches.

<sup>1</sup>: extrapolated

Appendix A



Figure A1: average blending research octane number of C<sub>5</sub>-C<sub>11</sub> paraffins as function of number of branching.

	Table A2: avera	ge blending research	octane numbers of	C <sub>5</sub> -C <sub>11</sub> olefins	divided into nu	mber of branches
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	number of branches					
	0	1	2	3	4	5
<b>C</b> 5	112	125	127			
<b>C</b> 6	100	112	120			
<b>C</b> 7	75	86	98	$110^{1}$		
<b>C</b> 8	61	72 <sup>1</sup>	85 <sup>1</sup>	$100^{1}$	115 <sup>1</sup>	
C9	48	$60^{1}$	72 <sup>1</sup>	$87^{1}$	$102^{1}$	
C10	35	$47^{1}$	591	75 <sup>1</sup>	90 <sup>1</sup>	
C11	$20^{1}$	32 <sup>1</sup>	46 <sup>1</sup>	63 <sup>1</sup>	78 <sup>1</sup>	90 <sup>1</sup>
1						

<sup>1</sup>: extrapolated

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Figure A2: average blending research octane number of C5-C11 olefins as function of number of branching.



Figure A3: blending research octane number of linear C5-C10 olefins as function of double bond position.

side chains							
	0	1	2	3	4	5	average
<b>C</b> <sub>6</sub>	108						108
<b>C</b> 7		120					120
C8		120.9	131.5				126
C9		124.1	$127^{1}$	131 <sup>1</sup>			127
C <sub>10</sub>		116.7	121.8	126.9	133		125
C11		101	112.7	120 <sup>1</sup>	125 <sup>1</sup>	127 <sup>1</sup>	117

Table A3: average blending research octane numbers of C<sub>6</sub>-C<sub>11</sub> aromatics divided into number of side chains.

<sup>1</sup>: extrapolated



Figure A4: average blending research octane number of  $C_6$ - $C_{11}$  aromatics as function of number of side chains.

Recent advances in bifunctional synthesis gas conversion to chemicals and fuels with a comparison to monofunctional processes



Figure A5: average blending research octane number of aromatics as function of carbon number.

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## **Appendix B**

#### **Supporting information Chapter 3**

Bifunctional Catalysis for the Conversion of Synthesis Gas to Olefins and Aromatics

Experiments in mixed bed configurations were performed up to a certain dilution of the iron catalysts to maintain an isothermal catalyst bed. The maximum dilution was determined using the dilution number  $B^{1}$ :

$$B = \frac{b \cdot d_p}{l \cdot \delta} < 4 \cdot 10^{-3}$$
Equation B1

with:

В	Dilution number
b	dilution (inert fraction)
$d_p$	particle diameter (m)
l	length of undiluted catalyst bed (m)
δ	relative experimental error (%)

Hence

$$B = \frac{b \cdot 1.125 \cdot 10^{-4} m}{5.21 \cdot 10^{-3} m \cdot 5} < 4 \cdot 10^{-3}$$
 Equation B2

Using Equation B2 we calculated the dilution number (*B*) of the catalyst bed of physical mixtures of the FTO catalyst with different amounts of zeolite (Table B1). With B > 0.004, an isothermal bed cannot be maintained.

	V	olume parts		_		
	FeP	Z	SiC	b	В	
FeP-2Z	1	2	6	0.889	0.00384	isothermal
FeP-3Z	1	3	8	0.917	0.00396	isothermal
FeP-4Z	1	4	10	0.933	0.00403	not isothermal
FeP-10Z	1	10	22	0.970	0.00419	not isothermal
FeP-20Z	1	20	42	0.984	0.00425	not isothermal

Table B1: Calculations of dilution numbers based on values shown above.

To avoid a non-isothermal catalyst bed, experiments were carried out with zeolite/iron catalyst ratio of 2 v/v for the mixed bed experiments.

catalyst	Fe (wt-%)	Na (wt-ppm)	S (wt-ppm)	Na/Fe (at/at)	S/Fe (at/at)
Fe	5.60	344	bdl. <sup>[a]</sup>	0.015	-
FeP	5.51	3270	294	0.144	0.0093

Table B2: Composition of iron catalysts according to ICP measurements.

[a] bdl.: below detection limit

**Table B3:** Results from Mößbauer spectroscopy of the unpromoted iron catalyst without the presence of the zeolite after calcination at 250°C for 2 h in static air, reduction at 350°C for 2 h in H<sub>2</sub>/Ar = 2, carburization at 290°C for 1 h in CO/H<sub>2</sub> = 1, reaction conditions at 400 °C after 5 h in CO/H<sub>2</sub> = 1 and reaction conditions at 400°C after 15 h in CO/H<sub>2</sub> = 1.

Sampla	IS	QS	Hyperfine field (T)	Г	Dhaco	Spectral contribution (%)
Sumple	(mm·s⁻¹)	(mm·s⁻¹)	nyperjine jiela (1)	(mm·s⁻¹)	PHUSE	spectral contribution (%)
Fe	0.38	-0.2	50.7	0.4	Fe <sup>3+</sup> (α-Fe <sub>2</sub> O <sub>3</sub> )	19
calcined	0.34	-0.06	44.7*	0.5	Fe <sup>3+</sup>	52
	0.34	0.84	-	0.82	Fe <sup>3+</sup> (SPM <sup>a</sup> )	29
Fe	0	-	33.1	0.31	Fe <sup>0</sup>	21
H <sub>2</sub> /Ar=2	-0.05	-	-	0.77	Fe <sup>o</sup> (SPM)	9
350 °C, 2 h	0.22	0.3	-	0.42	Fe <sub>x</sub> C (SPM)	8
	1.03	0.39	-	0.71	Fe <sup>2+</sup>	62
Fe	0.24	-	17.2	0.35	€ <sup>′</sup> -Fe₂.₂C	9
H <sub>2</sub> /CO=1	0.23	-	21.7	0.36	$\chi$ -Fe <sub>5</sub> C <sub>2</sub> (I)	4
290 °C, 1 h	0.17	-	19	0.35	$\chi$ -Fe <sub>5</sub> C <sub>2</sub> (II)	5
	0.21	-	11.3	0.35	χ-Fe₅C₂ (III)	2
	0.17	0.36	-	0.5	Fe <sub>x</sub> C (SPM)	12
	1.07	0.28	-	0.73	Fe <sup>2+</sup>	68
Fe	0.24	-	21.1	0.38	χ-Fe₅C₂ (I)	16
H <sub>2</sub> /CO=1	0.19	-	18.4	0.4	χ-Fe₅C₂ (II)	16
400 °C, 5 h	0.21	-	11.4	0.38	$\chi$ -Fe <sub>5</sub> C <sub>2</sub> (III)	8
	0.18	0.42	-	0.65	Fe <sub>x</sub> C (SPM)	15
	1.07	0.27	-	0.73	Fe <sup>2+</sup>	45
Fe	0.19	-	17.3	0.33	€ <sup>′</sup> -Fe₂.₂C	8
H <sub>2</sub> /CO=1	0.25	-	21.2	0.42	χ-Fe₅C₂ (I)	17
400 °C, 15 h	0.2	-	18.9	0.42	χ-Fe₅C₂ (II)	16
	0.21	-	11.3	0.42	$\chi$ -Fe <sub>5</sub> C <sub>2</sub> (III)	10
	0.18	0.52	-	0.7	Fe <sub>x</sub> C (SPM)	21
	1.05	0.35	-	0.69	Fe <sup>2+</sup>	28

Sampla	IS	QS	Hyperfine field (T)	Г	Phase	Spectral contribution /0/	
Sumple	(mm·s <sup>-1</sup> )	( <i>mm</i> ⋅s <sup>-1</sup> )	Hyperjine jielu (1)	(mm·s⁻¹)	Phuse	Spectrui contribution (%)	
Fe-Z	0.01	-	33.1	0.32	Fe <sup>0</sup>	30	
H <sub>2</sub> /Ar=2	-0.05	-	-	0.9	Fe <sup>0</sup> (SPM)	15	
350 °C, 2 h	0.21	0.3	-	0.42	Fe <sub>x</sub> C (SPM)	7	
	1.01	0.43	-	0.7	Fe <sup>2+</sup>	48	
Fe-Z	0.25	-	17.1	0.4	$\epsilon'$ -Fe <sub>2.2</sub> C	17	
H <sub>2</sub> /CO=1	0.27	-	22.1	0.49	χ-Fe <sub>5</sub> C <sub>2</sub> (I)	6	
290 °C, 1 h	0.18	-	18.7	0.49	$\chi$ -Fe <sub>5</sub> C <sub>2</sub> (II)	6	
	0.21	-	11.4	0.49	$\chi$ -Fe <sub>5</sub> C <sub>2</sub> (III)	3	
	0.15	0.44	-	0.73	Fe <sub>x</sub> C (SPM)	23	
	1.03	0.39	-	0.68	Fe <sup>2+</sup>	45	
Fe-Z	0.25	-	20.9	0.38	χ-Fe₅C₂ (I)	20	
H <sub>2</sub> /CO=1	0.19	-	18.2	0.39	χ-Fe <sub>5</sub> C <sub>2</sub> (II)	18	
400 °C, 5 h	0.18	-	11.4	0.38	χ-Fe <sub>5</sub> C <sub>2</sub> (III)	9	
	0.22	0.59	-	0.84	Fe <sub>x</sub> C (SPM)	26	
	1.06	0.3	-	0.76	Fe <sup>2+</sup>	27	
Fe-Z	0.25	-	17	0.4	€ <sup>′</sup> -Fe₂.₂C	8	
H <sub>2</sub> /CO=1	0.26	-	21	0.4	χ-Fe <sub>5</sub> C <sub>2</sub> (I)	18	
400 °C, 15 h	0.2	-	18.8	0.43	$\chi$ -Fe <sub>5</sub> C <sub>2</sub> (II)	17	
	0.21	-	11.4	0.4	χ-Fe <sub>5</sub> C <sub>2</sub> (III)	8	
	0.22	0.57	-	0.93	Fe <sub>x</sub> C (SPM)	30	
	1.06	0.23	-	0.89	Fe <sup>2+</sup>	19	

**Table B4:** Results from Mößbauer spectroscopy of the unpromoted iron catalyst with the presence of the zeolite after reduction at 350°C for 2 h in H<sub>2</sub>/Ar = 2, carburization at 290°C for 1 h in CO/H<sub>2</sub> = 1, reaction conditions at 400°C after 5 h in CO/H<sub>2</sub> = 1 and reaction conditions at 400°C after 15 h in CO/H<sub>2</sub> = 1.

	IS	QS		Г	21		
Sample	(mm·s⁻¹)	(mm·s⁻¹)	Hyperfine field (1)	(mm·s⁻¹)	Phase	Spectral contribution (%)	
FeP	0.31	0.01	44.1 <sup>*</sup>	0.54	Fe <sup>3+</sup>	52	
calcined	0.34	0.81	-	0.63	Fe <sup>3+</sup> (SPM)	48	
FeP	0.01	-	33.1	0.29	Fe <sup>0</sup>	35	
H <sub>2</sub> /Ar=2	0.21	0.3	-	0.42	Fe <sub>x</sub> C (SPM)	11	
350 °C, 2 h	1.06	0.5	-	0.58	Fe <sup>2+</sup>	54	
FeP	0.26	-	17	0.38	€́-Fe₂.₂C	26	
H <sub>2</sub> /CO=1	0.24	-	21.8	0.46	χ-Fe <sub>5</sub> C <sub>2</sub> (I)	5	
290 °C, 1 h	0.2	-	18.5	0.44	$\chi$ -Fe <sub>5</sub> C <sub>2</sub> (II)	9	
	0.21	-	10.9	0.41	$\chi$ -Fe <sub>5</sub> C <sub>2</sub> (III)	3	
	0.21	0.38	-	0.57	Fe <sub>x</sub> C (SPM)	14	
	1.06	0.41	-	0.67	Fe <sup>2+</sup>	43	
FeP	0.25	-	16.6	0.37	€́-Fe₂.₂C	9	
H <sub>2</sub> /CO=1	0.27	-	21.6	0.38	$\chi$ -Fe <sub>5</sub> C <sub>2</sub> (I)	24	
400 °C, 5 h	0.21	-	18.1	0.38	$\chi$ -Fe <sub>5</sub> C <sub>2</sub> (II)	23	
	0.18	-	10.3	0.38	$\chi$ -Fe <sub>5</sub> C <sub>2</sub> (III)	15	
	0.19	0.6	-	0.88	Fe <sub>x</sub> C (SPM)	21	
	1.06	0.47	-	0.71	Fe <sup>2+</sup>	8	
FeP	0.27	-	21.6	0.41	χ-Fe₅C₂ (I)	24	
H <sub>2</sub> /CO=1	0.22	-	18	0.41	$\chi$ -Fe <sub>5</sub> C <sub>2</sub> (II)	26	
400 °C, 15 h	0.18	-	10.3	0.41	$\chi$ -Fe <sub>5</sub> C <sub>2</sub> (III)	17	
	0.23	0.59	-	0.94	Fe <sub>x</sub> C (SPM)	33	

**Table B5:** Results from Mößbauer spectroscopy of the promoted iron catalyst without the presence of the zeolite after calcination at 250°C for 2 h in static air, reduction at 350°C for 2 h in H<sub>2</sub>/Ar = 2, carburization at 290 °C for 1 h in CO/H<sub>2</sub> = 1, reaction conditions at 400°C after 5 h in CO/H<sub>2</sub> = 1 and reaction conditions at 400°C after 15 h in CO/H<sub>2</sub> = 1.

Sampla	IS	QS	Hyperfine field (T)	Г	Phace	Spectral contribution (%)	
Sumple	(mm·s⁻¹)	(mm·s⁻¹)	Hyperjine jiela (1)	(mm·s⁻¹)	Phase	Spectrui contribution (%)	
FeP-Z	0.01	-	33	0.29	Fe <sup>0</sup>	52	
H <sub>2</sub> /Ar=2	0.2	0.22	-	0.88	Fe <sub>x</sub> C (SPM)	18	
350 °C, 2 h	1.05	0.37	-	0.72	Fe <sup>2+</sup>	30	
FeP-Z	0.25	-	17	0.4	€ -Fe₂.₂C	27	
H <sub>2</sub> /CO=1	0.28	-	21.5	0.41	$\chi$ -Fe <sub>5</sub> C <sub>2</sub> (I)	8	
290 °C, 1 h	0.21	-	18.5	0.42	χ-Fe₅C₂ (II)	10	
	0.21	-	10.8	0.41	$\chi$ -Fe <sub>5</sub> C <sub>2</sub> (III)	4	
	0.26	0.72	-	0.85	Fe <sub>x</sub> C (SPM)	34	
	1.1	0.47	-	0.75	Fe <sup>2+</sup>	17	
FeP-Z	0.25	-	16.8	0.38	€ -Fe₂.₂C	10	
$H_2/CO=1$	0.26	-	21.6	0.34	χ-Fe₅C₂ (I)	18	
400 °C, 5 h	0.24	-	18.5	0.34	χ-Fe₅C₂ (II)	16	
	0.18	-	10.2	0.34	χ-Fe₅C₂ (III)	10	
	0.23	0.61	-	1.42	Fe <sub>x</sub> C (SPM)	46	
FeP-Z	0.25	-	16.6	0.36	€ -Fe <sub>2.2</sub> C	7	
H <sub>2</sub> /CO=1	0.27	-	21.6	0.35	χ-Fe₅C₂ (I)	15	
400 °C, 15 h	0.23	-	18.3	0.35	χ-Fe₅C₂ (II)	14	
	0.18	-	10.1	0.35	$\chi$ -Fe <sub>5</sub> C <sub>2</sub> (III)	8	
	0.23	0.53	-	1.22	Fe <sub>x</sub> C (SPM)	56	

**Table B6:** Results from Mößbauer spectroscopy of the promoted iron catalyst without the presence of the zeolite after reduction at 350°C for 2 h in H<sub>2</sub>/Ar = 2, carburization at 290°C for 1 h in CO/H<sub>2</sub> = 1, reaction conditions at 400°C after 5 h in CO/H<sub>2</sub> = 1 and reaction conditions at 400°C after 15 h in CO/H<sub>2</sub> = 1.

**Table B7:** Summary of experiments conducted at elevated pressures of 5 bar in a mixed bed and stacked bed configuration at 400°C and GHSV of 24,000 h<sup>-1</sup> with synthesis gas compositions of  $CO:H_2 = 0.5$  (v/v) and 2 (v/v) after time on stream between 3 h and 6 h.

1 -	· · ·							
	F	еP	FeP	-2Z	FeP-2	2Z-SB	FeP-1	.0Z-SB
CO:H₂ v/v	0.5	2	0.5	2	0.5	2	0.5	2
Activity (10 <sup>-5</sup> mol CO g(Fe) <sup>-1</sup> s <sup>-1</sup> )	22.8	6.3	30.5	6.8	29.7	7.7	25.0	8.9
CO conversion (%)	18.1	6.0	23.4	8.2	22.7	6.2	18.8	6.1
H <sub>2</sub> conversion (%)	6.9	5.2	9.4	7.6	9.6	5.7	7.9	5.9
Hydrocarbon distribution								
CH <sub>4</sub> selectivity (% <sub>c</sub> )	28.9	21.8	31.2	19.9	32.0	23.4	33.7	23.8
C <sub>2</sub> -C <sub>4</sub> olefins selectivity (%c)	46.0	50.4	12.6	27.3	3.8	12.0	1.3	3.8
C <sub>2</sub> -C <sub>4</sub> paraffins selectivity (% <sub>c</sub> )	7.6	5.3	39.0	31.1	47.0	42.7	53.7	53.4
C <sub>5+</sub> aliphatics selectivity (% <sub>c</sub> )	17.5	21.5	16.1	19.2	15.6	18.9	9.9	15.9
$C_6$ - $C_8$ aromatics selectivity (% <sub>c</sub> )	0.00	1.00	1.17	2.53	1.63	3.02	1.46	3.10
$CO_2$ selectivity (% <sub>C</sub> )	51.9	69.9	50.3	64.8	50.9	68.5	50.1	67.8
Carbon balance (%)	84	62	85	67	79	64	83	61

Experiments performed at elevated pressure of 5 bar, 400°C, and GHSV of 24,000 h<sup>-1</sup> in a mixed bed as well as in a stacked bed configuration (Table B7) showed that the activity is not influenced as strongly as shown in experiments at low pressure, where the activity was doubled when the promoted iron catalyst was mixed with the zeolite in the mixed bed configuration. The high CO<sub>2</sub> selectivity of ~50%<sub>C</sub> for CO:H<sub>2</sub> = 0.5 v/v and ~67%<sub>C</sub> for CO:H<sub>2</sub> = 2 v/v is related to the Boudouard reaction that takes place under these reaction conditions. The pure promoted iron catalyst showed a selectivity towards C<sub>2</sub>-C<sub>4</sub> olefins of 46.0%<sub>C</sub> (CO:H<sub>2</sub> = 0.5 v/v) and 50.4%<sub>C</sub> (CO:H<sub>2</sub> = 2 v/v), while C<sub>2</sub>-C<sub>4</sub> paraffins were formed with 7.6%<sub>C</sub> (CO:H<sub>2</sub> = 0.5 v/v) and 5.3%<sub>C</sub> (CO:H<sub>2</sub> = 2 v/v) selectivity. When the promoted iron catalyst was combined with the zeolite in a mixed bed configuration (FeP-2Z) as well as a stacked bed configuration (FeP-2Z-SB and FeP-10Z-SB) the selectivity towards C<sub>2</sub>-C<sub>4</sub> olefins was decreased while C<sub>2</sub>-C<sub>4</sub> paraffins were formed with higher selectivity. This trend is more pronounced the more zeolite is present. The selectivity towards aromatics did not exceed 3.1%<sub>C</sub>.

The less significant influence of the zeolite on the activity of the promoted iron catalyst in the experiments performed at elevated pressure is due higher pressure of synthesis gas and the resulting enhanced carburization. This makes the influence of the zeolite less pronounced.



**Figure B1:** Activity during the initial phase of the reaction for the promoted iron catalyst with different zeolite amounts present in a stacked bed configuration, compared with FeP at 400°C, CO:H<sub>2</sub> = 1, GHSV: 7,200 h<sup>-1</sup>, 1 bar.



**Figure B2:** Thermodynamic equilibrium of propene dehydroaromatization to benzene as function of initial hydrogen/propene ratio at 400°C and 1 bar.



**Figure B3:** High Annular Angle Dark Field–TEM image of a calcined promoted iron catalyst particle (left) and High Annular Angle Dark Field–TEM image overlaid with Energy Dispersive X-ray spectroscopy to detect the elements iron and sodium (right).



**Figure B4:** X-ray diffraction measurement of the promoted iron catalyst on a Bruker D2 Phaser powder diffractometer equipped with a cobalt  $k_{\alpha}$ -source ( $\lambda = 1.78897$  Å), 2 $\Theta$  from 10° to 130° with 0.07°/step and a step time of 1 s.



**Figure B5:** Temperature programmed NH<sub>3</sub>-desorption of H-ZSM-5 with Si/Al = 15 with a heating 10 K/min to 700°C.

### References

 Van Den Bleek, C. M., Van Der Wiele, K. & Van Den Berg, P. J. The effect of dilution on the degree of conversion in fixed bed catalytic reactors. *Chem. Eng. Sci.* 24, 681–694 (1969).

# Appendix C

### **Supporting information Chapter 4**

Effect of Proximity and Support Material on Deactivation of bifunctional Catalysts for the Conversion of Synthesis Gas to Olefins and Aromatics



Figure C1: Temperature programmed NH<sub>3</sub> desorption of H-ZSM-5 zeolite.

	Fe (wt-%)	Na:Fe (at/at)	S:Fe (at/at)
AFe	5.75%	0.097	0.0091
CFe	2.96%	0.073*	0.036*

\*: nominal ratios



**Figure C2:** TEM images recorded in bright field mode. A+B: Sodium and sulfur promoted FTO catalyst supported on  $\alpha$ -alumina, C+D: Colloidal iron nano crystals without promoters, E+F: Colloidal iron nano crystals supported on CNT before the addition of promoters.

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Figure C3: Histogram of iron oxide particle size of sodium and sulfur promoted FTO catalyst supported on  $\alpha$ -alumina.



Figure C4: Histogram of iron oxide particle size of FTO catalyst supported on CNT before the addition of promoters.



Figure C5: Nitrogen physisorption isotherms of α-alumina and carbon nano tubes.

Table S2: Surface area and pore volume of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and CNT determined with N<sub>2</sub>-physisorption and water titration.

	Surface area (m <sup>2</sup> /g)	Pore volume (mL/g)
$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	6.7 (at p/p0 = 0.250)	0.4*
CNT	230 (at p/p <sub>0</sub> = 0.249)	1.55 (at p/p <sub>0</sub> = 0.994)
* 1		

\* determined by water titration



**Figure C6:** Selectivity to  $C_2$ - $C_4$  paraffins as function of time on stream for the alumina supported iron catalyst mixed with the zeolite in different proximities. Reaction conditions: 400°C, 1 bar, CO:H2 = 1 (v/v), GHSV: 14,400 h<sup>-1</sup>.



Figure C7: Iron time yield of the composite mixture of iron catalyst supported on CNT with the zeolite (CFeZ) as function of time on stream.

## Appendix D

#### **Supporting information Chapter 5**



**Figure D1:** Ammonia TPD measurement during heating step under helium. Temperature desorption of  $NH_3$  during heating from 25°C to 600°C of catalyst Fe/Z-P-W. This measurement was used to indicate that during drying at relatively low temperatures the ammonia, which was added to H-ZSM-5 during the washing step to remove the promoters from catalyst Fe/Z (and by consequence also Fe/Z-P), could be removed. The TCD signal shows that at 300°C ammonia is being desorbed from the zeolite surface after washing the Fe/Z-P catalyst with ammonium nitrate. This indicates that  $NH_3$  was desorbed at 350°C and therefore that proton form of ZSM-5 was recovered during heating at 350°C in particular the reduction prior to catalysis.



**Figure D2:** Argon physisorption (at  $-196^{\circ}$ C) measurements of H-ZSM-5. In (A) the adsorption and desorption isotherms are given. Pore size distribution from adsorption data analyzed by BJH model (B).



**Figure D3:** TEM images of the washed catalysts. Colloidal iron oxide nanoparticles attached to an H-ZSM-5 zeolite with organic ligands after washing step, Fe/Z-W (A). Inorganic ligand exchanged attached particles FeP/Z-W (B) and inorganic ligand exchanged after attaching Fe/Z-P-W (C). None of the above catalysts showed any change in particle size or distribution after this washing step.



**Figure D4:** Example of ammonium TPD measurements for H-ZSM-5 and the catalysts. (A) Ammonium TPD of H-ZSM-5 and (B) of Fe/Z-P-W representative for all results with iron nanoparticles (regardless of promoters). The NH<sub>3</sub>-TPD spectra were deconvoluted (using Fityk) to fit three peaks, corresponding to the weak Lewis acid sites (LAS) (around 150°C), Lewis acid sites in proximity of Brønsted acid sites (around 200°C) and solely strong Brønsted acid sites (BAS) (around 350°C) at respectively <sup>1</sup>. The black line shows the original spectrum, while the blue, pink, and red lines give the gaussian fits. The light blue line shows the cumulative fits. When iron particles are attached to the zeolite external surface, the plot changed dramatically.



**Figure D5:** Total acidity calculated from ammonium TPD measurements presented in a bar graph. Yellow shows the acidity of the blank H-ZSM-5 zeolites, blue indicates the Fe/Z while the green indicates Fe/Z and orange indicates Fe/Z-P. Moreover, the striped parts of the bar graph show the calculated Brønsted acid sites from ammonium TPD peaks. The total acidity of all catalysts is the same within the estimated error margins. Assynthesized indicates the catalysts after addition of Fe-NP or FeP-NP to the surface of the H-ZSM-5 support. Washed indicates the catalysts washed with ammonium nitrate. From the graphs it is noticeable that for the washed samples both Fe/Z and FeP/Z obtain more BAS than initially present. This indicated that the Na was most probably washed from the iron acid sites, leading to the conclusion that the deconvolution of these samples (Figure D4), in combination with iron on the support is challenging and can only be used for rough indications of the Brønsted acidity <sup>2</sup>.



**Figure D6:** Pyridine IR graph of silica as a blank experiment. No absorbance was found of pyridine between the wavelengths of  $1400 \text{ cm}^{-1}$  to  $1550 \text{ cm}^{-1}$  as shown by the inset. This indicated that pyridine did not absorb to silica acid sites. Accordingly, silica could be used as a blank support material to measure if any pyridine would absorb to the iron nanoparticle surfaces, see Figure D7.



**Figure D7:** Pyridine IR graph of Fe-NP on silica. This measurement was used to observe if any of the pyridine, just like the ammonium observed in Figure D5, would absorb on the iron acid sites. The Fe-NP absorb pyridine at the LAS sites at 25°C (shown by the black peak at 1450 cm<sup>-1</sup> in the inset). However, this pyridine is desorbed before 150°C was reached indicating that the pyridine only weakly interacts with the iron. Therefore, when the temperature (150°C) used to calculate the concentration of BAS and LAS on the H-ZSM-5 is reached, all the pyridine has desorbed from the iron nanoparticle's surface. This shows that final values obtained from pyridine IR for the concentration of BAS and LAS do not include any pyridine that might absorb to the surface of the nanoparticles.



**Figure D8:** Pyridine Infrared spectrum of an H-ZSM-5 zeolite with Si/Al=15. BAS can be found at 1543 cm<sup>-1</sup> while the LAS are at 1455 cm<sup>-1</sup>. The peak at 1490 cm<sup>-1</sup> is from BAS in the vicinity of LAS <sup>3</sup>. Pyridine IR spectra were used to calculate the BAS and LAS using the formulas Equation D1 and Equation D2, where C stands for the concentration acid sites (mmol/g), IA stands for the integrated area of the pyridine IR spectrum (cm<sup>-1</sup>), R stands for the radius of the pallet (cm) and W stands for the weight of the pallet (mg). The 1.88 and 1.42 are calculated for the extinction coefficient from LAS and BAS at 150 °C which were used from Emeis, et al <sup>4</sup>.

$C(pyridine \text{ on } BAS) = 1.88 \ \mu mol/cm \ IA(B)R^2/W$	Equation D1
$C(pyridine \text{ on } LAS) = 1.42 \mu mol/cm  IA  (L)R^2/W$	Equation D2



**Figure D9:** Calculated Brønsted acid sites from pyridine IR spectra. The blue indicates the Fe/Z while the striped green indicates Fe/Z and striped orange indicates Fe/Z-P. As synthesized indicates the catalysts after addition of Fe-NP or FeP-NP to the surface of the H-ZSM-5 support. Washed indicates the catalysts washed with ammonium nitrate. As can be observed in this histogram, all catalysts retain the same BAS within the estimated error margins. Seemingly sodium did not deactivate the zeolite Brønsted acid sites. However, a noticeable difference can be found between the NH<sub>3</sub>-TPD and the pyridine IR. Ammonium TPD was found less specific, as the ammonium can bind on the acid sites of the iron oxide nanoparticles as well as on the zeolites' acid sites. The pyridine IR, however, has much more defined peaks (Figure D5) compared to the ammonium TPD.



**Figure D10:** Thermogravimetric analysis coupled with mass spectrometry (TGA-MS) of colloidal iron oxide nanoparticles on ZSM-5. **A**) TGA-MS of blank ZSM-5 zeolite and of **B**) ZSM-5 zeolite treated with all organic solvents from the attachment step (toluene, hexane, acetone and octadecene). **C**) TGA-MS of the Fe/Z and **D**) of FeP/Z catalysts. **E**) TGA-MS data of Fe/Z during the reduction for 2 hours at 350°C and **F**) data of Fe/Z after the reduction. The black line and right axes show the unsubstracted weight from the TGA measurement while the colored lines and the left axes show the ion current from the MS with weights of water (green), CO (light blue), CO<sub>2</sub> (dark blue) and the specific weight m/z = 55 of fraction C<sub>4</sub>H<sub>7</sub><sup>+</sup> (pink) coming from either organic ligands oleic acid (OLAC), oleylamine (OLAM) or the solvent octadecene (ODE) <sup>5</sup>. As the m/z = 55 signal was low, an inset was added to show the magnified area between temperatures 150°C – 450°C where the signal of ligands was typically found.



**Figure D11:** Methane selectivity as function of time on stream. To observe the effect of possible sodium and sulfur migration from the iron particles to the support, the methane selectivity over time was observed. This showed no change over the short reaction time, indicating no migration.

### Appendix D



**Figure D12:** Histograms and TEM micrographs of the used catalyst' particle size at 10 bar. Both Fe/Z (A) and Fe/Z-W (D) sustain the particle size similar to fresh catalysts and show carbon formation. The biggest difference could be found in the growth of FeP/Z (B) and FeP/Z-W (E) where both samples have obtained a broad particle size distribution with particles obtain large sizes up to 35 nm. Fe/Z-P (C) and Fe/Z-P-W (F) have grown into bimodal particle size distributions indicating an Ostwald ripening process.



**Figure D13:** Magnified TEM images of the FeP/Z-W catalyst, after catalysis at 1 bar. As can be observed, in image A) there are small particles present of which some are highlighted with arrows. These nanoparticles are < 5 nm and therefore show that the original size particles with a homogeneous size distribution have shrunken due to Ostwald ripening effects. In image B) the Fe-NP size distribution of the fresh catalyst can be found (light blue) next to the size distribution of the used catalyst (dark blue). The used catalyst has a clear broadening of particle size forming larger as well as smaller particles compared to the original size.

#### Table D1: Nomenclature of catalysts

Sample name	Attachment procedure	Washing	Promotion
Fe/Z	Attachment to H-ZSM-5	-	-
Fe/Z-W	Attachment to H-ZSM-5	Washed with ammonium nitrate solution	-
FeP/Z	Promoted before attachment	-	Inorganic ligand exchange with Na <sub>2</sub> S
FeP/Z-W	Promoted before attachment	Washed with ammonium nitrate solution	Inorganic ligand exchange with Na <sub>2</sub> S
Fe/Z-P	Promoted after attachment	-	Inorganic ligand exchange with Na <sub>2</sub> S
Fe/Z-P-W	Promoted after attachment	Washed with ammonium nitrate solution	Inorganic ligand exchange with Na <sub>2</sub> S

Sample	X(CO) %	FTY <sup>1</sup>	Selectivity							
	70		CH <sub>4</sub>	total	C <sub>2</sub> -C <sub>4</sub> <sup>2</sup>	C <sub>5</sub> <sup>+</sup> aliphatics	<i>i</i> -C <sub>4</sub>	Benzene	Toluene	C <sub>8</sub> aromatics <sup>3</sup>
				aromatics						
Fe/Z	1.2	0.07	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Fe/Z-W	1.2	0.06	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FeP/Z	0.2	0.02	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FeP/Z-W	3.1	0.24	40	7	52	1	2	1	2	3
Fe/Z-P	0.3	0.01	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Fe/Z-P-W	5.1	0.29	15	11	69	5	3	2	3	3

**Table D2:** Catalyst performance of H-ZSM-5 supported iron catalysts under FTO conditions at 340°C, 1 bar,  $H_2/CO = 1$  (v/v), GHSV = 4,200 h<sup>-1</sup>, TOS = 15 h

 $^1$  FTY in  $10^{\text{-5}} mol_{\text{CO}}\,\text{g}^{\text{-1}}{}_{\text{Fe}}\,\text{s}^{\text{-1}}$ 

<sup>2</sup> sum of olefins and paraffins

<sup>3</sup> sum of m-/o-/p-xylene and ethylbenzene

n.d.: not determinable, below detection limit

**Table D3:** Catalyst performance of H-ZSM-5 supported iron catalysts under FTO conditions at 340°C, 10 bar,  $H_2/CO = 2$  (v/v), GHSV = 6,900 h<sup>-1</sup> after TOS = 50 h.

Sample	X(CO)	FTY <sup>1</sup>	Selectivity					
	%		%c					
			CO <sub>2</sub>	CH <sub>4</sub>	$C_2-C_4^=$	$C_2 - C_4^0$	C₅ <sup>+</sup> -aliphatics	Aromatics
H-ZSM-5	0.5	0	0	0	0	0	0	0
H-ZSM-5-W	0.5	0	0	0	0	0	0	0
Fe/Z	9	0.8	40	59	15	14	7	5
Fe/Z-W	13	1.4	50	53	15	14	12	6
FeP/Z	1	0.2	40	49	38	13	0	0
FeP/Z-W	11	1.0	40	55	14	19	9	6
Fe/Z-P	4	0.3	40	43	23	19	11	4
Fe/Z-P-W	15	1.5	50	50	15	19	11	5

 $^1$  FTY in 10  $^4 mol_{CO}\,g^{\text{--}1}{}_{Fe}\,\text{s}^{\text{--}1}$ 

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Conversion of synthesis gas to aromatics at medium temperature with a Fischer Tropsch and ZSM-5 dual catalyst bed

# Appendix E

### **Supporting information Chapter 6**

Conversion of synthesis gas to aromatics-rich gasoline at medium temperature with a Fischer-Tropsch and ZSM-5 dual catalyst bed



**Figure E1:** Nitrogen physisorption isotherms at -195.8°C as function of relative nitrogen pressure of the calcined FeK. Solid line: Adsorption profile; dashed line: Desorption profile.



**Figure E2: A:** Activity as iron time yield (FTY) of FeK as function of dilution of the FeK bed with silicon carbide. Reaction conditions:  $300^{\circ}$ C, 20 bar, CO:H<sub>2</sub>=1 v/v, TOS=50 h. **B:** Illustration of inter-particle filling with products and resulting channeling (top) and sufficient dilution to avoid channeling (bottom).

Figure E2-A shows the effect of dilution of the FeK bed with inert silicon carbide on the CO conversion activity normalized to the mass of iron per time (iron time yield, FTY). Insufficient dilution can lead to a strong decrease in activity. We assigned this to condensation of heavy hydrocarbon products and/or carbon in the interparticle space, resulting in partial clogging of the catalyst bed. This might eventually lead to channeling, where only certain routes in the catalyst bed are available for the synthesis gas to flow through, not utilizing the whole catalyst (Figure E2-B). Conversion of synthesis gas to aromatics at medium temperature with a Fischer Tropsch and ZSM-5 dual catalyst bed



**Figure E3:** Illustration of reaction intermediates of the FTO reaction with  $C_2H_5$  intermediate adsorbed on the catalyst surface. a) chain propagation with  $CH_2$  species inserted in M-C bond of adsorbed  $C_3H_7$  intermediate, b)  $\alpha$ -hydrogenation forming ethane, c)  $\beta$ -hydride abstraction forming ethene.

The mechanism of the Fischer-Tropsch synthesis follows surface polymerization of adsorbed  $CH_2$  species, whereas adsorbed  $CH_3$  species act as chain starter <sup>1–3</sup>.

For adsorbed intermediate species (i.e.  $-CH_2-CH_3$  in Figure E3) three option are possible to proceed with the reaction. **a**) The intermediate can undergo further chain propagation by insertion of another  $CH_2$  species resulting in an adsorbed  $CH_2-CH_2-CH_3$ species. **b**) The  $CH_2$  group attached to the catalyst surface (in  $\alpha$ -position) can be hydrogenated and desorb from the surface, resulting in a paraffin molecule. **c**) The  $CH_3/CH_2$  group in second position to the catalyst surface ( $\beta$ -position) can lose hydrogen (so-called  $\beta$ -hydride abstraction) followed by desorption from the catalyst surface, forming an olefin molecule.

These processes have different kinetic rates and can be controlled with the process parameters, such as reaction temperature. The ratio of  $\frac{a}{a+b+c}$  describes the chain growth probability ( $\alpha$ -value of ASF).

With increasing temperature from 250°C to 300°C, we observed an increase in olefin/paraffin ratio, whereas the  $\alpha$ -value of the ASF distribution did not change. This indicates that  $\beta$ -hydride abstraction of the adsorbed intermediates is increased on the expense of  $\alpha$ -hydrogenation, whereas the chain propagation was not influenced.



**Figure E4:** Selectivity of methane, the C<sub>2</sub>-C<sub>4</sub> fraction and the C<sub>6</sub>-C<sub>10</sub> fraction as function of chain growth probability ( $\alpha$ ) according to the ASF distribution. The selectivity to the C<sub>6</sub>-C<sub>10</sub> fraction shows a maximum between  $\alpha$ =0.75-0.8.



**Figure E5:** Contribution of **A:** Ethylmethylbenzene to the C<sub>9</sub> fraction of aromatics and **B:** the contribution of ethylmethylbenzene and toluene to  $C_6$ - $C_{10}$  aromatics. Values are given in % (mol/mol). Reaction conditions: 300°C, 20 bar, CO:H<sub>2</sub>=1 v/v, GHSV of 40000 h<sup>-1</sup> CO conversion of 15-20%. The volume of the zeolite bed was varied to achieve zeolite based GHSV between 4500 h<sup>-1</sup> and 40000 h<sup>-1</sup>.

Conversion of synthesis gas to aromatics at medium temperature with a Fischer Tropsch and ZSM-5 dual catalyst bed



**Figure E6:** Selectivity of C<sub>2</sub>-C<sub>3</sub> olefins, C<sub>4</sub>-C<sub>8</sub> olefins and C<sub>6</sub>-C<sub>10</sub> aromatics as function of zeolite bed height for stacked bed experiments with FeK and H-ZSM-5 zeolite at **A:** 250°C and **B:** 275°C. Reaction conditions: 250°C and 275°C, 20 bar, CO:H<sub>2</sub>=1 v/v, GHSV of 10000 h<sup>-1</sup> and 20000 h<sup>-1</sup>, respectively. The CO conversion was between 15-20%. The volume of the zeolite bed was varied to achieve zeolite based GHSV between 6000 h<sup>-1</sup> and 18000 h<sup>-1</sup>.

FeK without zeolite showed selectivity to  $C_2$ - $C_3$  olefins of 19%<sub>C</sub> and to  $C_4$ - $C_8$  olefins of 17%<sub>C</sub> with no aromatics formed. By placing H-ZSM-5 zeolite downstream of FeK,  $C_6$ - $C_{10}$  aromatics were formed with 3%<sub>C</sub> selectivity, whereas the selectivity to  $C_2$ - $C_3$  olefins and  $C_4$ - $C_8$  remained relatively constant with 18-20%<sub>C</sub> and 16-17%<sub>C</sub>, respectively.

Operating at 275°C showed similar results compared to the experiments at 250°C. FeK without zeolite showed  $21\%_{C}$  C<sub>2</sub>-C<sub>3</sub> olefins and  $18\%_{C}$  C<sub>4</sub>-C<sub>8</sub> olefins, with no aromatics formed. Loading zeolite downstream of FeK led to the formation of  $2.5\%_{C}$  C<sub>6</sub>-C<sub>10</sub> aromatics, whereas C<sub>2</sub>-C<sub>3</sub> olefins with selectivity of 23-24%<sub>C</sub> and C<sub>4</sub>-C<sub>8</sub> olefins with selectivity of 17-20%<sub>C</sub> remained constant.

This shows that temperatures of 250°C and 275°C are too low to convert olefins into aromatics within the range of zeolite bed height tested in this study.

Appendix D



**Figure E7:** Bright field transmission electron microscopy (BF-TEM) images of **A:** spent FeK at 250 °C, **B:** spent FeK at 275 °C and scanning electron microscopy (SEM) images of **C:** spent FeK at 250 °C, **D:** spent FeK at 275 °C. Reaction conditions: 250 °C at GHSV=10,000 h<sup>-1</sup>, 20 bar, CO:H<sub>2</sub>=1 v/v, TOS=50 h, 275 °C at GHSV=20,000 h<sup>-1</sup>, 20 bar, CO:H<sub>2</sub>=1 v/v, TOS=50 h.

Conversion of synthesis gas to aromatics at medium temperature with a Fischer Tropsch and ZSM-5 dual catalyst bed



**Figure E8:** Derivative weight change of TGA analysis in mg weight loss per Kelvin of the spent iron catalyst after 50 h on stream at 250-300°C. Reaction conditions: 250-300°C, 20 bar,  $CO:H_2=1 \text{ v/v}$ . The stacked bed experiments of FeK and zeolite were tested at 250°C with FeK based GHSV of 10,000 h<sup>-1</sup>, at 275°C with GHSV of 20,000 h<sup>-1</sup> and at 300°C with GHSV of 40,000 h<sup>-1</sup> to reach same conversion levels in the initial phase of the reaction of 15-20%. TGA measurement conditions: heating rate: 15°C/min to 700°C in 60 mL/min synthetic air flow.



**Figure E9:** Derivative weight change of TGA analysis in mg weight loss per Kelvin of the spent zeolite with zeolite bed height of 4 mm and 13 mm after 50 h on stream at 250-300°C. Reaction conditions: 250-300°C, 20 bar, CO:H<sub>2</sub>=1 v/v. The stacked bed experiments of FeK and zeolite were tested at 250°C with FeK based GHSV of 10000 h<sup>-1</sup>, at 275°C with GHSV of 20000 h<sup>-1</sup> and at 300°C with GHSV of 40000 h<sup>-1</sup> to reach same conversion levels in the initial phase of the reaction of 15-20%. TGA measurement conditions: heating rate: 15°C/min to 700°C in 60 mL/min synthetic air flow.


Conversion of synthesis gas to aromatics at medium temperature with a Fischer Tropsch and ZSM-5 dual catalyst bed

**Figure E10:** Derivative weight change of TGA analysis in mg weight loss per Kelvin of **A**: the spent iron catalyst with GHSV of 14,000 h<sup>-1</sup> and 20,000 h<sup>-1</sup> and **B**: the spent zeolite with zeolite bed height of 9 mm after 20 h on stream at 300°C. Reaction conditions: 300°C, 20 bar, CO:H<sub>2</sub>=1 v/v, GHSV of 40000 h<sup>-1</sup>. TGA measurement conditions: heating rate:  $15^{\circ}$ C/min to 700°C in 60 mL/min synthetic air flow.

The areas indicated in blue in Figure E9 and Figure E10 indicate the temperature range, where we expect hydrocarbon products to be decomposed, whereas the green areas show the temperature range for decomposition of coke species.

The rate of carbon deposition on the individual catalysts upon reaction was determined by burning off the carbon of the spent catalysts in TGA and is shown in Table S1 as mg carbon deposit per gram of individual catalyst averaged over the total runtime of the experiment.

The iron catalyst showed a carbon deposition of 2.9-3.1 mg<sub>C</sub>  $g_{cat}^{-1}$  h<sup>-1</sup> at 250°C reaction temperature. Increasing the reaction temperature to 275°c and 300°C resulted in an increase in carbon deposition of 3.3-3.5 mg<sub>C</sub>  $g_{cat}^{-1}$  h<sup>-1</sup> and 8.4-8.5 mg<sub>C</sub>  $g_{cat}^{-1}$  h<sup>-1</sup>, respectively, when the reaction was operated with 15-20% CO conversion.

The zeolite catalyst showed a carbon deposit of 6.7 mg<sub>C</sub>  $g_{cat}^{-1}$  h<sup>-1</sup> at 250°C with a zeolite bed of 4 mm. With increasing zeolite bed height to 13 mm, the carbon deposit decreased to 4.3 mg<sub>C</sub>  $g_{cat}^{-1}$  h<sup>-1</sup>. The decomposition temperature of the carbon deposit indicated that hydrocarbon products rather than coke is responsible for the high deposit rate (Figure E8, Figure E9, and Figure E10). The carbon deposit rate in the 13 mm zeolite bed is decreased due to the same amount of products condensed over more mass of zeolite.

The carbon deposit on the zeolite decreased to 1.2-1.6 mg<sub>C</sub>  $g_{cat}$ <sup>-1</sup> h<sup>-1</sup> when operated at 275°C. Furthermore, the weight loss in the TGA measurement was shifted to higher temperatures, indicating the formation of coke rather than hydrocarbon products.

In contrast to the experiments performed at 250°C, the carbon deposit on the zeolite increased with increasing zeolite bed height at 300°C, which is caused by coke formation as result of enhanced formation of aromatics at 300°C with increasing zeolite bed height.

A decrease in FeK based GHSV and resulting increase of CO conversion to 50-60% enhanced the carbon deposition on the iron catalyst to 10.8-11.2 mg<sub>C</sub>  $g_{cat}$ <sup>-1</sup> h<sup>-1</sup> at 300°C reaction temperature. Also, we observed higher carbon deposition rates on the zeolites of 4.4-4.8 mg<sub>C</sub>  $g_{cat}$ <sup>-1</sup> h<sup>-1</sup> caused by higher concentration of olefin intermediates entering the zeolite bed.

### Conversion of synthesis gas to aromatics at medium temperature with a Fischer Tropsch and ZSM-5 dual catalyst bed

**Table E1:** Rate of carbon deposition and total carbon loading of spent catalysts determined with TGA and calculated as mg carbon species per gram of catalyst and hour of runtime. TGA measurement conditions: heating rate: 15 K/min to 700°C in 60 mL/min synthetic air flow.

FeK based GHSV	Zeolite bed height	Reaction temperature	carbon deposit		carbon loading	
(h-1)	(mm)	(°C)	(mg <sub>C</sub> g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> )		(wt-%)	
		_	FeK	Zeolite	FeK	Zeolite
10,000	4	250ª	3.1	6.7	6.6	33.7
10,000	13	250ª	2.9	4.3	6.4	21.6
20,000	4	275ª	3.5	1.2	16.5	6.2
20,000	13	275ª	3.3	1.6	14.5	7.9
40,000	4	300ª	8.4	1.5	40.9	7.3
40,000	13	300ª	8.5	2.2	40.4	11.2
20,000	9	300 <sup>b</sup>	11.2	4.8	20	9.6
14,000	9	300 <sup>b</sup>	10.8	4.4	17.1	8.7

a: after TOS of 50 h.

b: after TOS of 20 h.

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# List of Publications and Presentations

## **Publications in this Thesis**

- Chapter 2 Weber, J.L., Hernández Mejía, C., de Jong, K.P., de Jongh, P.E. Recent advances in bifunctional synthesis gas conversion to chemicals and fuels with a comparison to monofunctional processes. *Catal. Sci. Technol.* **14**, 4799-4842 (2024)
- Chapter 3 Weber, J. L., Dugulan, I., de Jongh, P. E. & de Jong, K. P. Bifunctional Catalysis for the Conversion of Synthesis Gas to Olefins and Aromatics. *ChemCatChem* **10**, 1107–1112 (2018)
- Chapter 4 Weber, J. L., Krans, N.A., Hofmann, J.P., Hensen, E.J.M., Zecevic, J., de Jongh, P.E., de Jong, K.P. Effect of Proximity and Support Material on Deactivation of bifunctional Catalysts for the Conversion of Synthesis Gas to Olefins and Aromatics. *Catal. Today* 342, 161–166 (2020)
- Chapter 5 Krans, N. A., Weber, J. L., Van Den Bosch, W., Zečević, J., De Jongh, P. E., & De Jong, K. P. Influence of Promotion on the Growth of Anchored Colloidal Iron Oxide Nanoparticles during Synthesis Gas Conversion. ACS Catal. 10, 1913–1922 (2020)
- Chapter 6 Weber, J. L., Martínez del Monte, D., Beerthuis, R., Dufour, J., Martos, C., de Jong, K. P., & de Jongh, P. E. Conversion of Synthesis Gas to Aromatics at Medium Temperature with a Fischer Tropsch and ZSM-5 Dual Catalyst Bed *Catalysis Today* 369, 175–83 (2021)

## **Other Publications**

- Hernández Mejía, C., den Otter, J. H., Weber, J. L., de Jong, K. P. Crystalline Niobia with tailored porosity as support for cobalt catalysts for the Fischer–Tropsch synthesis. *Applied Catalysis A: General* **548**, 143–149 (2017)
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- Cui, M., Kulkarni, S.R., Abu-Naaj, Y. Y., Wagner, S., Berger-Karin, C., Weber, J. L., Nagy, A., Pedro Castaño, P. Coupling catalytic bed fluidization with impeller rotation for improved hydrodynamic characterization of Berty reactors. *React. Chem. Eng.* (2024) DOI: 10.1039/D4RE00074A

### **Oral Presentations**

"Bifunctional Catalysis for Synthesis Gas Conversion to Olefins and Aromatics." EuropaCat Florence, Italy August 27<sup>th</sup>-31<sup>st</sup> 2017

"Conversion of Synthesis Gas to Olefins and Aromatics" CHAINS Veldhoven, The Netherlands December 5<sup>th</sup>-7<sup>th</sup> 2017

"Catalyst deactivation and Promoter Migration during the Conversion of Syngas to Chemicals using bifunctional Catalysis." Syngas Convention 3 Cape Town, South Africa March 25<sup>th</sup>-28<sup>th</sup> 2018

"Effect of Proximity and Support Material on Deactivation of bifunctional Catalysts for the Conversion of Synthesis Gas to Olefins and Aromatics." Multi Scale Catalytic Energy Conversion (MCEC) Mini Conference Utrecht, The Netherlands September 10<sup>th</sup> 2018

"Conversion of Synthesis Gas to Olefins and Aromatics using Bifunctional Catalysis at Industrially Relevant Conditions." 20<sup>th</sup> The Netherlands' Catalysis and Chemistry Conference (NCCC) Noordwijkerhout, The Netherlands March 04<sup>th</sup>-06<sup>th</sup> 2019

### **Poster Presentations**

"Direct Conversion of Synthesis Gas to Aromatic Hydrocarbons" 17<sup>th</sup> The Netherlands' Catalysis and Chemistry Conference (NCCC) Noordwijkerhout, The Netherlands March 7<sup>th</sup>-9<sup>th</sup> 2016

"Bifunctional Catalysis for the Conversion of Synthesis Gas to Olefins and Aromatics" 18<sup>th</sup> The Netherlands' Catalysis and Chemistry Conference (NCCC) Noordwijkerhout, The Netherlands March 6<sup>th</sup>-8<sup>th</sup> 2017

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During our time at the UU, we created the FT corner consisting of **Tom**, **Carlos**, myself and **Martin**, and **JX** in the Post-Doc office. A special thanks to **Lisette** for finally giving up your desk and letting me join the FT corner.

**Carlos** (aka Karl Hans Meyer), you are a great scientist and an even greater friend. I like thinking back to our holidays in Florence, Italy after the EuropaCat conference. "What a profitable day". We were roommates on various conferences and always spent time together, mainly during *smokey-smoke*, discussing our secret projects. If we were not outside, we were either fixing the FT1/2 or putting the sponge in the oven for yet another secret project. BTW, is it still in there? Also, thank you for introducing me to the magical world of color combinations.

**Tom** (aka the fine gentleman), I am really happy that you were my buddy during my initial period in the group and introduced me to everything. Thank you for hosting the first FT-BBQ at your place (with the two balconies). We should keep this up.

Many thanks are due to *mi amigo* **Miguel**. We were living together for almost four years in what can be considered the diamond of Utrecht (but only if you take into account blood diamonds). I remember great evenings with heavy metal slug or dragon ball on PS4 or cheering for Kruseman on Ink Master Season 6. Also, you made the best *Tortilla de Patatas* I have ever tried.

During my PhD I had the honor to supervise several theses, study project, or internship. I want to thank **Dylan**, **Max**, **Wolfer**, and **Dmitry** for helping me learn to become a good supervisor. I especially want to acknowledge **Dani** for doing part of his PhD in Utrecht. We were working on a joint project, which resulted in *Chapter 6* of this thesis. I wish you all the best and much success with your band.

In a group focusing on catalysts and catalysts synthesis, catalyst characterization and catalytic testing is essential and plays an important role in everyone's research. I was allowed to contribute by performing physisorption measurements together with **Peter B.**, **Remco, Nazila, Nikos, Silvia,** and **Pasi**. The groups of ICC and MCC of the Utecht University own incredibly special pieces of equipment, which is not a given for universities. On the one hand, I had access to electron microscopy (TEM/SEM) with special detectors. These were operated by **Savannah**, **Jessi, Jovana, Hans, Wouter, Nynke, Mark,** and **Lars**. On the other hand, I could evaluate the catalytic performance of my catalysts on two special units (Flowrence I and II) and I want to acknowledge **Tom, Arjan, Carlos, JX, Nynke, Jogchum, Kang, Justine, Rolf,** and **Remco** for always helping out, performing maintenance and planning the experiments.

The second lunch round initially started with 2-3 people at M4 and grew over time to more than 10 participants. I want to thank the following people for discussing wild theories, plans to save the world and alternative career options: **Katharina**, **Stano**, **Silvia**, **Egor, Bea**, **Miguel**, **Carlos**, **Rolf**, **Ana**, **Baira**, **Oscar**, **Donglong**, **Kang**, **Justine**, **Ioannis**, **Nikos**, and everyone else that participated. Özgün, thank you for the many MTG rounds (that I mostly lost against your strong green deck).

Das Wichtigste kommt zum Schluss. Vielen Dank an meine Familie, **Vaddern**, **Mutti**, **Eike** und **Amelie**. Und am meisten an meine Frau **Tomke** und an unsere wunderbaren Töchter **Janneke** und **Nienke**. Ohne eure ständige Unterstützung hatte ich diese Arbeit nicht zu Ende bringen können. Ihr habt mich wieder auf die Beine gebracht und mir Motivation gegeben, wenn mir alles über den Kopf gewachsen ist.

# **Curriculum Vitae**

Jan Lennart Weber was born on March 8th, 1985, in Oldenburg, Germany. After completion of high school, he started an apprenticeship to become a chemical laboratory technician at LUFA Nord-West in Oldenburg in 2004 and passed with distinction in 2007. Afterwards he started the Bachelor course of studies in chemistry at the University of Oldenburg, Germany. The Bachelor thesis with the title "Examination of the transesterification of performance pilot-scale-synthesized



hydrotalcites" was prepared in the group of Technische Chemie II under Prof. Frank Rößner and in collaboration with Südchemie (today Clariant) in Heufeld. During the Master studies at the University of Oldenburg, he performed a research project with Symrise on alkylation reactions using zeolites and other solid acids. He finished the master's degree in 2014 with the thesis titled "In-situ preparation and Fischer Tropsch testing of cobalt nano particles", which was conducted at the University of Cape Town, South Africa in the group of Prof. Michael Claeys.

In 2015, Lennart started a PhD research project supervised by Prof. Krijn de Jong and Prof. Petra de Jongh at Utrecht University, The Netherlands, in the group of Inorganic Chemistry and Catalysis. This project was part of the Netherlands Center for Multiscale Catalytic Energy Conversion (MCEC). The research focused on the combination of different catalysts to convert synthesis gas to chemicals and fuels in a single step and understanding the interaction between the different catalysts. The results of this research are described in this thesis.

Lennart joined Integrated Lab Solutions GmbH in Berlin, Germany in 2019 as project leader. Here, he was responsible for the design of catalytic test units and the management of all (internal and external) parties, from technical design to commissioning. Additionally, from 2021 he was leader of the analytics competence center. In 2023 he started at Tree Energy Solutions GmbH in Wilhelmshaven, Germany, as Senior Process Engineer and became Process Engineering Lead in 2024 for the e-NG (electric natural gas) terminal project in Wilhelmshaven.