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Catalysis for Sustainable Aviation Fuels: Focus on Fischer-Tropsch Catalysis

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6.1 Introduction

6.1.1 Sustainable Aviation Fuels (SAF) via Fischer-Tropsch-based Routes

Not only does air transport allow billions of passengers to access some of the most distant locations in the globe, it also accounts for 35% of world trade by value and provides jobs for 60–90 million people [1–3]. In 2019, the aviation industry consumed around 360 billion liters of jet fuel and produced 915 million tons of CO_2 [4]. This represents 12% of the transport sector CO_2 emissions and 2% of all anthropogenic emissions [2]. The industry is forecasted to grow at an average rate of 4.3% a year for the next 20 years resulting in projected CO_2 emissions of 3.1 billion tons by 2050 [5]. Tangible steps have already been taken to improve on energy efficiency and reduce CO_2 emissions through technological advances such as wing tip device retrofits, resulting in avoidance of 80 million tons of CO_2 since the year 2000 [2]. Incremental improvements such as these are significant but can be expected to plateau in such a mature industry.

For most ground-based transport, hydrogen and electricity are anticipated to largely replace existing liquid fuels like gasoline and diesel. However, the substitution of jet fuel is less trivial. Around 80% of aviation's CO_2 emissions are from flights over 1,500 km for which substitution with less energy dense fuels is difficult. Figure 6.1 shows that although liquid hydrogen has the highest gravimetric energy density, potentially allowing for greater passenger and cargo loads, the low volumetric energy density would severely limit flight range [6]. Current lithium-ion batteries have specific energy and energy densities of under 0.94 MJ/kg and 2.63 MJ/L respectively, well below that of jet fuel (43.2 MJ/kg and 34.7 MJ/L) [7]. Battery recharge rates are also comparatively slower than refueling an aircraft. Future technology developments may unlock more viable alternatives, although these would require some time to implement globally to ensure that aircraft can safely fill up with compatible fuels.

Aviation fuel is produced primarily from the distillation and refining of the crude-oil derived kerosene cut [8]. This material has a typical boiling range between 150 and 270 °C and consists of predominantly C_8 to C_{16} alkanes (linear, branched, and cyclic) and aromatics. Achieving the right
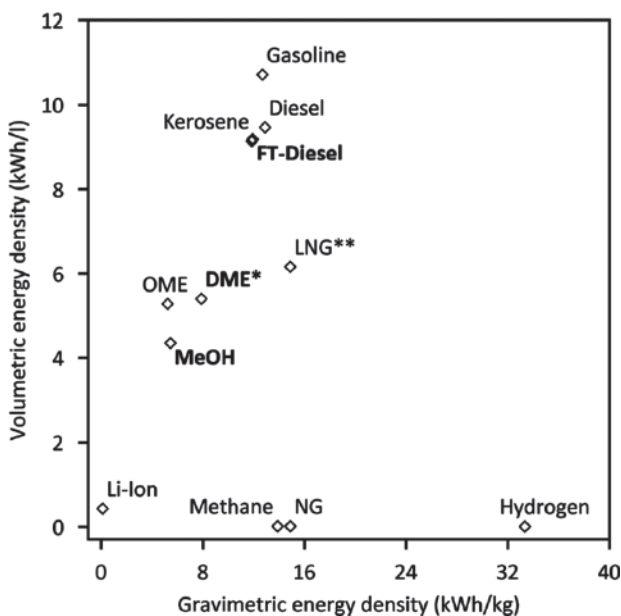
Figure 6.1 Mass and volumetric energy density for different liquid and gaseous fuels, with Li-ion batteries for comparison (*at 10 bar; **at −160 °C). Reproduced with permission from Ref [6] / Royal Society of Chemistry.

mix of these components is key. For example, aromatics provide seal swell characteristics but tend to increase particulate matter emissions. Branched alkanes have good cold flow characteristics and high specific energy, but do not provide the same seal swell characteristics as aromatics [9].

SAF look and perform similarly to existing jet fuels and therefore provide an opportunity to reduce CO_2 emissions with minimal to no aircraft adaptation. SAF is described as a fuel that emits fewer greenhouse gases (GHGs) on a life-cycle basis than conventional aviation fuel. Feedstocks used to produce SAF can be either from biogenic sources such as vegetable oil, crops, woody waste, municipal solid waste, inedible waste fats, oils, and greases, or non-biogenic sources such as renewable H_2 and CO_2.

Various pathways exist to produce SAF, many of which have been certified for use in commercial aviation. Sugar and starch crops can be upgraded through fermentation, followed by dehydration and oligomerization via the Alcohol to Jet (AtJ) conversion process. Microbial conversion of C_6-sugars affords farnesene which can be hydrotreated to yield the corresponding iso-paraffin in the Synthesized Iso-Paraffin (SIP) process. Fatty acid esters and free fatty acids may be treated using catalytic hydrothermolysis (CHJ) or directly hydroprocessed (HEFA) to afford jet fuel blend components.

Fischer-Tropsch synthesis (FTS) is a process whereby syngas, a mixture of CO and H_2, is converted over a suitable catalyst to hydrocarbons. Although commonly generated from natural gas reforming or coal gasification, syngas can also be obtained from renewable feedstocks such as biomass (Figure 6.2a). Alternatively, hydrogen can be generated from electrolysis of water using renewable electricity and combined with unavoidable CO_2 in a Reverse Water Gas Shift (RWGS) reaction to form syngas (Figure 6.2a). CO_2 and H_2 can also be converted in a single step in an iron-catalyzed high temperature Fischer-Tropsch (HTFT) process (Figure 6.2b).

Several companies are researching the FTS route to produce sustainable synthetic kerosene and have announced plans to deploy the technology commercially. Some of these include: BP and Johnson Matthey (JM) together with Fulcrum Bioenergy, INERATEC, Red Rock Biofuels under license from Emerging Fuels Technology, Sasol, Shell, Sunfire, and Velocys.
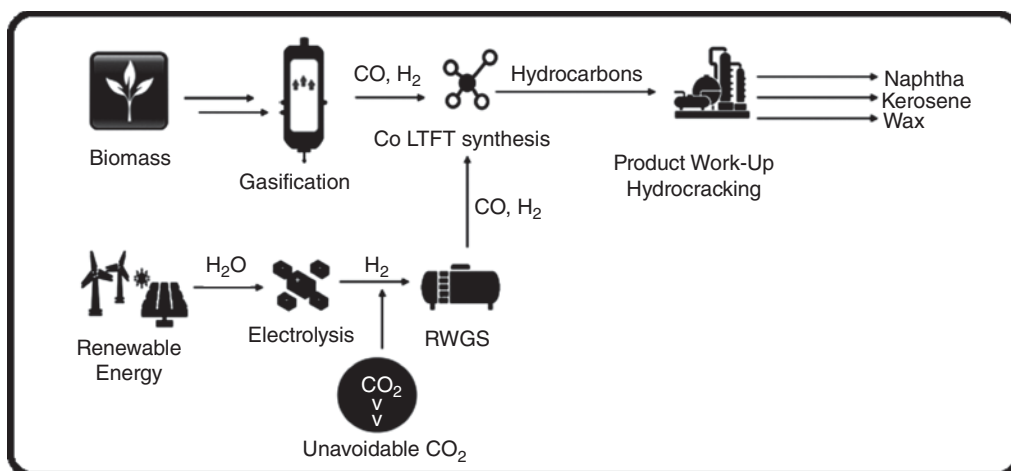
(a)
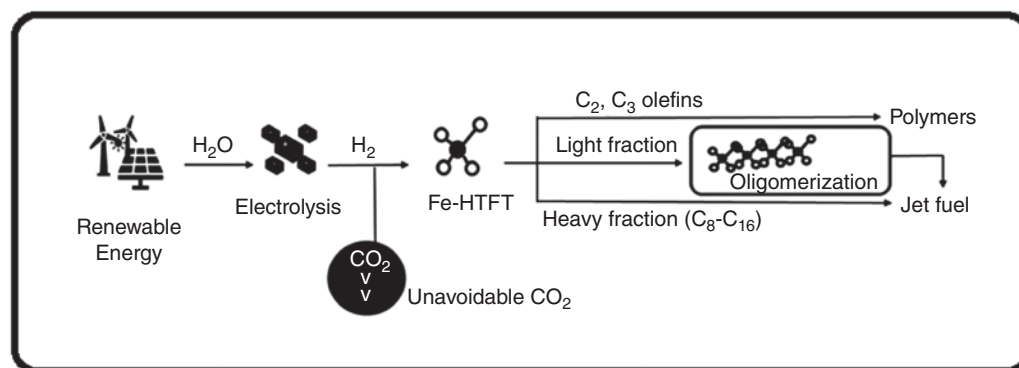
(b)

Figure 6.2 (a) Conversion of syngas from renewable feedstocks to products via FTS. (b) Single step CO_2 and H_2 conversion over an iron-catalyzed high temperature Fischer-Tropsch (HTFT) process.

6.1.2 Introduction to FT Chemistry

FTS comprises simultaneous CO hydrogenation and polymerization reactions. The overall process involves a network of elementary bond-breaking and bond-formation steps, including CO and H_2 dissociation as well as hydrogenation and chain growth (step-wise carbon coupling) on the metal surface. Various competitive insertion reactions can also occur on the surface of the catalyst and hence the product spectrum contains a wide distribution of hydrocarbon products, including paraffins, olefins, alcohols, carboxylic acids, aldehydes, and ketones.

As the reaction is a polymerization reaction, it follows a statistical function described by the Anderson–Schulz–Flory (ASF) relationship. This statistical distribution is characterized by the chain growth probability factor (α-value), defined as the rate of chain propagation relative to the sum of the rates of chain propagation and chain termination. In the ideal case where the α-value is independent of carbon number, it follows that:
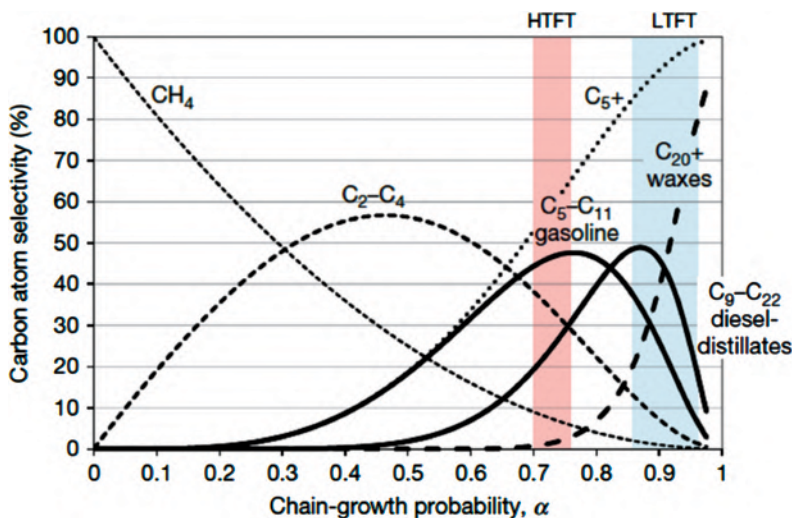
$$C_{n+1} / C_n = \alpha$$

Figure 6.3 Product selectivity in Fischer-Tropsch synthesis (FTS) as a function of the chain growth probability (α). The selectivity is expressed as the molar percentage of a range of products on a carbon basis.

where C_n and C_{n+1} are the mole fractions of species with n and n+1 carbon number, respectively, in the FT product spectrum. Based on the ASF distribution, more lighter (C_1–C_4) hydrocarbons are expected at a smaller α value, while higher selectivity of heavier (C_{21+}) hydrocarbons can be obtained at a larger α value (Figure 6.3). For a catalyst, the value of α is determined mainly by the temperature, pressure and syngas H_2/CO ratio. The carbon number distribution of the product can therefore be predicted with reasonable accuracy.

The choice of metal for the FT catalyst determines the balance of the bond-breaking and bond-formation processes on the metal surface. Transition metals to the left in the periodic table (e.g. Mo) will easily dissociate CO, but the products (i.e. surface C and O_2) are too strongly bound to the surface, thus blocking subsequent hydrogenation and carbon coupling reactions. On the other hand, transition metals to the right (e.g. Cu and Rh) are not active enough to dissociate CO. The optimal metals are those which can promote CO dissociation along with a balanced degree of surface carbon hydrogenation and carbon coupling in order to produce longer chain hydrocarbon products. It is known that the Group VIII transition metals are active for FTS. However, the only FTS-active metals which have enough CO hydrogenation activity for commercial application are Ni, Co, Fe, or Ru [10]. The choice of active metal has important implications for the selectivity of the catalyst toward desired products as well as cost of the final catalyst.

Iron catalysts are known to make large amounts of carbon dioxide via the water-gas shift (WGS) reaction (CO + H_2O → CO_2 + H_2) [11], which can be an environmental concern. On the other hand, the WGS activity of a Fe-based catalyst gives it flexibility for use with coal or biomass derived synthesis gas that has an inherently lower H_2/CO ratio, especially when operated at moderate to high temperatures (270 to 350 °C) where the WGS reaction is in equilibrium. Iron catalysts tend to produce predominantly linear alpha olefins as well as a mixture of oxygenates such as alcohols, aldehydes, ketones, acids, and esters. Of the other metals active for CO hydrogenation, nickel is too hydrogenating and consequently produce excessive amounts of methane. It also tends to form carbonyls and sub-carbonyls at FTS conditions which facilitates sintering via Oswald Ripening [12] and contamination of downstream systems. Ruthenium is the most active FTS catalyst, producing long chain products at around 140 °C [13, 14]. However, it is prohibitively expensive

and the supply of Ru is limiting for large scale application. Bimetallic catalysts such as Ni–Co [15] and Co–Fe [16] can be advantageous from a cost and synergistic property perspective, but these systems are still academic in nature. Combining cobalt with Cu [17] and Rh [18] to form alloys, could allow tuning the selectivity of these catalysts more toward oxygenated components.
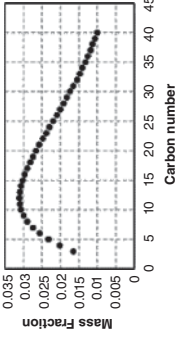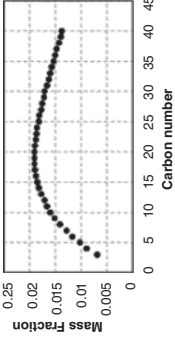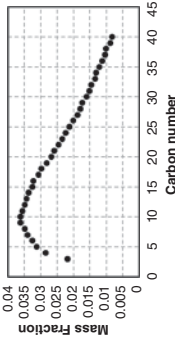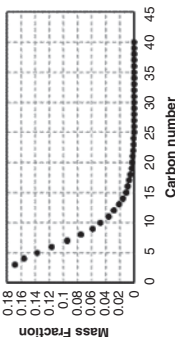
The only two catalysts that are used at commercial scale are Co- and Fe-based systems that can be employed in different modes with respect to reactor technology, catalyst morphology, and process conditions (Table 6.1 and Figure 6.2). Cobalt catalysts are a good choice for FTS from natural gas derived synthesis gas and have a good balance between cost and stability. The water-gas shift activity of cobalt-based catalysts is low and hence water is the main oxygen containing reaction product. Cobalt-based catalysts are employed at temperatures between 190 and 240 °C and are suitable for wax production in either fixed-bed, micro channel, or slurry bubble column reactors, while operating at high per pass syngas conversion (>60% CO conversion).

To maximize the use of cobalt metal, most FTS catalysts contain nanoparticles of cobalt anchored onto high surface area refractory supports. Although a number of cobalt phases (carbidic, oxidic, mixed cobalt-promoter, and support phases) can co-exist during realistic FT synthesis conditions, the major phase is metallic cobalt and is widely considered to be the active phase for FTS [10]. The size, uniformity of dispersion, phase, and stability of the metallic cobalt nanoparticles plays an important role in the performance of the catalyst with respect to activity, stability, and selectivity. Recent studies have indicated that CoO in conjunction with reducible oxides such as MnO_x and TiO_x, can act as active sites for CO_2 hydrogenation, a reaction that does not readily occur over metallic cobalt catalysts [19, 20]. Whereas cobalt carbide is mostly considered to be inactive for CO dissociation, its formation is typically associated with lower reaction rates and higher methane formation [21, 22]. Reports have indicated that depending on the morphology [23], and chemical environment of the carbide phases, they can act as catalysts for olefin or oxygenate formation [19].

Iron-based catalysts are employed in three modes, these being low temperature (c. 210–240 °C), medium temperature (c. 270–290 °C) [24], and high temperature (c. 330–350 °C) (see Table 6.1). Depending on the reaction temperature employed, various product distributions can be obtained. The CO_2 conversion efficiency and build-up of carbon on the catalyst will also be impacted by reaction temperature. The active phase of Fe-based catalysts for CO hydrogenation is considered to be Fe-carbide [25, 26] as this phase has optimal bond breaking and bond formation strength for FTS. Fe-based catalysts can directly convert CO_2 into products via RWGS, and literature consensus is that CO_2 conversion to CO occurs on Fe-oxide phases also present in the working catalyst [27]. The preparation of Fe-based catalysts can vary significantly depending on their application. For example, fusion of iron oxide together with relevant structural and chemical promoters, similar to ammonia synthesis catalyst manufacture, is used to produce a catalyst suitable for the large scale Secunda and Mosselbay HTFT plants, whereas precipitation methodology is used for the LTFT Sasolburg site and is also believed to be the preferred route for the preparation of Synfuels China's slurry phase MTFT iron catalyst [28].

The various reactor types applied in commercial scale conventional FT applications are shown in Figure 6.4. These consist of both stationary and moving bed reactors and a specific catalyst morphology needs to be targeted for each specific reactor. Currently the most widely used reactors are fixed beds, slurry beds and fixed-fluidized beds. These conventional FT reactors are designed to work on a large scale, and traditional FT plants are built to process substantial amounts of synthesis gas from a single large gas or coal reserve. These plants require large capital investment: for example Shell's Pearl plant, including both FTS production and the upstream natural gas condensates, was built at a cost of around $20 billion [29]. The viability of these large plants is also dependent on factors such as the natural gas price and economy of scale.

Table 6.1 Overview of Fischer–Tropsch (FT) catalyst and reactor XTL (X = coal and natural gas or combinations) technology currently in commercial operation, using low temperature FT (LTFT), medium temperature FT (MTFT), and high temperature FT (HTFT) modes of operation.

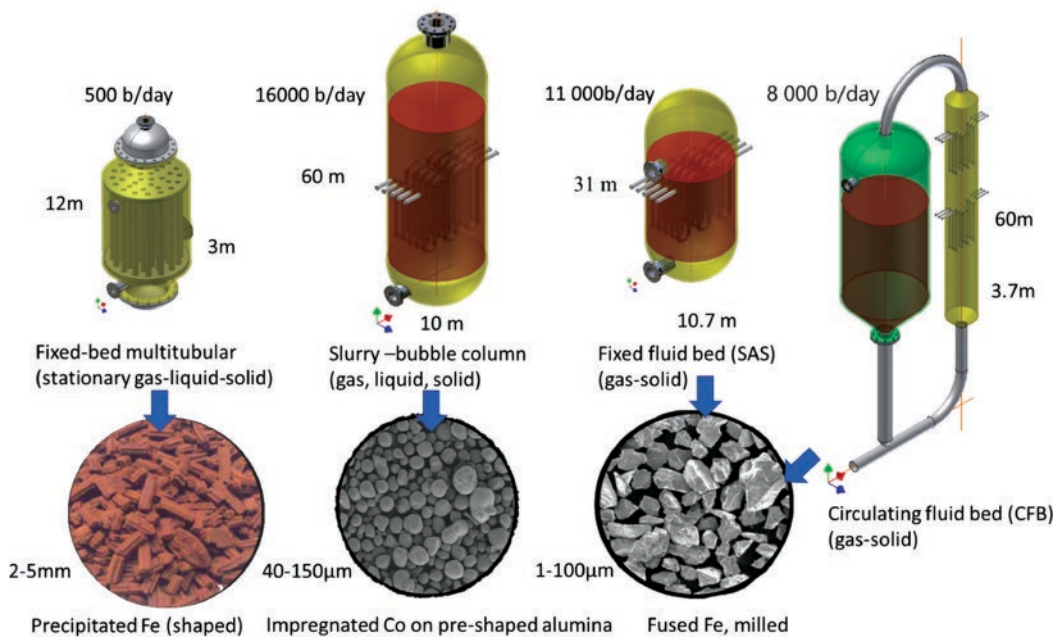| Parameter	Co-based	Fe-based		
Temperature classification	LTFT (190–240 °C)	LTFT (210–240 °C)	MTFT (270–290 °C)	HTFT (330–350 °C)
Catalyst preparation route	Supported and precipitated, spray-dried, or extruded	Precipitated, spray-dried or extruded	Precipitated and spray-dried	Fused and milled
Synthesis gas-feed	Natural gas	Natural gas	Coal	Coal & Natural gas
Example of commercial applications	ORYX-GTL, Qatar (34 000b/d) Shell Pearl GTL, Qatar (140 000 b/d)	Sasol Sasolburg operations, South Africa (7500b/d)	Synfuels China CTL (various locations in China) (>150000 b/d est.)	Sasol Secunda Operations South Africa (160 000b/d), PetroSA, South Africa (22 000b/d)
Reactor type	Slurry bed and fixed bed multi-tubular	Slurry bed and fixed bed multi-tubular	Slurry bed	Fixed-fluidized bed and circulating fluid bed (CFB)
Carbon number distribution				
Typical product profile and characteristics	Mainly straight chain paraffins with negligible amounts of oxygenated, branched, and aromatic components; most suitable for diesel fuel, wax, and synthetic lubricant production	Mainly normal paraffins (saturated, straight chain hydrocarbons) typically produces a heavy product slate (wax) with small amounts of olefins, alcohols, and acids; very high alpha (0.95); most suitable for hard wax production	Mostly n-paraffins with small amounts of branched paraffins, olefins, and oxygenates; wax production	Mainly olefin and aromatic hydrocarbons with very small amounts of heavier (wax) products and high C_1–C_3 gas yield and large amounts of oxygenated compounds; gasoline and chemicals applications

Figure 6.4 Schematic representation of Fischer-Tropsch (FT) reactors and images of catalysts employed for stationary and moving bed reactors.

6.1.3 FT Catalysts for SAF Production

Cobalt and iron based FTS catalysts are two contenders for the production of jet fuel products from renewable CO_2/syngas and H_2, each having their own strengths and weaknesses (Table 6.2). Because cobalt catalysts have negligible activity for CO_2 hydrogenation (particularly in the presence of CO), it is necessary to convert the CO_2 either via co-electrolysis or RWGS to CO and H_2 in an intermediate step. This green syngas is then readily converted to products over the cobalt catalyst. In contrast, iron catalysts possess RWGS activity and can convert CO_2 in situ to CO,

Table 6.2 Comparison of Co-low temperature Fischer-Tropsch Fischer (LTFT) and Fe-HTFT systems for Fischer-Tropsch synthesis (FTS) to produce sustainable aviation fuels (SAF).

Cobalt LTFT catalysts	Iron HTFT catalysts
High activity catalyst with established regeneration protocols enabling materials circularity. However, cobalt and noble metal promoters are relatively expensive, and catalysts are sensitive to poisons.	Inexpensive catalyst, robust to a variety of feed poisons, but used in large quantities and has a short life-time (limited by carbon formation)
Metallic cobalt cannot convert CO_2 and H_2 directly, need separate RWGS reactor or co-electrolysis unit to produce synthesis gas	Can do tandem catalysis, combining RWGS and FT in one catalyst system
Good water tolerance enabling higher per pass conversion, minimizing the need for large recycle streams	Greater sensitivity to water, per pass conversion is limited, requiring recycles. Especially problematic with CO_2 hydrogenation which produces an addition mole of water for every mole of C converted
Primary product is alkanes. Can maximize wax selectivity leading to higher overall kerosene yields post hydrocracking.	Complex product spectrum (olefins, oxygenates, aromatics). Needs oligomerization for high kerosene yield, but can provide benefit for chemicals production.

followed by FTS. While the RWGS activity is favorable, it produces additional water. This can be problematic for iron catalysts, which are oxidized to FT inactive oxide phases. On the other hand, cobalt catalysts are much more likely to be able to run at high conversions due to their stability against oxidation. Iron catalysts typically run at around 3 bar water partial pressure [30], whereas cobalt systems are reported to be capable of running at 8–10 bar water partial pressures [31]. The important parameter for stability appears to be the $p_{water}/p_{hydrogen}$ ratio. The stability of nano-sized Co- and Fe-carbides as a function of CO conversion and crystallite size is shown in Figure 6.5. The data indicates that even small cobalt crystallites (8–10 nm) are unlikely to be oxidized at high CO conversions (70–80%); conversely Fe carbide crystallites, even if they are fairly large (>20nm), can oxidize at over 60% conversion levels [32].

The product spectrum obtained from typical cobalt catalysts is primarily straight chain, paraffinic wax products with high alpha values. These waxes can then be hydrocracked directly to the desired kerosene range hydrocarbons, ensuring high jet fuel yields. Iron systems, particularly at higher temperatures, have a more complex product spectrum, including more isomerized hydrocarbons, olefins, aromatics, and oxygenates. Although these components are attractive from a chemical value perspective, they require complex downstream product work-ups and jet-fuel yields (per mass catalyst) are significantly lower. Strategies to improve kerosene production, such as oligomerization of $C_{3/4}$'s, add capital intensity to the process [33].

Iron-based catalysts have a much shorter lifetime than their cobalt counterparts, typically lasting weeks or months whereas cobalt catalysts can last years [34] and are relatively easily regenerated. As iron is a cheaper starting material, it is often discarded and not re-used, potentially causing environmental concerns. Iron-based catalysts do have a higher threshold for poison in the feed-gas and are able to tolerate oxygen and nitrogen containing poisons at higher levels, sometimes incorporating them into the product spectrum [35]. Poison tolerance or utilization of appropriate gas-clean-up technologies is especially important when using waste or biomass as a renewable feedstock as these sources possess oxygen, nitrogen, halides, and sulfur-containing contaminants, which poison FTS catalysts [36].

As indicated, cobalt catalysts are preferred for application in FT-based SAF processes. This is mainly due to the propensity of cobalt-based systems to produce straight chain hydrocarbons that can be used to derive synthetic kerosene at high yields. Many of the announced FT plants that will be used to generate SAF are envisaged to use cobalt catalysts [37]. This review will therefore focus
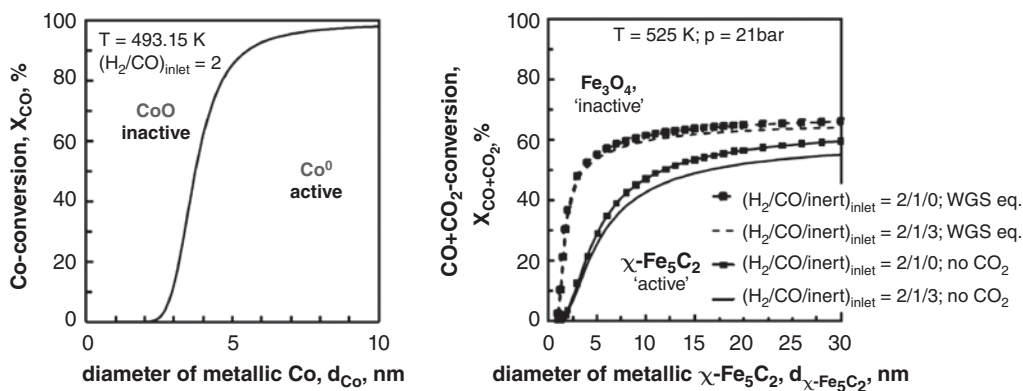

Figure 6.5 Oxidation propensity of cobalt (left) and iron (right) as a function of crystallite size and CO conversion in the reactor as determined by surface thermodynamic calculations. Reproduced with permission from Ref [32] / Elsevier.

more on cobalt-based catalysts for production of SAF. The key challenge for FTS in a PtL process is to ensure that syngas conversion is as high as possible to minimise recycles, while still achieving the required selectivity to produce high jet fuel yield.

Iron-based catalysts can be important for directly producing sustainable chemicals from CO_2 and H_2 and there are opportunities to make these systems more sustainable and water tolerant. These will be touched on briefly in this chapter.

6.1.4 Reactor Technology for SAF Production Using FTS

In contrast to the large-scale FT plants described in the previous section, the first commercial biomass-to-liquid (BtL)/PtL plants are expected to be much smaller, less complex, and decentralized. The small-scale FT concept is not new and was first discussed in a gas-to-liquids (GTL) context about a decade ago [38]. By taking advantage of new or adapted reactor technologies, GTL plants can be scaled down and operated on a distributed basis, providing a more cost effective a more cost effective to take advantage of smaller gas resources with smaller plants located near gas resources and potential markets. The lower capital cost also establishes a lower hurdle to market entry. Due to the high costs of green H_2 production and localized sources of renewable carbon sources, the initial PtL landscape is also expected to start at a significantly smaller scale (500–2500 b/d)

This will allow use of reactor technologies having a smaller footprint, but also needs to be highly efficient to process the relatively expensive renewable resource. Some examples of smaller scale reactors for FT for production of sustainable fuels are shown in Figure 6.6. BP and JM [39] have developed the novel CANs™ reactor design which combines the advantages of fixed bed reactors with a slurry phase system allowing the use of smaller catalyst particle sizes, with lower pressure drops. The new reactor system consists of modular catalyst containers, stacked within a fixed bed reactor, providing modified reactant flow paths down a porous central channel. This configuration delivers improved mass transfer and kinetics, aiding in reactor intensification. It is claimed that this configuration allows reduction of unit cost by half, while at the same time increasing product volumes by 50% and operating at >90% overall CO conversion with a C_{5+} selectivity around 90–92% [40].

The stainless-steel microstructure reactor concept used by INERATEC [41, 42] consists of a 2 cm^3 reactor volume and consists of eight parallel catalyst sections sandwiched between
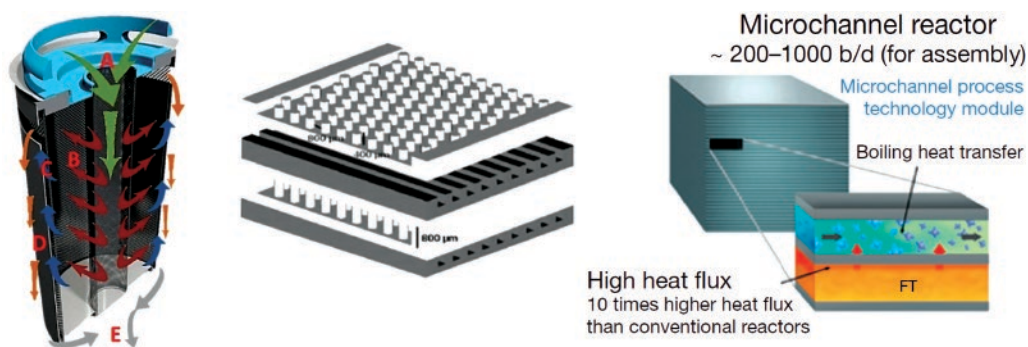

Figure 6.6 Examples for novel small-scale Fischer-Tropsch synthesis (FTS) reactors. Left: BP/JM/Davy CANS™. Reproduced with permission from Ref [39] / Johnson Matthey Plc; Middle: microstructure reactors as used by INERATEC. Reproduced with permission from Ref [42] / Elsevier. Right: Microchannel reactors as used by Compact GTL and Velocys. Reproduced with permission from Ref [51] / Elsevier.

cross-flow oil channels for heat exchange. Each catalyst section consists of two foils with an etched 400 μm deep pillar structure, hexagonally arranged with 800 μm distance between the pillars. The foils are stacked opposite to each other, giving 800 μm channel height. INERATEC reactors will be used in the first containerized SAF plant in Germany (8b/d) with a Sasol Co catalyst, affording high CO conversions and C_{5+} selectivity [43].

In the Velocys [44] microchannel set-up, each reactor block has thousands of process channels (~0.1–1.0 mm) filled with active cobalt FT catalyst interleaved with water filled coolant channels. The microscale dimensions of the channels increase the surface area per unit volume and thus increase the overall productivity of the process per unit volume. This allows significant process intensification, whereby the reactor volume to produce a given amount of product is reduced by an order of magnitude or more. The systems are capable of running for more than a year 70% CO conversion, with C_{5+} selectivity around 88–90% without requiring any regeneration [45]. Velocys plans to use this technology on two commercial SAF projects in the UK and United States, one using municipal solid waste as feed stock (c. 1550 b/d) and one utilizing woody biomass (2750 b/d) [46].

More conventional multi-tubular fixed bed reactors can also be used for SAF production and do possess a degree of modularity and scalability, as shown by Shell [47]. These are expected to be a preferred choice for small scale PtL/BtL plants. Sunfire is another company that intends to use tubular fixed bed reactors to produce aviation fuel [48] using renewable feed from water electrolysis, direct air capture (DAC), and waste CO_2, with the intention of deploying the technology to produce 420b/d of product by 2026 for the Norsk e-Fuel project [49].

Small scale slurry reactors may also be viable for SAF plants in the 2000–2500 b/d range. Sasol has operated small scale slurry reactors since the 1980s, using commercial slurry bubble columns in Sasolburg with capacities of 100 and 2500b/d. Dynamic modelling simulations [50] indicate that slurry reactors containing cobalt catalysts could also operate well at variable feed loads, which would be a requirement for PtL applications, with good temperature distribution in the reactor and no detrimental influence on FT product selectivity.

It is likely that new or adapted reactor technologies, could play a key role in the initial deployment of FT plants for small scale SAF production due to their efficiency, cost and lower footprints. However, smaller versions of conventional technologies such as small scale multi-tubular fixed bed and slurry, are also envisaged to play a role as well. As the SAF market ramps up and reaches maturity, much larger plant capacities will be required that could again favor the larger, more traditional reactor technologies.

6.2 State-of-the-art Cobalt Catalysts

In the century since Fischer and Tropsch published their first article [52] and patent [53] on CO hydrogenation [54], more than 13,500 patent families were filed on the subject. Although FT-patent filing numbers showed a slight decline since the oil price crash of 2014, there is renewed interest in the process as it is perceived to be viable for the production of SAF.

Developing a commercially viable FT catalyst must consider the targeted commercial process which includes reactor type, gas loop impacts, and the envisaged commercial production cost of the catalyst. The reactor type not only impacts the catalyst and support morphology (size and shape), but also which type of support and modifiers are required. For example, in a slurry bubble reactor the catalyst must survive a high attrition, abrasion, and hydrothermal environment for at least two to three years which can be stretched to 10^+ years with regeneration.

The synthesis gas and recycle loops determine the following:

- Poison levels: Poisons can be split into permanent poisons (e.g. sulfur, alkali/alkali earth metals, and halogens) and non-permanent poisons (e.g. nitrogen poisons) [55]. Promoters can be added to capture poisons (e.g. Mn/Mo for S) or limit the enhanced hydrothermal impact caused by NH_3 (from nitrogen poisons) and water. Cobalt phases (face-centered cubic/hexagonal closed packet; FCC/HCP) could also be impacted by poisons and thereby impact catalyst performance.
- CO_2 content: CO_2 slippage from synthesis gas production and WGS builds-up in the internal recycle, especially when maximizing overall conversion. Cobalt catalysts have inherently low WGS activity but addition of promoters (such as precious metal reduction promoters, Pt [56], etc.) can increase the WGS activity. Some cobalt FT-catalyst systems were reported to be CO_2 sensitive [57].
- Water partial pressure: Although water is the main product from FT-synthesis and hence dependent on per pass conversion, there is also water in the synthesis gas inlet, depending on the efficiency of water removal from upstream units such as RWGS and/or Autothermal Reformer units. Water impacts will be discussed later.
- H_2/CO ratios and gradients: Low H_2/CO ratios can enhance polymeric carbon formation and carbon deposition [58]. Reduction promoters usually minimize carbon formation. The literature also indicates that the partial pressure ratio of $(H_2+CO)/H_2O$ can impact sintering.

Due to these factors, it is essential to test and develop commercial FT-catalysts using representative synthesis gas and targeted conditions, which can increase the cost and timeline of FT-process development. Shell invested around $1 billion to develop their GTL process [59] with catalyst cost expected to contribute a significant portion. FT catalyst developments therefore focus on stability and selectivity to drive down the catalyst contribution to production costs. This is evident from published presentations showing how Shell [60] (Figure 6.7) and Sasol [61] have improved their commercial offerings to target C_{5+} selectivities in excess of 95% and alpha values larger than 0.94.

A list of commercial cobalt catalysts and commercial reactor selection for these catalysts can be found in Table 6.3. It should be noted that the actual composition of the commercial catalysts employed may be slightly different to the published information. In general compositions of commercially relevant cobalt catalysts are very similar, usually containing:

- Nanosized cobalt as the FTS active metal (typically 10–30 wt%).
- A second metal (usually noble) as a reduction promoter (0.05–1 wt%) to facilitate H_2 spillover during reduction.
- A structural oxidic promoter (e.g. Zr, Si, and La) (1–10 wt%), which is used to protect the support and impart stability.
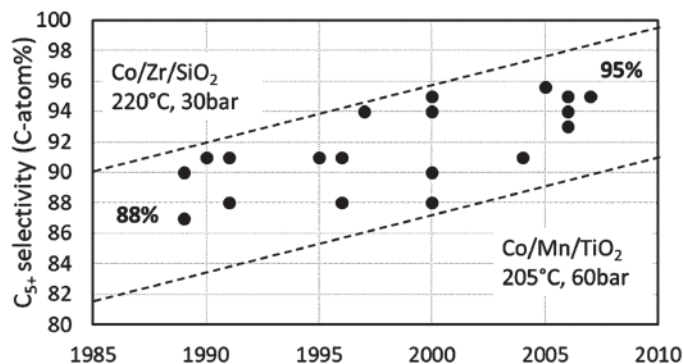

Figure 6.7 Improvement in Shell catalyst selectivity with time, based on analysis of patent data [62].

Table 6.3 List of commercial cobalt catalysts and reactors. Adapted from [63].

Technology provider	Support	Support modifier	Promoter	Reactor type
BP/JM [64]	ZnO [65] & TiO_2		Mn	FB or Davy CANS™
Exxon Mobil [66]	TiO_2	γ-Al_2O_3	Re	Bubble bed
CompactGTL [67]	γ-Al_2O_3		Re	Microchannel
Conoco-Philips [68]	γ-Al_2O_3	B	Ru/Pt/Re	Bubble bed
EFT [69]	γ-Al_2O_3			Fixed bed
ENI/IFP/Axens [70]	γ-Al_2O_3	Si	Pt(?)	Bubble bed
GTLF1 [71]	Ni-Aluminate	α-Al_2O_3	Re	Bubble bed
INERATEC [72]	γ-Al_2O_3	Si	Pt	Microchannel
Nippon [73]	Silica	Zr	Ru	Bubble bed
Sasol–Topsoe (a)	γ-Al_2O_3	Si/C	Pt	Bubble bed
Sasol–Topsoe (b) [74]	SiO_2	Ti	Mn/Pt	Bubble bed
Shell [75]	TiO_2		Mn/V	Fixed bed
Syntroleum [76]	γ-Al_2O_3	Si/La	Ru	Bubble bed
Velocys [77]	Silica	Ti	Re	Microchannel

- A selectivity promoter (e.g. Re and Mn), specifically to target longer chain products.
- A refractory oxidic support such as titania, alumina, silica, or combinations thereof.

The various considerations that need to be taken into account when designing an optimal cobalt catalyst with required activity, stability, and selectivity are described in Figure 6.8 [51, 78–80]. Aspects of these will be discussed in the next section.
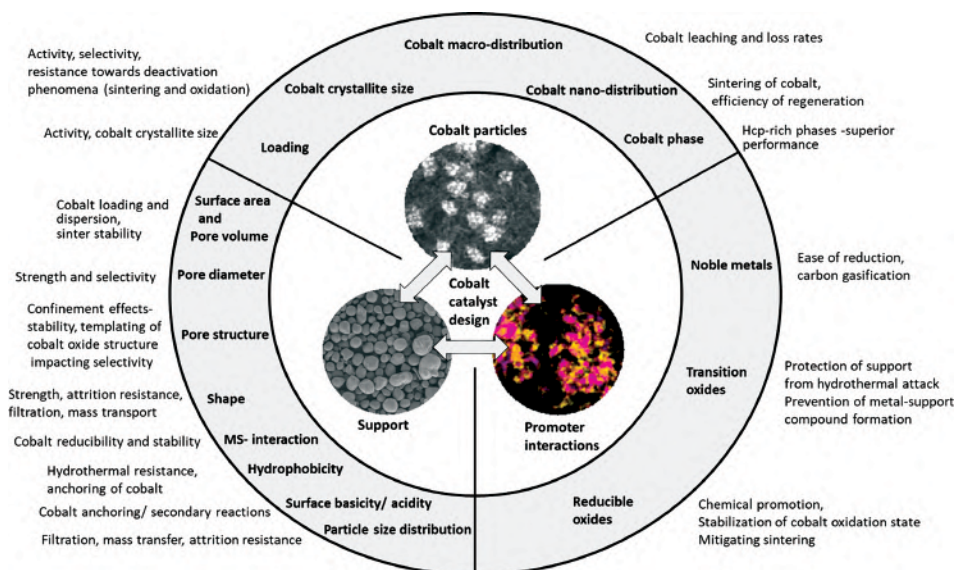

Figure 6.8 Considerations for the design of efficient supported cobalt catalysts with high water tolerance and high selectivity in PtL applications, consolidated from information in Refs [51, 78–80].

6.2.1 Catalyst Preparation Routes for Cobalt-based Catalysts

6.2.1.1 Precipitation Methodology – a Short Summary

Co-precipitation was initially the preferred FTS-catalyst preparation method (e.g. Co/ThO$_2$/kiesel-guhr during the second World War) [81]. More recently, co-precipitation has been applied, such as for the BASF (formerly Engelhard) Co/ZnO catalyst [82]. Co-precipitation follows a five-step process that includes precipitation, washing to remove unwanted salts, and drying followed by shaping and calcination [83]. For bubble bed application, the drying and shaping steps are usually replaced by re-slurrying and spray drying. Washing out of the residual alkali metals and/or halogens is important as ppm levels thereof can degrade both selectivity and activity of the catalyst. The active metal (Co) crystallite size and composition of the precipitate can be controlled by the precipitation agent, organic hydrolysis reagents, precursor salts, temperature, and ageing time. As disposal of salts can pose an environmental risk, care must be taken in the choice of precipitation agents so that the resulting salts can be recycled, re-used or decomposed. Although batchwise precipitation is still employed, continuous processes are preferable for large scale production. The choice of precipitation chemicals can also impact side reactions such as the formation of cobalt aluminates and cobalt silicates (e.g. using Na$_2$CO$_3$ or KOH as precipitation agents for Co/SiO$_2$ FTS-catalysts) [84]. Cobalt silicate formation can be limited by adding the silica after precipitation.

6.2.1.2 Preparation Methods Using Pre-shaped Supports

6.2.1.2.1 Support Modification

Homogeneous covering of the support surface by the modification promoter is important to ensure optimal hydrothermal protection and/or promotional impacts [85–87]. This can be achieved by either organic based slurry impregnations [88], aqueous phase impregnations or grafting [89]. Some aqueous phase modifications may require extensive washing steps to remove residual sulphates, alkali metals or halogens as they can negatively impact catalyst performance. During organic base modifications it is important to choose a solvent with a sufficiently different boiling point to the modifier precursor to minimize losses. To achieve optimum modifier distribution, precursors with optimum interaction with the support surface are required and/or optimal drying and calcination procedures must be targeted.

6.2.1.2.2 Cobalt Impregnation

While bubble bed and micro channel reactor catalysts usually target homogeneous cobalt distributions, larger fixed bed catalyst particles often target an egg-shell cobalt distribution to limit the impact of diffusion limitations during FTS [90].

When targeting a homogeneous distribution of cobalt and promoter, the desired cobalt crystallite size is another critical parameter. To achieve this, the following aspects should be considered:

- Pore volume determines the maximum amount of precursor that can be added [91]. Slurry impregnations can usually target 95% of pore volume occupation by precursors, whereas incipient wetness (IW) preparations at times require lower concentration solutions to simplify the precursor addition process.
- To obtain a homogeneous impregnated cobalt distribution throughout the support particle, the particle geometry (diffusion path length, 2 or 3D pore structure, pore geometry, and size), interaction between precursor and support surface (point of zero charge [PZC] of the support, pH of the solution, contact angle, and surface tensions), viscosity of the precursor, suspension, and diffusion coefficients need consideration to determine optimum impregnation and drying [92, 93]. These impacts are demonstrated in Figure 6.9, showing the cobalt distribution for optimized slurry impregnation compared with IW impregnation followed directly by similar calcination procedures.
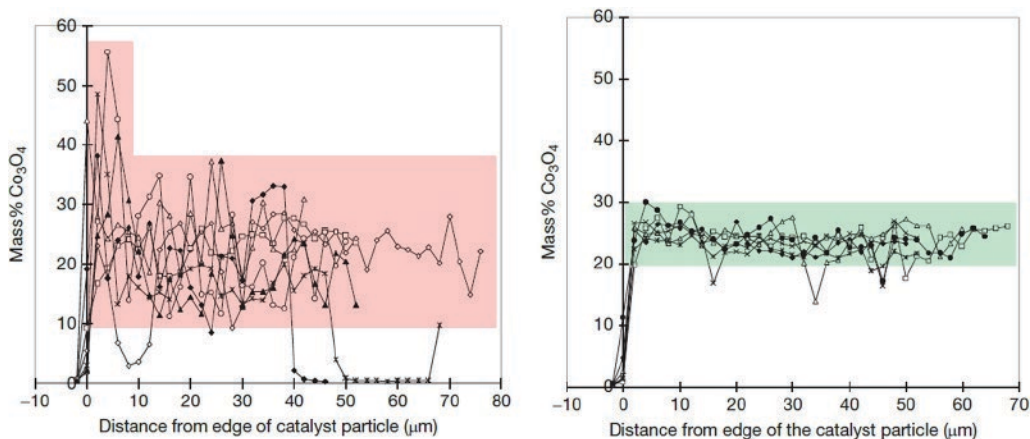
Figure 6.9 Scanning electron microscope/energy-dispersive x-ray spectroscopy (SEM/EDX) line scans show the heterogeneous cobalt oxide distribution for incipient wetness (IW) impregnation followed directly by fast drying (left) compare to the more homogeneous distribution from optimized slurry impregnation (three hours slow drying) followed by fast drying (right) [94, 95]. Reproduced with permission from Ref [51] / Elsevier.

The addition of viscosity enhancers, chelating agents [96, 97], organic metal precursors [98], organic acids [99], and binary acids [100] can further enhance the cobalt crystallite size distribution.

When targeting egg-shell type impregnations for fixed bed applications, addition of viscosity enhancers or using cobalt salt melts are preferred during impregnation [101]. For deposition-precipitation onto pre-shaped supports, both the precipitation agent and cobalt precursor's diffusion into the pre-shaped support and interaction with the support surface are important and must be controlled to obtain homogeneous distributions and crystallite size distributions [102].

Metal precursors can migrate out of the pores if care is not taken during the drying phase from the point of IW until the metal precursor decomposition (calcination) starts. The same parameters for impregnation and deposition should be considered to prevent the cobalt precursor (if not chemically fixed to the support) from migrating out of the particle. In addition, heat transfer coefficients, evaporation enthalpy and particle outer surface area need consideration for optimizing the drying stage of the cobalt catalyst preparation. Models are available that describe the impacts of convective flows, diffusion and adsorption of metals over the surface of the porous support. From these models, targeted conditions can be used to either obtain homogeneous, egg-shell or egg-yolk distributions [103]. Even the drying atmosphere (e.g. using air or N_2) can impact the final cobalt distribution [104]. Each preparation method needs to be optimized carefully and one cannot assume that the optimum procedure for one type of support and support particle shape will be the same for all other supports and support particle shapes. The interaction between the support surface and cobalt precursor may differ from the promoter precursor and surface. If care is not taken during the drying phase as well as any storage time between drying and calcination, cobalt-promoter segregation may occur.

6.2.1.2.3 Calcination

Storage time between drying and calcination must be limited as precursor migration may occur. Most calcinations are performed in air, but organic precursors may require the use of nitrogen or diluted air to control the exothermic decomposition [21]. Alternatively, reactive gases such as NO can be added to assist in the decomposition of the cobalt precursor [105, 106].

To maintain the cobalt distribution achieved by impregnation and drying, cobalt precursor mobility must be prevented. This can be achieved by controlling the heating rate and removal of

decomposition products in such a manner that the cobalt precursor stays in a highly viscous or solid form [107]. The mobility of the cobalt precursors can be further limited by flash or high heating rate calcinations. Care should be taken regarding the heat flow into the system as both the drying and nitrate decomposition are endothermic [108, 109]. Reductive calcinations that use H_2 or CO as decomposition medium can also be used if care is taken regarding explosive limits [110, 111]. Organic additives counteract the overall endothermic nature of cobalt nitrate decompositions as their decomposition is exothermic, thereby accelerating the calcination process. The transmission electron microscopy (TEM) images in Figure 6.10 illustrate how optimal cobalt distributions can be achieved by employing different calcination strategies.
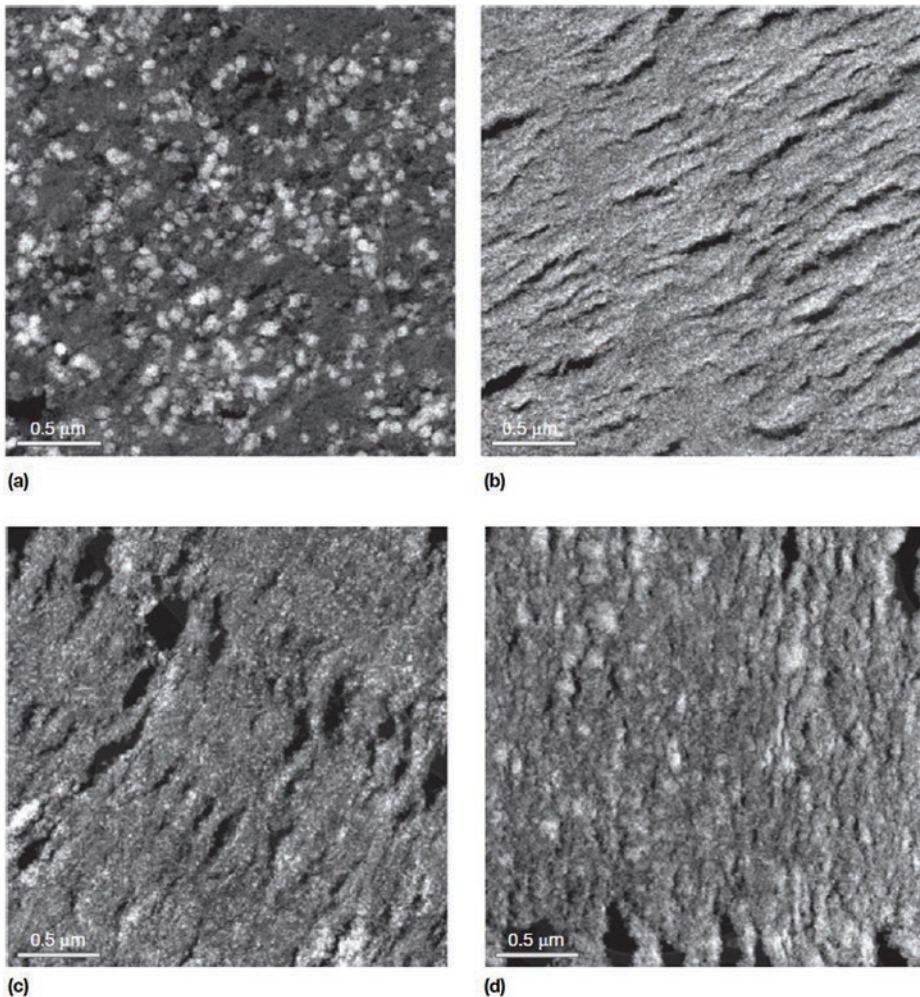

Figure 6.10 Transmission electron microscopy (TEM) images of cobalt crystallite distributions in cobalt alumina catalysts employing different calcination strategies. (a) Cobalt oxide microglobule formation of a 30 g Co/100 g alumina catalysts using a heating rate of 1°C/min and an air space velocity of 1 m^3 / kg $Co(NO_3)_2.6H_2O$ / hour. (b) Cobalt oxide distribution of a 30 g Co/100 g alumina catalysts using fast heating rate and air space velocity to ensure optimum calcination (flash calcination). (c) Cobalt oxide distribution of a 30 g Co/100 g alumina catalysts using carbon coated alumina (C as accelerator for calcination), using the same heating rate and air flow rate as in (a). (d) Cobalt oxide distribution of 30 g Co/100 g alumina catalysts using the same heating rate and flow rate as (a), but with 1% NO in He as in the calcination atmosphere. Reproduced with permission from Ref [51] / Elsevier.

6.2.1.2.4 Reduction

Activation of cobalt catalysts requires a reduction step in hydrogen or a diluted hydrogen atmosphere. CO reductions can be performed if carbon formation can be limited. Co_3O_4 is first reduced to CoO, followed by further reduction to cobalt metal. Both these steps are exothermic; hence care must be taken to optimize heat transfer during commercial reductions as well as minimizing hydrogen diffusion and mass transfer limitations. Efficient removal of reduction products such as water and ammonia (from residual nitrates) is reliant on high hydrogen space velocities and use of low heating rates [112, 113]. The impact of water partial pressure during reduction on the performance of a 30 g Co/100 g Alumina is clearly demonstrated in Figure 6.11.

The lowest commercially possible water partial pressure is targeted to maximize performance and to achieve the optimal reduction rate in agreement with the thermodynamics of reduction. Therefore, the hydrogen stream used for reduction must be as dry as possible. In fluidized bed reduction of catalyst powders these criteria are easily met, while for fixed bed reductions care must be taken to overcome the limitations particularly toward the reduction reactor outlet. Reduction promoters (Pt, Ru, Pd, and others) lower the maximum reduction temperature required. A lower reduction temperature is sometimes required to limit side reactions such as silicate formation and sintering.

Catalyst performance depends critically on the reduction procedure [114] and sometimes intermediate hold steps are required to obtain optimum promoter interaction with the cobalt [115]. Catalyst performance can further be enhanced by up to 30% with a reduction–oxidation–reduction (ROR) [116, 117] sequence. This improvement from ROR treatment is linked to rougher cobalt crystallites with more steps on the surface, increased degree of reduction, and re-dispersion of the cobalt on the support surface.

To secure the more active Co-HCP phase, a reduction-carbiding-reduction (RCR) activation step can be employed [118]. The Co-HCP phase improves both the activity as well as the selectivity toward longer chain products [119].

6.2.2 Challenges for Catalysts Operating with High Carbon Efficiency: Water Tolerance

To maximize the carbon efficiency for PtL processes conversions should be high, while at the same time not compromising the selectivity to the desired products. Due to the inherent stoichiometry of the FT reaction, a mole of water is produced for every mole of CO converted. Thus, higher conversions afford high reactor water partial pressures, particularly in the case of cobalt (which has negligible water-gas shift activity).
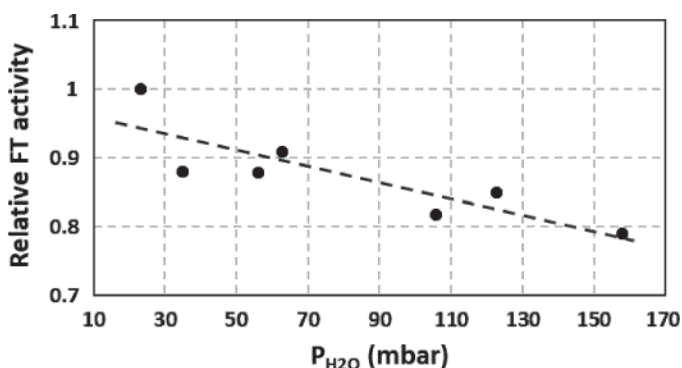

Figure 6.11 Impact of water partial pressure during reduction of a 30 g Co/0.075 g Pt/100 g alumina catalyst on initial Fischer–Tropsch (FT) synthesis performance (Sasol in-house data, redrawn from Ref [51] / Elsevier).

The positive and negative impacts of water on FTS catalysts have been widely studied and there are several reviews on the topic [120–122]. Water may affect the activity, selectivity, and deactivation of the catalyst, and its impact is related to the amount of water present (CO conversion level), catalyst structure, and catalyst composition as well as the reactor employed. At realistic syngas conversions (50–70%), several bars of steam will be generated, which could have a negative impact on catalyst performance.

In general, this would be more problematic in a slurry bed reactor since there is substantial back-mixing compared to fixed-bed reactors. This in turn implies that a comparatively large part of the circulating slurry bed catalyst is exposed to high water partial pressures. In a fixed-bed reactor the particles are stationary and there is a gradient across the bed resulting in water partial pressure increasing from inlet to outlet. Thus, a smaller part of the catalyst is exposed to higher water partial pressure. Therefore, slurry bed catalysts require a greater water tolerance than fixed bed catalysts when targeting the same overall outlet FTS conditions.

The positive effects of water include enhancement in long chain hydrocarbon selectivity [120–122]. Water is known to enhance C_{5+} selectivity by increasing the chain propagation α-value. The exact mechanism of this improvement is not conclusively known but seems to be linked to the observation that water increases the coverage of monomeric CH_x species that are responsible for chain growth. Water assisted-CO activation may also play a role [123]. The observed impact on selectivity is also related to the level of water in the reactor. Tucker and van Steen [124] showed that after a certain level of water in the system is reached (CO conversion >75%), the selectivity to longer chain products can in fact worsen. At these conditions excess amounts of CO_2 can be formed due to water gas shift caused by oxidized cobalt species. Hydrogenation and thus CH_4 selectivity is also enhanced due to an increased H_2/CO ratio on the surface due to water gas shift. At very high water partial pressures, there is also a possibility of capillary condensation in the catalyst pores at low reaction temperatures. For catalysts with very narrow pores, this can become problematic for reactant diffusion to the active metal, impacting coverages of H_2 and CO on the cobalt nanoparticles buried in the pores and negatively impacting selectivity.

The deleterious effects of high water partial pressures on alumina- [124], silica- [125], and titania- [126] based catalysts have been well documented in literature. Van Berge et al. found that an alumina-supported cobalt FTS catalyst was inherently susceptible to hydrothermal attack under typical FTS conditions [127]. This increased the rate of deactivation and resulted in contamination of the wax product with ultra-fine cobalt-rich particulate matter. The problem was solved by pre-coating the support with a silica structural promoter. High water partial pressures (c. 10 bar) during FTS also contributed to significant amounts of cobalt aluminate formation as indicated by a XANES study conducted by Moodley et al. [128]. It was shown that due to the isostructural nature of Co^{2+} and Al^{3+}, cobalt ions from the unreduced oxide can diffuse into the support in the presence of a hydrated surface resulting in the production of difficult to remove cobalt aluminate. Higher water partial pressures also promote the sintering rate of nano-sized cobalt particles [129]. Fundamental work studying the impact of process conditions on Co/Pt/Alumina catalysts in an in situ magnetometer indicated that the presence of high water partial pressure in combination with high CO partial pressures can cause enhanced sintering of the cobalt phase [130].

Thus, the literature indicates that although water can have a positive impact on long chain selectivity at certain levels, very high water partial pressures can be detrimental to both activity and selectivity. Robustness toward water is therefore an important aspect to consider when designing catalysts for PtL processes that run at high conversion levels. Various approaches will be discussed in the next section.

6.2.3 Strategies to Increase Water Tolerance and Selectivity for Cobalt Catalysts

6.2.3.1 Optimizing Physico-chemical Support Properties for Stability at High Water Partial Pressure

In order to optimize catalyst performance at high syngas conversion, one would need to consider the physico-chemical properties of the support such as surface area, pore volume, pore diameter, and thermal conductivity as well as surface acidity and basicity that can affect the stability at elevated water partial pressures [131]. The pore volume has to be matched to the loading of an appreciable quantity of active metal precursor (at least 15–20 wt % Co in order to obtain a catalyst that is active enough for commercial purposes) to limit pore blocking and ensure a homogeneous macroscopic cobalt distribution [132]. Support hydrophobicity can stabilise catalyst performance at higher CO conversion by decreasing the interactions of water with the support and the active metal surface. Post-preparation silylation with 1,1,1,3,3,3-hexamethyldisilazane (HDMS) improved catalyst stability at higher CO conversion conditions relative to an unmodified catalyst. However, hydrocarbon selectivity did not significantly improve [133].

Of the various porous supports (such as alumina, silica, titania, zirconia, SiC, zeolites, and carbon fibers or nanotubes) used for cobalt catalysts, carbon and SiC exhibit superior thermal conductivity that has been linked to improvements in heat removal capacity from the catalyst surface [85, 134, 135]. This is specifically relevant to the FT reaction which is quite exothermic ($\Delta H = -166 \text{ kJ/mol}_{CO}$) and could lead to local hot spots on the catalyst surface, particularly at higher conversion. Shaped carbon (nanotubes and fibers) has been investigated extensively due to the weaker metal-surface interaction and smaller effect on reducibility (making crystallite size effects more facile to evaluate). To date, commercial applications are limited mainly due to sintering and degradation of the support during regeneration [136]. There have been many improvements in the porosity and shaping of SiC supports in recent years which is essential to achieve the required metal loading and mechanical and abrasion resistance that are required for a commercial cobalt catalyst [137]. Compared to an alumina support, the use of SiC in a slurry reactor improved stability at high water partial pressures (c. 10 bar) with only 10% deactivation observed after 50 days on stream (Figure 6.12) [31].

An aggressive acid wash further improved anchoring and dispersion of cobalt oxide, likely due to removal of alkali impurities, surface roughening, and the introduction of additional acid sites. Uniform Ti modification of the SiC surface further improved FT activity. This has been linked with literature citing an improvement in metal dispersion and interaction with the support surface after Ti addition to SiC [138].
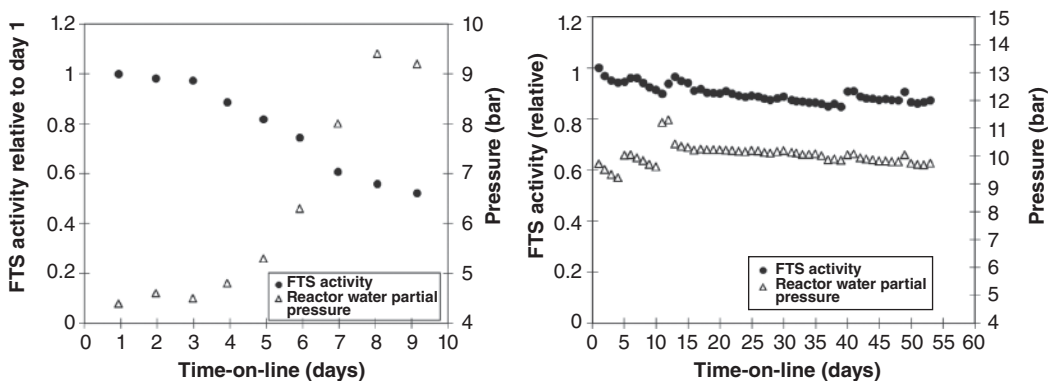

Figure 6.12 FT evaluation of Co/Al$_2$O$_3$ catalyst (left) and Co/SiC catalyst (right) in a slurry reactor at 230 °C, 30 bar, synthesis gas as feed of composition: 60 vol% H$_2$, 30 vol% CO and 10 vol% inerts. In all other experiments the gas space velocity was adjusted to keep the water partial pressure constant at 9–10 bar (syngas conversion of 50–80%). Redrawn with data from Re [31] / Elsevier.

6.2.3.2 Stabilizing the Support by Surface Coating

Surface hydroxyls act as anchoring points for cobalt nitrate during impregnation (irrespective of the type of support). By altering the impregnation pH and the subsequent electrostatic interaction with the support surface, the dispersion of cobalt nitrate may be optimized significantly (Figure 6.13) [85, 132]. Surface hydroxyls are vulnerable to secondary reactions with organic acids and water that are formed during the FT process. There is an interplay between ensuring an optimal number of anchoring points for the active metal phase whilst making the surface inert enough toward chemical attack. Surface modifiers such as Al, Ba, Ce, La, Mn, Si, Ti, or Zr have been added to Al_2O_3, SiO_2, or TiO_2 (at a loading of 1–10%) to coat the surface hydroxyls thereby improving hydrothermal stability especially at conditions favoring higher syngas conversion and water partial pressures [132].

By carbon-coating alumina supports, the cobalt oxide dispersion over the support surface can be improved (Figure 6.14) [139]. High angle annular dark-field transmission electron microscopy (HAADF-TEM) showed smaller, more evenly spaced crystallites and a narrower cobalt size distribution that could limit the thermodynamic drive toward sintering due to surface migration and Ostwald ripening. There was a marked improvement in activity and sintering stability for the carbon coated catalyst over the conventional system. This is evidenced by the smaller change in % ferromagnetic fraction (FM) for the former which can be used to gauge the sintering extent, with sintering being the predominant deactivation mechanism in the early stages of the reaction. This corresponds with findings of Khodakov et al. showing that optimizing dispersion by the addition of carbon had the additional benefit of stabilizing catalyst performance at higher CO conversion relative to the unmodified catalyst [140].

6.2.3.3 Impact of Crystallite Size on Selectivity

The support may be viewed as a mechanical scaffold that can be used to direct cobalt crystallite size through the selection of an appropriate pore diameter and other physico-chemical properties. Depending on the FT application, these physical properties of the support may be tailored to produce a catalyst with the desired cobalt crystallite size.
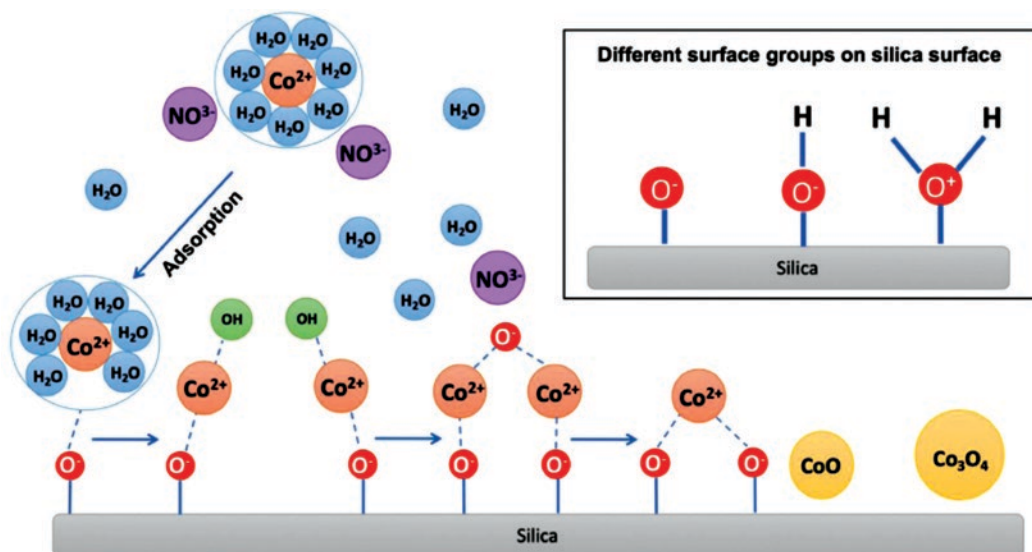

Figure 6.13 Interaction between Co nitrate and the silica gel surface during impregnation based on interfacial coordination chemistry. The progression from solution through formation of hydrosilicates and silicates to formation of CoO and Co_3O_4 is depicted. Reproduced with permission from Ref [132] / Elsevier.
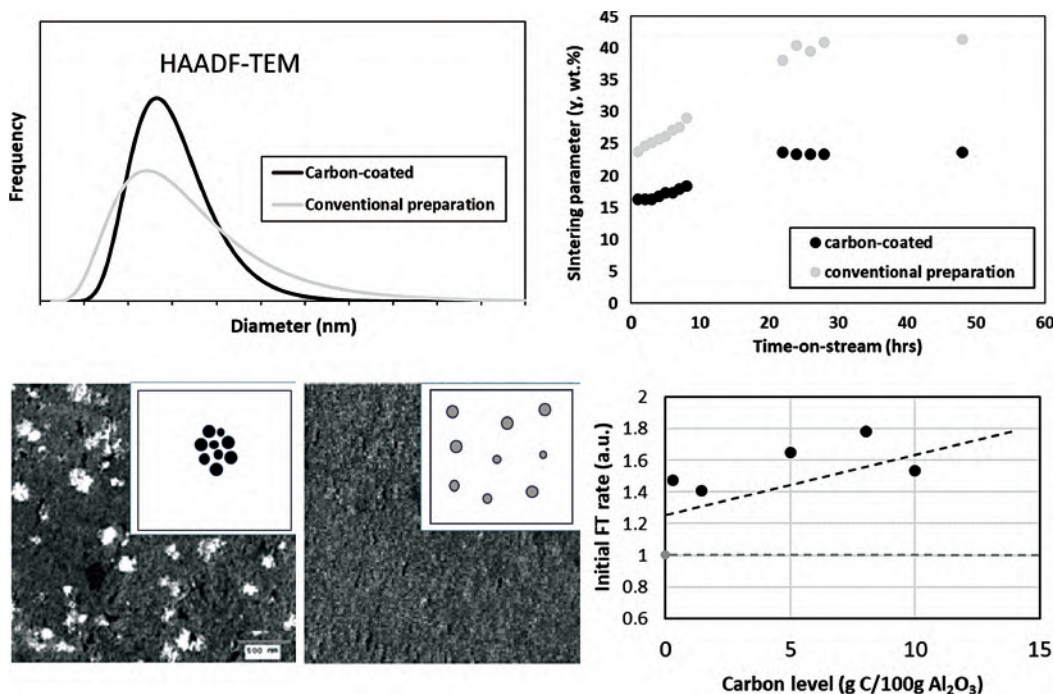
Figure 6.14 Impact of carbon coating on performance of Co/Alumina catalysts. Carbon coating results in improved dispersion and nanoparticle spacing as well as narrowing the cobalt size distribution (left). These effects impact both the activity and stability toward sintering (right). Reproduced with permission from Ref [139] / Springer Nature.

The cobalt crystallite size distribution influences catalyst activity, stability, and selectivity. The selectivity impact levels out for metal crystallites greater than 8 nm [51, 141]. Although activity relates to metal surface area, larger crystallites are more stable toward oxidation and sintering. Therefore, a narrow crystallite size distribution is preferred to optimally utilize the cobalt. Literature consensus is that cobalt-based FTS is a structure sensitive reaction (Figure 6.15). Metallic cobalt particles that are too small do not contain the necessary B_5 step-edge sites required for CO dissociation [142] and subsequent C-C bond formation and thus don't have optimal activity and selectivity.

Salmeron et al. have proposed that the low activity and higher methane selectivity observed for small crystallites is linked to slower hydrogen dissociation on the surface rather than effects such as sintering, deactivation by carbon deposition or oxidation. This is in agreement with the conclusions of van Helden et al. that more highly defective Co sites (associated with smaller Co crystallites) exhibited a larger hydrogen sticking coefficient than the more planar sites found on larger crystallites [143]. Moreover, x-ray absorption spectroscopy (XAS) experiments showed that CO is adsorbed molecularly on very small Co nanoparticles but that the fraction of dissociated CO increases with crystallite size. This was proposed to be an effect of the hydrogen-assisted mechanism of CO dissociation for FT [144].

Smaller crystallites will therefore favor hydrogenation of CH_x intermediates to methane but larger cobalt crystallites ($\geq$10 nm) while being less active will be more selective towards longer chain hydrocarbons due to surface coverage effects and the more facile dissociation of CO and H_2.

6.2.3.4 Metal Support Interactions with Cobalt Crystallites of Varying Size

Strong metal support interaction (SMSI) can negatively influence reducibility of small cobalt crystallites supported on alumina, silica, or titania due to the formation of cobalt silicates, aluminates
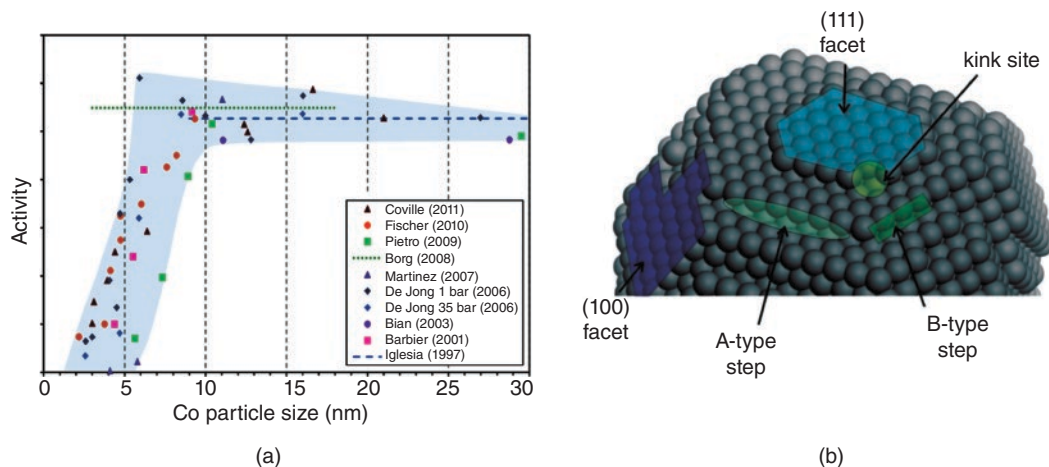
(a)

(b)

Figure 6.15 (a) Fischer-Tropsch synthesis (FTS) activity as a function of the cobalt metal particle size, showing structure sensitivity in cobalt FTS. Reproduced with permission from Ref [143] / Elsevier. (b) Atomic model of a ∼4.6 nm Co particle (4603 atoms), terminated predominantly by (1 1 1) and (1 0 0) facets. A significant portion of defects are present, in particular, ad-islands terminated by mono-atomic step edges. Reproduced with permission from Ref [142] / Elsevier.

and titanates [145]. This can shift the required reduction temperatures above 450 °C and reduce the active metal surface area available for FT reaction through sintering (Figure 6.16).

Titania has been shown to migrate over the surface of cobalt crystallites after reduction at 450 °C forming partially reduced TiO_x which covers active sites and leads to a decrease in hydrocarbon selectivity due to site blocking [146]. This strong-metal support interaction (SMSI) effect becomes more pronounced if high surface area supports are used [147]. It has been postulated that water

Figure 6.16 Temperature programmed reduction (TPR) patterns for a spherical Co/SiO_2 model catalyst following calcination with (a) large Co crystallites (Co-28 nm); (b) medium Co crystallites (Co-13 nm); and (c) small Co crystallites (Co-4 nm). TPR conditions: 5% H_2/N_2, 25–800 °C, 10 °C/min. Reproduced with permission from Ref [145] / Elsevier.
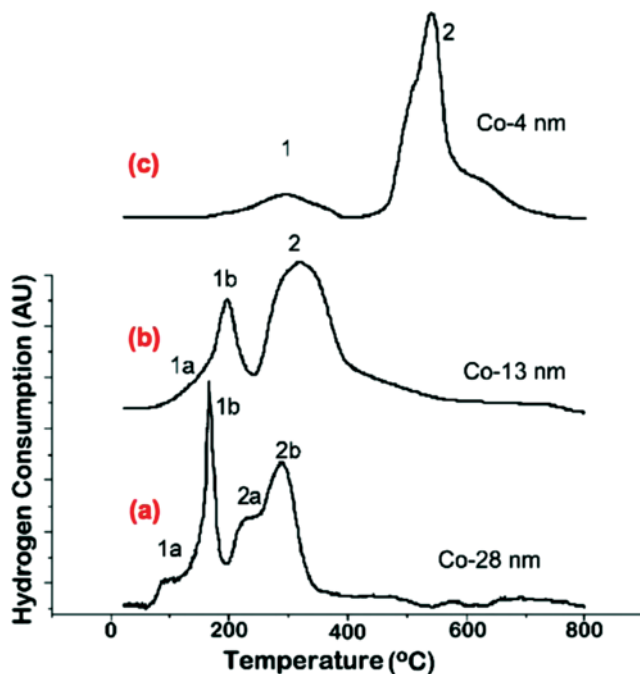
can reverse this encapsulation effect and this is the reason that titania supports respond positively to increasing water partial pressure during FTS [148].

6.2.3.5 The Role of Reduction Promoters and Support Promoters in Optimizing Selectivity

The addition of a reduction promoter such as Pt, Ru, or Re will facilitate reduction to cobalt metal by increasing hydrogen availability on the surface through a spill-over mechanism [149]. Noble metal promotion will also influence selectivity and hydrocarbon productivity for catalysts with similar crystallite size (12 nm using x-ray diffraction [XRD] analysis) (Table 6.4).

Mn is an important catalyst promoter patented by companies such as Shell and BP as well as receiving considerable attention in the academic literature. A component such as Mn not only limits migration of Ti during reduction (structural promoter), but also optimizes electronic interaction with cobalt crystallites at the support/crystallite interface [150, 151]. FTS inactive mixed Mn-Ti spinels can be formed on the support as well as mixed $Mn_{1-x}Co_xO$ compounds. The latter has been found to retard reduction of cobalt while improving catalyst stability as well as selectivity (more so for large Co crystallites than small ones where Mn coverage of active sites might start playing a role).

Similarly, it was shown that Mn-promoted alumina (20wt% Co/xMn/0.05%Pt/Al_2O_3) can shift the Schultz-Flory carbon distribution of a cobalt catalyst toward lighter hydrocarbons (Figure 6.17) [152]. Careful optimization of the Mn/Co ratio was reported to maximise C_{5+} selectivity for different TiO_2 and SiO_2 supports [153–155]. The impact of Mn on the FT rate and selectivity for Sasol-prepared Co/Alumina catalysts was also evident and an optimal loading is required for balancing rate and selectivity. The data indicates that Mn can poison catalyst selectivity and activity at higher loadings, with Mn:Co mole ratio of around 0.179 being optimal.

Researchers at Shell prepared a series of catalyst with various Mn loadings on Co/TiO_2 and subsequently tested them in a fixed bed reactor [156]. The experimental data (Figure 6.18) showed that the presence of MnO significantly increased the catalyst activity by c. 80% and C_{5+} selectivity from 88 to 91 wt %, mostly by suppressing the methane selectivity at 50% conversion and 20 bar. The olefin/paraffin ratio was enhanced, indicating reduced hydrogenation compared to the unpromoted Co catalyst. The maximum activity was obtained at a Mn loading of 0.48 wt% (Mn:Co mole ratio = 0.034). The authors utilized DFT calculations on a Co (0001) model surface to help understand the electronic impact of the decoration of manganese oxide particles on cobalt. It was found that Mn weakens the C–O bond and reduces the barrier for direct CO dissociation while at the same time destabilizing hydrogen on the surface, thereby enhancing selectivity for olefin and long chain production.

Of direct relevance to high conversion operation, Tucker et al. [157], added Mn to Co/Pt/Alumina catalysts in an attempt to improve the water tolerance and selectivity (see Figure 6.19). The addition of Mn: Co in 0.15 mol ratio significantly improved the selectivity of the catalysts compared to unpromoted

Table 6.4 Effect of Pt promotion on activity and selectivity for 20wt%Co/Mn/Ti-SiO$_2$ catalysts containing Mn as a structural promoter. Temperature programmed reduction (TPR) in hydrogen with ramp rate of 1 °C/min to 1,000 °C, Fischer-Tropsch synthesis (FTS) conditions: Slurry reactor, 230 °C, H$_2$/CO = 1.5, 15 bar total pressure evaluated at isoconversion (Sasol in-house data).

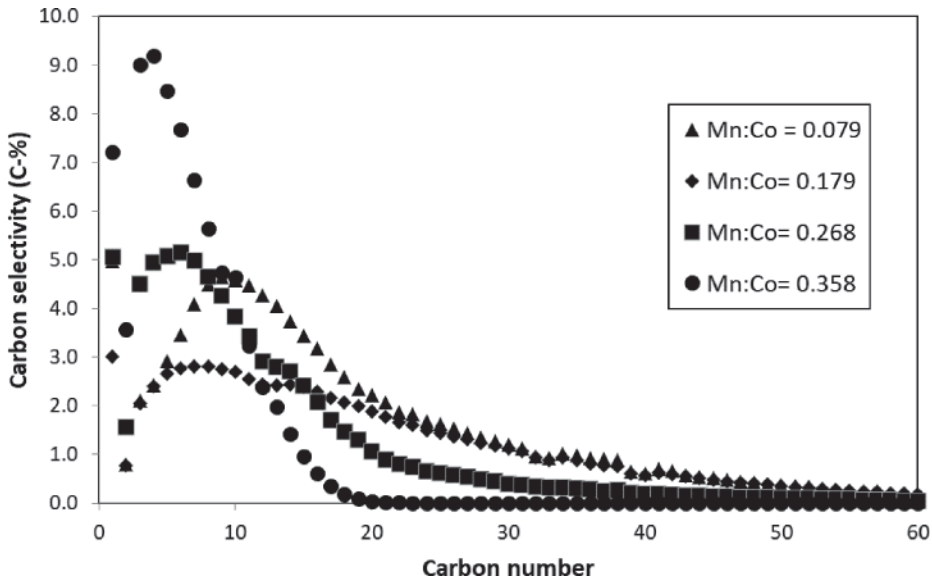| Pt loading (wt%)	Co$_3$O$_4$ reduction to CoO (°C)	CoO reduction to Co (°C)	Normalised FT activity at day 5	Normalised methane selectivity at day 5	Normalised hydrocarbon productivity at day 5
0.05	161	233	1	1	1
0	211	289	0.85	1.22	0.83

Figure 6.17 Commercial type cobalt on Mn-modified alumina (20 wt% Co/xMn-Al$_2$O$_3$) showing that carbon distribution shifts toward lower carbon-number with increasing Mn loading [152].
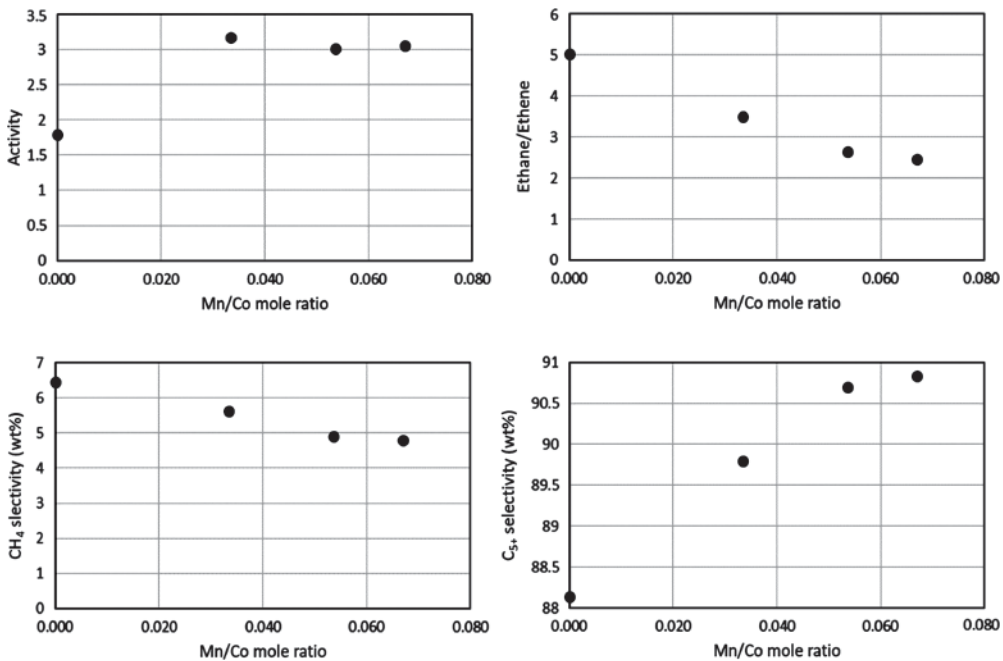

Figure 6.18 Trends of activity and selectivity (210 °C, 50% CO conversion, 20 bar H$_2$/CO), for 16 wt% Co/TiO$_2$ catalyst as a function of Mn:Co mole ratios as reported by Shell. Redrawn from data in Ref [156] / American Chemical Society.

catalysts, especially at high conversion conditions (>70% CO conversion). The manganese-promoted catalyst decreased the selectivity toward methane and CO$_2$ at high CO conversion (X$_{CO}$ = 90%) with significant enhancement of fuel yield (C$_{5+}$) up to 14 C-%. It was reported that Mn addition changed the reducibility and Co crystallite size of Mn-Pt-Co/Al$_2$O$_3$ significantly. Manganese seems to be
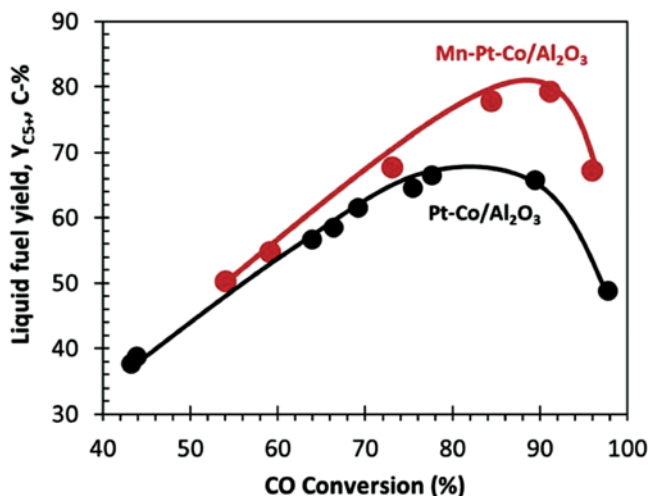
Figure 6.19 The yield of C_{5+} as a function of CO conversion for standard industrial Pt–Co/Al$_2$O$_3$ and industrial Mn–Pt–Co/Al$_2$O$_3$ Mn: Co = 0.15 mol/mol. Reproduced with permission from Ref [157] / Royal Society of Chemistry.

incorporated in the spinel structure of the calcined catalyst. This study provided convincing evidence that Mn as a promoter can boost selectivity at high conversion conditions.

6.2.3.6 Role of Pore Diameter in Selectivity

Pore diameter has the potential to determine cobalt crystallite size and therefore influence the C_{5+} selectivity. Diffusion of long-chain hydrocarbon products occurs more easily from larger pores due to the removal of transport restrictions via the formation of water-rich intra-particle liquids [158]. If all the cobalt nitrate is impregnated into the pores during catalyst preparation and migration of nitrate out of the pores during calcination is limited, the cobalt oxide crystallites that are formed inside the support pores should not exceed the pore diameter [159].

In alumina, a linear relationship between pore diameter and C_{5+} selectivity was found for large-pore supports (large crystallites) vs narrow-pore supports (small crystallites) (Figure 6.20) [160]. The amount of crystallite contraction after reduction increased for large pore aluminas, as evidenced by the ratio of crystallite diameter analysed with XRD (Co$_3$O$_4$) to TEM diameter (Co).
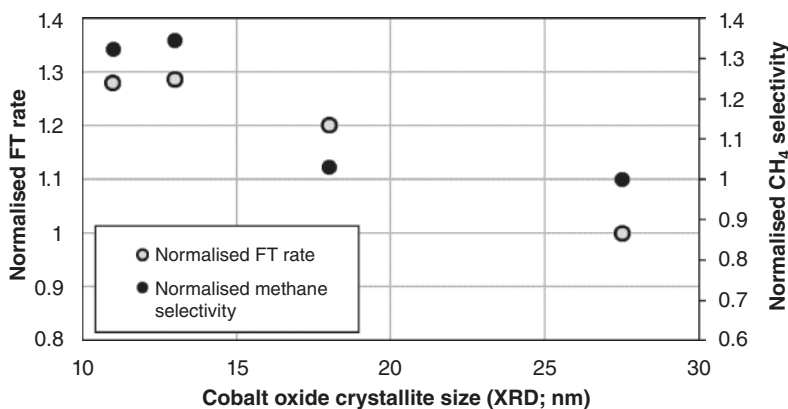

Figure 6.20 Effect of varying cobalt oxide crystallite size (XRD) on selectivity and Fischer-Tropsch (FT) rate at a constant optimal pore diameter.
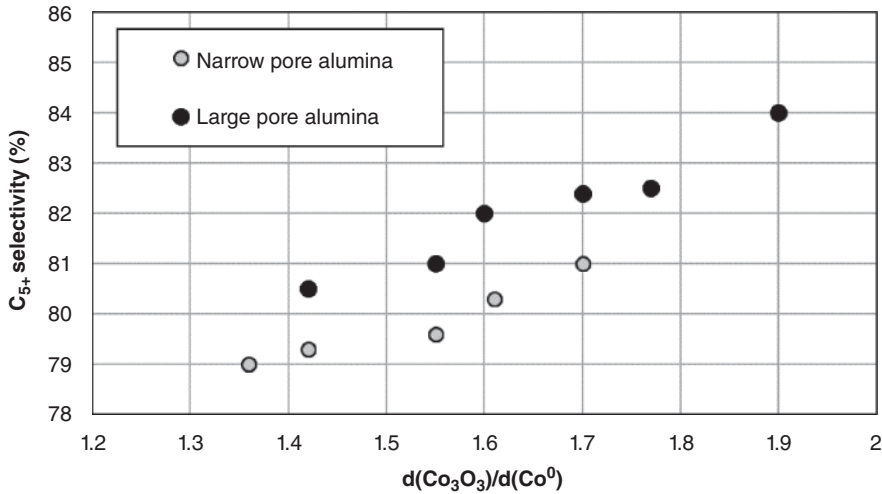
Figure 6.21 Effect of cobalt particle break-up on the C_{5+} selectivity at 483 K, 20 bar, $H_2/CO = 2.1$, and 50% CO conversion for 20% Co/0.5%Re/Al$_2$O$_3$ tested in a fixed bed reactor. Adapted from Ref [160].

This was linked to an increase in C_{5+} selectivity, most probably due to more steps, edges and kinks present on the larger crystallites. A similar link between crystallite size and pore diameter for a series of Co catalysts supported on Ti/Mn-modified silica at a constant pore diameter (Figure 6.21) was observed. The addition of a dispersant could decouple crystallite size from the pore diameter to give small crystallites inside a larger pore due to the formation of smaller cobalt crystallites after reduction, in agreement with results from Borg et al. [160], which showed improved selectivity.

Process conditions (such as temperature, H_2/CO ratio, and CO conversion) will influence selectivity as is clear from the plots in Figure 6.22 which depicts C_{5+} selectivity for various Co/SiO$_2$ catalyst systems as a function of increasing pore diameter. Even though conditions for these runs were dissimilar, the general trend of increasing hydrocarbon chain length with
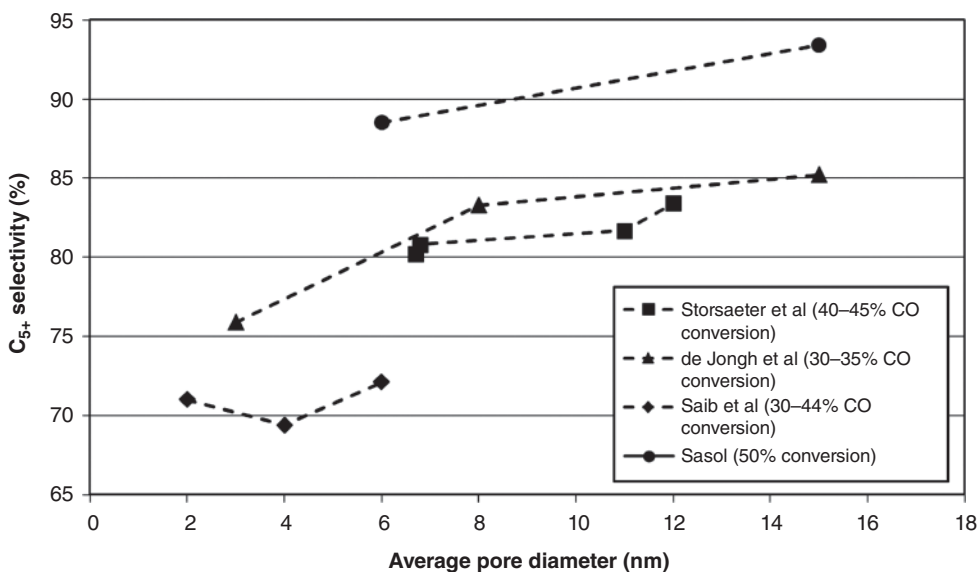

Figure 6.22 Link between pore diameter and C_{5+} selectivity for different silica-based catalysts evaluated in fixed-bed reactors as reconstructed. Adapted from Refs [104, 161, 162].

larger pores was the same. Notable from the work of de Jong et al. was the focus on improvements in dispersion during catalyst preparation which also benefitted selectivity toward longer chain hydrocarbons. Appropriate surface modification with the same pore diameter, allowed for an improvement in selectivity irrespective of higher temperature and CO conversion conditions.

6.2.3.7 Effect of Activation Conditions on Selectivity

The activation of the catalyst prior to FT synthesis can radically affect activity and selectivity. Metallic cobalt can assume either the face-centered cubic (FCC) crystallographic phase or hexagonal closed packed (HCP) phase. The HCP phase is more stable at a low temperature, whereas the FCC phase becomes more stable when the crystalline size of the cobalt is less than 20 nm and at temperatures above 450 °C [163].

Wulf constructions and DFT calculations suggest that the extra steps and kinks on HCP-Co crystallites would lead to an improvement in FT activity for HCP-enriched catalysts [164]. An *ab initio* study of the thermodynamics of the relative interaction between CO and the HCP vs FCC cobalt crystallites indicated that as the CO pressure (and chemical potential) on the surface of the crystallite increases, a morphology change is induced which will change the exposed facets at high coverage [165]. Work done at Sasol indicated that for the same corresponding size of cobalt nanoparticle there are some noticeable differences in morphology for FCC and HCP particles (Figure 6.23). Most noticeable is that HCP structures expose a larger variety of site arrangements than FCC. There are four additional unique sites on the HCP structure, with the notable absence of square sites that are thought to be FT inactive. If these additional sites are FT active, it could be expected that the FT rate and selectivities could differ between FCC and HCP nanocrystals, in agreement with the findings of Liu et al. [164].

Experimentally, the most reliable method of producing HCP-rich cobalt catalysts is by a reduction-carburisation-reduction activation protocol, forming an intermediate cobalt carbide phase
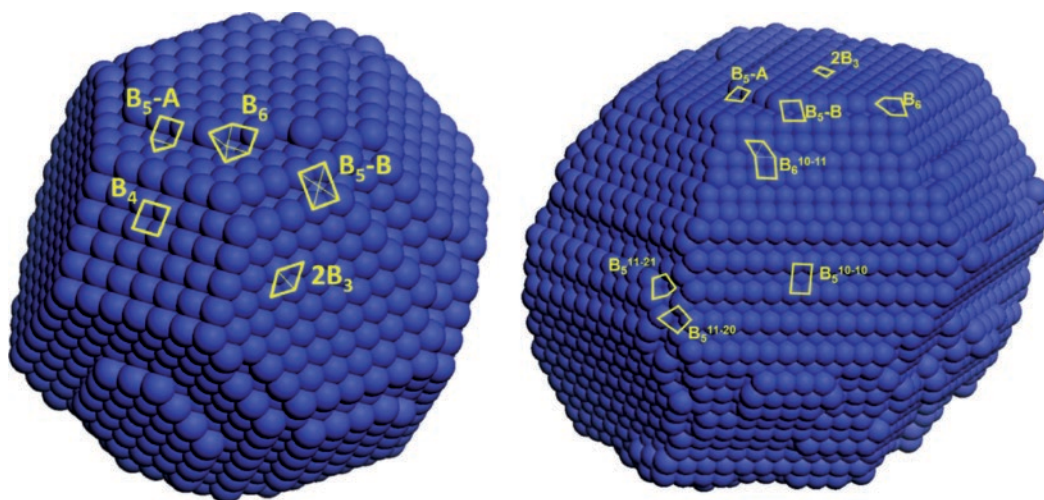

Figure 6.23 A 4 nm face-centered cubic (FCC) (left) and hexagonal closed packet (HCP) (right) Co particle showing the defined sites and their locations on one particle. Left figure reproduced from Ref [143] with permission from the American Chemical Society. Copyright 2012. Right figure courtesy Pieter van Helden (Sasol).

which preferentially decomposes to HCP-Co [21]. This has been observed experimentally over various types of supports such as alumina, silica (with Ru-promotion being mentioned to form more HCP-phase after activation), and even ZnO [166]. Alumina supports retained some FCC-Co after the RCR activation cycle whereas the defective surface of silica paired with Ru-promotion was postulated to be responsible for preferential formation of pure HCP-Co after completion of the RCR cycle [167]. The addition of Re as promoter to Co/TiO_2 catalysts (0.5 and 1 wt%) was also found to increase the fraction of HCP-Co after a standard reduction in hydrogen. However, the influence on turnover frequency (TOF) relative to the FCC-Co catalyst was insignificant [168]. Experimentally, the performance impact can be seen in Sasol fixed-bed data on Co/Alumina catalysts activated in H_2 only (to produce an FCC-rich particle) and via RCR activation (to produce a HCP-rich particle) (Figure 6.24).

The performance improvement noted for the HCP phase was also observed experimentally on other catalyst systems regardless of support, including unsupported cobalt [169], alumina [170], silica [171] and titania [172] supported cobalt catalysts.

To summarize, support properties can influence the stability of the final catalyst through direction of cobalt oxide crystallite size and how those crystallites interact with the support surface, the reactants (H_2 and CO), and the products that are formed (water and hydrocarbons). Through careful selection of the support material and final catalyst properties, stability at high water partial pressures can be achieved and the selectivity toward longer chain hydrocarbons may be optimized.
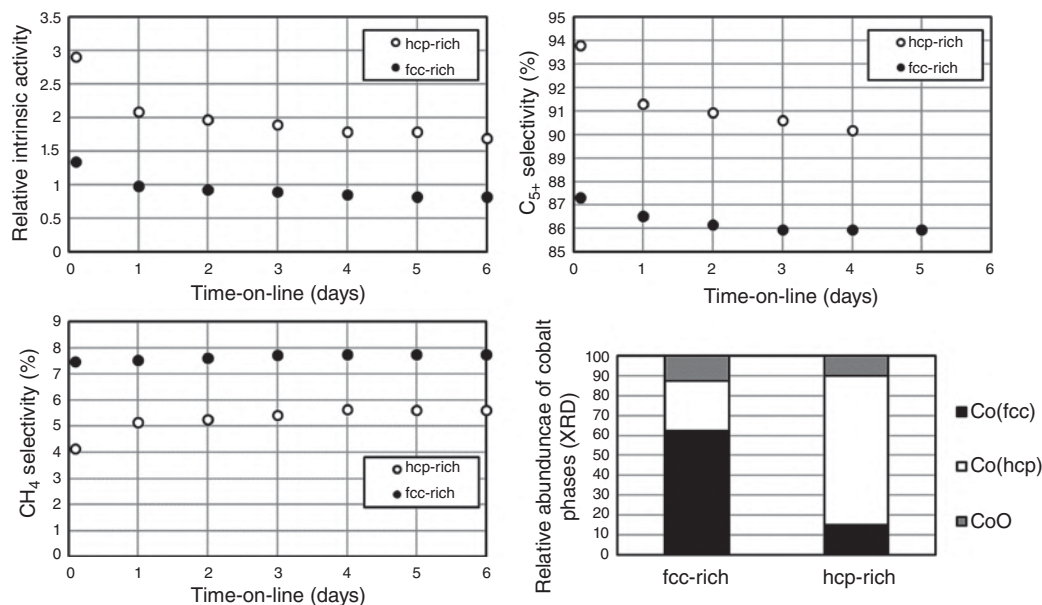

Figure 6.24 Activity and selectivity improvement of hexagonal closed packet (HCP)-rich (●) and face-centered cubic (FCC)-rich (○) Sasol lab -prepared 20 wt%Co/Alumina catalysts in a fixed bed reactor (16 bar, 230 °C, H_2/CO = 2, c. 55% CO conversion). The HCP-rich catalyst was produced in a similar manner to Adapted from [21]. The composition of the cobalt phases for the fresh catalysts as determined by XRD is shown on the bottom right.

6.2.4   Regeneration of Cobalt PtL Catalysts- Moving Toward Materials Circularity

The typical life cycle of a cobalt slurry phase catalyst used in a FT plant can be described as follows:

- Raw materials such as cobalt salts, noble metal salts and support are used to manufacture the catalyst at a manufacturing facility. The reduced and wax-embedded catalyst is then transported to the GTL facility where it is used in the FTS section, to convert synthesis gas primarily to waxy hydrocarbons.
- After the catalyst has reached the end of its useful life, it is then transported to a metals reclamation [173] facility to remove the hydrocarbon wax and recover cobalt and promoter metals for return to the manufacturing facility where they are reworked into the process. Drawbacks of this approach include that the catalyst support is currently not re-used and that a portion of the expensive metals cannot be reclaimed. There is also an additional carbon footprint associated with the logistics and re-preparation routes.

Circularity of materials is a topic that will become increasingly important for sustainability in catalysis. Regeneration and re-use of the spent catalyst is therefore a critical focus area for FTS. On-site regeneration provides logistical benefits as it reduces the amount of spent catalyst sent for metals reclamation, simplifying the catalyst supply chain. Regeneration further allows re-use of the support and a significant reduction in the solid waste footprint. For regeneration to be successful, an understanding of the deactivation mechanisms at play is important [174] so that they can be reversed, and catalyst properties can be returned as close as possible to that of the fresh catalyst. The regeneration concept has been around since the early days of FT research and is well documented in a number of reviews [175–177].

Shell has used regeneration as a tool to manage the lifetime of their fixed bed cobalt HPS (heavy paraffin synthesis) catalyst. They previously reported that in situ regeneration (required every 9 to 12 months) is routinely applied with great efficiency [178]. Their initial regeneration patents involve the use of solvent washing or hydrogen treatment, oxidation, and reduction [179, 180]. Regeneration in a fixed bed reactor can be performed in situ without removal of spent catalyst. However, the reactor needs to be taken offline to perform the regeneration, which results in some down time and may require additional capital cost to ensure sufficient reactor capacity to achieve production targets. Later regeneration patents of Shell involve a process in which the spent FT catalyst particles are first oxidized, then treated with a solvent containing ammonium carbonate and ammonium hydroxide in water [181]. This seems to be significantly better than the standard procedure and may result in dissolving and redispersion of cobalt in sintered spent catalyst.

BP also reported that regeneration was crucial for their catalyst to achieve a lifetime of four years. [182]. The main purpose for regeneration was to remove the extremely low levels of carbon deposited on the cobalt crystallites, which caused catalyst deactivation. Regeneration of a slurry phase catalyst requires that the catalyst be removed from the reactor and regenerated externally. An operational advantage is that with online catalyst removal and addition, the slurry bed reactor does not need to be taken off-line for catalyst replacement and allows continuous running of the reactor.

Regeneration of spent slurry phase catalysts has also been reported by both Exxon-Mobil [183] and Syntroleum [184]. Exxon's initial regeneration involved a low temperature oxidation step followed by reduction. According to a review by Bartholomew [175], Syntroleum uses an oxidation−reduction regeneration process. Syntroleum's patents and publications indicate that the first step involves concentrating the wax/catalyst slurry. The concentrated slurry is then dewaxed to convert it into a free-flowing powder. Oxidation is then initiated to combust the remaining hydrocarbons on the surface and pores of the catalyst. The final step is the hydrogen reduction step at high temperatures after which the catalyst is re-slurried before being returned to the FT reactor.