**Chapter - 5**

**Heterogeneous Hydrogenation of CO2**

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* 1. **Heterogeneous Hydrogenation of CO2: Scope and Importance**

Carbon dioxide is used in the production of chemicals, fuels or intermediates such as methanol, cyclic carbnonates and dimethyl carbonates in chemical industries via CO2 hydrogenation, CO2 cycloaddition to epoxides and by reacting CO2 with acetals, or ortho-ester, or methanol, with or without epoxides respectively. Considerable R&D efforts have been made to convert CO2 to useful chemicals through homogeneous and heterogeneous catalysis, as each of these pathways has its own advantages and disadvantages. Homogeneous catalytic systems typically exhibit higher catalytic activities than their heterogeneous catalysts counterparts. Yet, heterogeneous catalysts are preferable due to the simplicity in reactor design, separation, handling, stability, and reusability of catalysts. Advancing the efficiencies of heterogeneous catalysts could reduce the production cost in large-scale industrial processes [1]. The key challenge is to couple the unique homogeneous catalysts properties with specialized technical part of heterogeneous catalysts to create hierarchical catalysts. This chapter presents an overview and in-depth discussions on the potentialities of heterogeneous catalysis for CO2 utilization in the synthesis of various chemicals and fuels, focusing on the properties of heterogeneous catalysts, CO2 conversion, product yields, reaction conditions, limitations and reaction mechanisms.

* + 1. **Synthesis of carbon monoxide via reverse water-gas shift reaction**

Catalytic conversion of CO2 to carbon monoxide via reverse water-gas shift (RWGS) reaction has been generally deemed as one of the most promising processes for CO2 conversions (Eq. 5.1) [2].

CO2 + H2 ↔ CO + H2O ΔH298K = 41.2 kJ mol-1 (Eq. 5.1)

The RWGS reaction takes place in many processes, wherever CO2 and H2 are present in a reaction mixture. The importance of this reaction from both fundamental and practical points of view has attracted considerable attention in the design and characterization of RWGS catalysts.

* + - 1. **Metal Based Heterogeneous Catalysts**

As RWGS is a reversible reaction, catalysts active in the water gas shift (WGS) reaction are often active in the reverse reaction [3]. Copper-based catalysts are the most studied systems for the WGS reaction, and hence employed also to the RWGS reaction. Liu et al., [4] developed a series of bimetallic Cu-Ni/γ-Al2O3 catalysts for CO2 hydrogenation. The ratios of Cu/Ni show a significant influence on the conversion and selectivity. Cu favors CO formation, while Ni is active for CH4 production. The Cu/ZnO and Cu-Zn/Al2O3 catalysts used for methanol synthesis and WGS reaction have also been tested for the RWGS reaction [5]. The most active catalyst for the reaction is reported to be Cu rich (Cu/Zn > 3) system with alumina as a support. A linear relationship between the activity of the catalyst and the surface area of metallic Cu was obtained [5]. Chen et al. reported that Cu/SiO2 with potassium as a promoter offers better catalytic activity (12.8% of CO2 conversion at 600 °C) than the catalytic system without the promoter (5.3% of CO2 conversion at 600 °C) [6]. The newly formed active sites located at the interface between copper and potassium appears to favor the formation of formate (HCOO) species - a key intermediate for CO production. The major role of K2O is to provide active sites for decomposition of formates, in addition to its role as a promoter for CO2 adsorption.

RWGS reaction is an endothermic reaction, and hence high temperature would facilitate the formation of CO. However, copper-based catalysts are not suitable at high temperatures due to their poor thermal stability (for instance, sintering of copper nanoparticles) unless modified with the addition of a thermal stabilizer. For example, with the addition of a small amount of iron, catalytic activity and stability of Cu/SiO2 at high temperatures were effectively improved [7, 8]. Large copper surface area is provided by Cu-Fe catalysts, even if the catalysts are pretreated at high temperature. At 600 °C in atmospheric pressure, the Cu-Fe catalysts exhibit highly stable catalytic activity for up to 120 h. In contrast, 10 wt% Cu/SiO2 without Fe additives deactivated rapidly, due to the decreased surface area of copper and oxidation of copper at high temperature [8]. The new active species around the interface between Cu and Fe particles were proposed to account for the enhanced catalytic activity. At high temperature, the sintering of Cu is effectively prevented by the formation of small particles of iron species around Cu particles [8]. Chen et al. [9] have developed a Cu/SiO2 catalyst by atomic layer epitaxy (ALE), to provide thermal stability to resist the sintering of Cu particles under high temperature condition. Due to the formation of small Cu particles, the ALE-Cu/SiO2 catalysts could strongly bind CO and provide high catalytic activity for the RWGS reaction. Cerium-based catalysts are also active in both WGS and RWGS reactions [10]. Ni/CeO2 (2 wt% Ni) showed excellent catalytic performance in terms of activity, selectivity, and stability for the RWGS reaction [11]. CO yield is around 35% at 600 °C for a continuous period of 9 h. Oxygen vacancies formed in the lattice of ceria and highly dispersed Ni are key active components for the reaction, and bulk Ni favors the formation of methane. However, deactivation of ceria supported catalysts is a crucial issue that needs to be addressed. It has been reported that a very small coverage of deposited carbon on the ceria support leads to strong deactivation of the catalyst, indicating that the fraction of the support involved in the reaction is small, probably located next to the supported metal [12]. Supported noble metal catalysts (e.g., Pt, Ru, and Rh) typically have high ability toward H2 dissociation, and thus they have been used as efficient catalysts for CO2 hydrogenation. Bando et al. [13] performed CO2 hydrogenation over Li-promoted Rh ion-exchanged zeolites (Li/RhY). Main product transforms from methane to CO with increased amount of Li. When an atomic ratio of Li/Rh is higher than 10, the main product becomes CO (87% of selectivity) and formation of methane is greatly suppressed (8.4% of selectivity). The presence of Li atoms on the surface creates new active sites that enhance CO2 adsorption and stabilization of adsorbed CO species [13]. Moreover, the type of metal precursor employed in the catalyst preparation affects catalytic reactivity. Arakawa et al. [14] prepared silica-supported Rh catalysts (Rh/SiO2) from acetate, chloride, and nitrate precursors via impregnation for CO2 hydrogenation. The main product was CO over the catalysts prepared from acetate and nitrate, whereas the amount of CH4 was relatively high using the catalyst synthesized from the chloride precursor. Detailed X-ray photoelectron spectroscopy (XPS) measurements elucidated the effect of metal precursor on the CO2 hydrogenation reactivity. It was found that the ratio of hydroxyl species to Rh atoms on SiO2 surface determined reactivity (high ratio favors the formation of CO). The ratio based on different metal precursors follows the order: chloride < nitrate < acetate [14].

* + - 1. **Reactor aspects**

Generally, fluidized beds can be utilized efficiently for multiphase reactions such as the catalytic hydrogenation of CO2, because it can achieve higher mass and heat transfer rates compared to any other contacting mode [15]. For instance, a fluidized bed reactor was used to investigate the characteristics of the RWGS reaction with Fe/Cu/K/Al catalyst; CO2 conversion in the fluidized bed reactor (46.8%) was higher than that in the fixed bed reactor (32.3%) [16]. Electrochemical promotion of the RWGS reaction has been studied in the solid oxide fuel cell (SOFC). For Cu/SrZr0.9Y0.1O3-α catalyst system, higher reaction rates were observed when hydrogen was electrochemically supplied as H+ rather than as molecular hydrogen [17]. In case of Pt/YSZ (yttrium-stabilized zirconia), the rate-determining step of the RWGS reaction is the formation of surface-bound carbon and its interaction with adsorbed hydrogen [18]. This observation is due to the combination of direct electrocatalysis (electrodecomposition of CO2, electro-oxidation of H2) and electrochemical promotion. For Pd/YSZ, CO formation is improved by six fold upon employing either negative or positive overpotentials [19]. SOFC displays great stability and durability in the RWGS reaction, and can be considered as one of the alternative routes for the production of renewable energy.

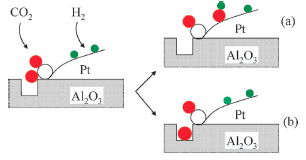
* + - 1. **Reaction mechanism**

Various advanced characterization techniques were employed to unravel the mechanism of the RWGS reaction. The mechanism has been primarily discussed over Cu-based catalysts, which is, however still controversial. Two major reaction mechanisms - redox and formate decomposition - have been proposed. The redox mechanism for the RWGS reaction has been modeled by the following scheme:

CO2  + 2Cu0 → Cu2O + CO (Eq. 5.2)

H2  + Cu2O → 2Cu0  + H2O (Eq. 5.3)

Cu0 atoms actively dissociate CO2, and therefore the reduction of oxidized Cu catalyst has to be faster than the oxidation process [20-22]. Hydrogen is proposed to be a reducing reagent without direct participation in the formation of intermediates in the RWGS reaction. The other model based on the formate decomposition suggests that CO is formed from decomposition of formate intermediate, derived from the association of hydrogen with CO2 [6, 23, 24]. Chen et al. [25] have examined the desorption energies of CO2, active sites, and reaction mechanism of the RWGS reaction on Cu nanoparticles. The Cu nanoparticles strongly bind CO2 molecules, as evidenced by two main peaks with maxima at 353 K (α peak) and 525 K (β peak) in CO2-TPD (temperature programmed desorption of CO2 - figure not shown) spectra. β-type CO2 is substantiated as the major species for the RWGS reaction. Since an infrared band at 2007 cm-1 was observed and assigned to CO adsorbed on low-index copper facets, the authors proposed that the reaction pathways mainly include the formation of the formate species [26, 27]. Different mechanisms were proposed for the reaction over Pd- and Pt-based catalysts. In a study using Pd/Al2O3 catalysts and supercritical mixture of CO2 and H2, infrared spectra indicated the formation of surface species such as carbonate, formate, and CO [28]. However, only carbonate and formate were observed on a bare alumina support. From these contrast observations, one can deduce that Pd facilitates the dissociative adsorption of H2 and the formation of formates and CO. Another proposed mechanism over Pt/Al2O3 is shown in Scheme 5.1 based on the results acquired from in situ attenuated total reflection infrared spectroscopy (ATR-IRS) [29].



Scheme 5.1. Schematic representation of the proposed mechanism of CO2 reduction on a Pt/Al2O3 model catalyst. Red, white, and green balls depict carbon, oxygen, and hydrogen atoms, respectively. [Reproduced with permission from Ref. 29. Copyright 2002 Royal Society of Chemistry]

The reaction of CO2 and hydrogen takes place at the interface between Pt and Al2O3, and the CO formed could serve as a probe molecule for the boundary sites. CO2 adsorbs on oxygen defects of Al2O3 thin film to form carbonate-like species, and then reacts with hydrogen to form CO. In order to dynamically identify the surface species over a Pt/CeO2 catalyst, Goguet et al., [30] developed a detailed spectrokinetic analysis monitored by diffuse reflectance Fourier transform infrared spectroscopy (DRIFT) and mass spectrometry (MS) using steady-state isotopic transient kinetic analysis (SSITKA). A reaction model involving three kinds of mechanism is proposed in Fig. 5.1. Both formates and Pt-bound carbonyls species were observed, but neither of them was the main reaction intermediate, although the formation of CO from formates was likely to occur to a limited extent. The RWGS reaction proceeds mainly via surface carbonate intermediates, including reaction between the surface carbonates and oxygen vacancies or the diffusion of the vacancies in ceria.



Fig. 5.1. Model for the reaction mechanism of the RWGS reaction over Pt/CeO2  [Reproduced with permission from ref. 30. Copyright 2004 American Chemical Society].

Theoretical investigations using model systems may assist to unravel the nature of molecular interactions. Qin et al. [31] investigated the mechanism of the RWGS reaction on a Ni surface using density functional theory (DFT) calculations and predicted that the C-O bond cleavage of CO2 occurred before the dissociation of the H2. The H2 moiety could promote the charge transfer in the Ni insertion process and facilitate the dissociation of coordinated CO2 molecule by reducing the energy barrier. The rate-determining step for the reaction is the migration of hydrogen atom from Ni center to oxygen atom with the formation of water. Liu et al. [32] reported the modeling of the reaction mechanism for the RWGS reaction with first-row transition metal catalysts L’M (L’ = C3N2H5- ; M = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn). The first step of catalytic reaction is the coordination of a CO2 molecule (L’M(CO2)). The second step is the scission of L’M(CO2) to produce L’M(CO) and L’M(O)

by adding L’M, which is followed by hydrogenation of the oxo complex L’M(O) to generate L’M(H2O). The last step involves the dissociation of H2O and CO. Reaction enthalpies for all the steps are depicted in Fig. 5.2.



Fig. 5.2. Reaction enthalpies (kcal mol-1) for each metal based enthalpies calculations. [Reproduced with permission from Ref. 32. Copyright 2010 American Chemical Society]

For catalytic cycle of the RWGS reaction, the key discriminating steps are the coordination and reduction of CO2. Early metals favor these steps thermodynamically, while late metals are more feasible for the hydrogenation of oxo complex [32].

* + 1. **Methanation of Carbon Dioxide**

The methanation of CO2 has wide range of applications such as formation of syngas and production of compressed natural gas. National Aeronautics and Space Administration (NASA), USA has conducted research on the application of this reaction in manned space colonization on Mars [33] to convert the Martian CO2 atmosphere into methane and water for fuel and astronaut life-support systems [34]. Catalytic hydrogenation of CO2 to methane is an important catalytic process named as Sabatier reaction (Eq. 5.4).

CO2 + 4H2 → CH4 + 2H2O ΔH298K = -252.9 kJmol-1 (Eq. 5.4)

Though the methanation of CO2 is thermodynamically favorable (ΔG298K = -130.8 kJ mol-1), the reduction of fully oxidized carbon to methane is an eight-electron process with significant kinetic limitations, catalyst is necessary to attain acceptable rates and selectivities [35]. Extensive studies have been carried out on the metal-based catalytic systems for the hydrogenation of CO2 to methane.

* + - 1. **Metal Based Heterogeneous Catalysts**

Hydrogenation of CO2 to methane formation has been investigated using a number of catalytic systems based on VIIIB group metals (e.g., Ru and Rh) supported on various oxides with high surface areas (e.g., SiO2, TiO2, Al2O3, ZrO2, and CeO2). Supported nickel catalysts remain as the most widely studied materials. The nature of support plays a key role by influencing the interaction between nickel and support, and thus determines catalytic performances toward activity and selectivity for CO2 methanation [36]. Amorphous silica extracted from rice husk ash (RHA) has high specific surface area (125-132 m2 g-1), melting point, and porosity. Chang et al. [37-39] reported that nickel catalysts supported on amorphous silica are active for methanation of CO2. In Table 5.1 the turnover frequency (TOF) of methane (methane produced per nickel site per second) for hydrogenation of CO2 on highly dispersed nickel catalysts prepared by various methods is given. Hydrogenation activity of nickel nanoparticles supported on amorphous silica is better than those on silica gel [39]. Amorphous silica is also used as a raw material for preparing a series of silica-alumina composites as supports for nickel-based catalysts (Ni/RHA-Al2O3) synthesized via ion exchange method [41]. The reduction of NiO from the layered nickel compound is difficult due to the presence of alumina trapped in the NiO particles, which lead to an increase in activation energy of reduction [41]. The calcination and reduction temperatures employed for the catalysts preparations influence the ability of the catalysts, impacting the extent of CO2 conversion and yields of CH4. Hydrogenation activity decreases as the content of alumina increases, indicating that acidic sites are not uniquely responsible for the reaction. Ni/RHA-Al2O3 catalyst was also prepared through incipient wetness impregnation method and it had exhibited favorable catalytic activity owing to the mesoporous structure and high surface area [36]. A strong interaction between metal and oxide (SIMO) was found for this system. Consequently, highly dispersed nanocrystallites of nickel oxide (e.g., NiO and NiAl2O4) were formed. At an optimized reaction temperature (773 K), maximized yield (~ 58%) and selectivity of CH4 (~ 90%) were obtained [36]. Ni/RHA-Al2O3 exhibited higher catalytic activity than Ni/SiO2-Al2O3, due to better metal dispersion and higher chemical reaction rate.

Table 5.1. Comparison of activities of CO2 methanation on nickel catalysts

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Catalyst | Preparation Route | Dispersion (%) | T/K | TOF (103 s-1) | Ref. |
| 4.3wt% Ni/SiO2-RHA | Ion-Exchange | 40.7 | 773 | 17.2 | [39] |
| 4.1 wt% Ni/SiO2-gel | Ion-Exchange | 35.7 | 773 | 11.8 | [39] |
| 3.5 wt% Ni/SiO2-RHA | Deposition - Precipitation | 47.6 | 773 | 16.2 | [38] |
| 3.0 wt% Ni/SiO2 | Impregnation | 39.0 | 550 | 5.0 | [40] |

Highly dispersed metal supported catalysts are of interest due to enhancement of the support effect on dispersion of the active phase. Du et al. [34] employed Ni/MCM-41 catalysts with different amounts of Ni for CO2 methanation. High selectivity (96.0%) and space-time yield (STY, 91.4 g kg-1 h-1) were achieved on 3 wt% Ni/MCM-41 at a space velocity of 5760 kg-1 h-1, superior to those of Ni/SiO2 catalysts and comparable to Ru/SiO2 catalysts [40, 42, 43]. The high selectivity is maintained at higher reaction temperature (673 K) with increased STY (633 g kg-1 h-1). Reduction at 973 K produces stable catalyst exhibiting the best activity and selectivity since most Ni species is reduced to highly dispersed Ni0 due to the surface anchoring effect [34]. ZrO2 is another support of interest due to its acidic/basic features and CO2 adsorption abilities. Ni/ZrO2 catalysts with various amounts of ZrO2 polymorph have been prepared from amorphous Ni-Zr alloys [44]. Fraction of tetragonal ZrO2 (t-ZrO2) increases with increasing nickel content, influencing the methanation activity. Nickel nanoparticles supported on t-ZrO2 show a higher TOF (5.43 s-1 at 473 K) and better CO2 adsorption than those loaded on the monoclinic ZrO2 (m-ZrO2) (0.76 s-1 of TOF at 473 K) [44]. Ce-Zr binary oxides have also been used in CO2 methanation as supporting materials for supplying oxygen species with high mobility. Ocampo et al. [45] studied Ni/Ce0.72Zr0.28O2 catalysts for the synthesis of methane. A catalyst with 10 wt% Ni exhibits excellent catalytic activity and stability in the reaction during 150 h on stream, yielding CO2 conversion and CH4 selectivity to the extents of 75.9% and 99.1%, respectively. The high oxygen storage capacity of Ce0.72Zr0.28O2 and its ability to enhance nickel dispersion is the origin of the high performance. The incorporation of nickel cations into the Ce0.72Zr0.28O2 structure and the higher dispersion of Ni improve the redox properties of the material, and prevent sintering of the metal. Perkas et al.[46] developed Ni/ZrO2 catalysts doped with Ce or Sm cation and found that the catalyst containing maximum pore volume and size are obtained with 30 mol% Ni loading, showing higher catalytic activity towards CO2 methanation (1.5 s-1 of TOF at 573 K) and this observation could be ascribed to the synergistic effect between the surface area and the doping of the rare earth elements. The surface area of the catalyst is increased due to the mesoporous structure of the support, which leads to the insertion of the Ni particles into the pores. The catalytic activity could be further improved by a redox pretreatment [46].

Raney nickel is a well known active catalyst for hydrogenation that appears to exhibit high reactivity in the methanation reaction [47]. The notable catalytic performance is attributed to its unique thermal and structural stability as well as a large BET surface area. CH4 and CO have been found to be the main products over Ni-Al alloys [48]. An increase in Ni content leads to higher selectivity to methane (100%), since Ni (compared to Al) readily dissociates CO. A series of mono- and bi-metallic Ni-based catalysts supported on alumina were examined through computational study [49]. The conversion of CO2 to methane is significantly increased over Ni-Fe alloy compared to pure nickel or iron catalyst, and the catalyst with a Ni/Fe ratio higher than 1 showed excellent performance.

The major problem with Ni-based catalysts is the deactivation at low temperature due to the interaction of the metal particles with CO and formation of mobile nickel subcarbonyls [50]. Instead, noble metal (e.g. Ru, Pd, and Pt) is stable at operating conditions and more active for CO2 methanation than nickel [51]. Kowalczyk et al. [52] studied the effect of the support on catalytic properties of Ru nanoparticles in CO2 hydrogenation, and found that TOFs of Ru-based catalysts were dependent on the Ru dispersion and the type of supports. For high metal dispersion, the following order of TOFs (x103 s-1) for the reaction was obtained: Ru/Al2O3 (16.5) > Ru/MgAl2O4 (8.8) > Ru/MgO (7.9) > Ru/C (2.5) [52]. The catalytic activity of ruthenium nanoparticles is strongly affected by the metal-support interaction. In the case of Ru/C systems, the carbon moiety partially covers the metal surface and reduces the number of active sites (i.e., site blocking effect) [52]. Under steady-state conditions, reaction rate of a highly loaded 15 wt% Ru/Al2O3 is about 10 times higher than that of Ni-based catalysts. Highly dispersed Ru nanoparticles were also synthesized on TiO2 through a barrel sputtering method [53]. Remarkably, a 100% yield was achieved over this catalyst at 433 K, which was significantly higher compared to that prepared by conventional wet impregnation. The prepared Ru/TiO2 sample could catalyze the methanation reaction at low temperature (300 K) with a reaction rate of 0.04 mmol min-1g-1. Further, the addition of yttrium to Ru- based catalysts not only increases the active surface area and the dispersion of ruthenium but also improves the catalytic activity and anti-poisoning capacity of the catalysts [54]. Ru/γ-Al2O3 was also used as a probe catalyst to determine kinetic parameters for CO2 methanation [55]. Apparent activation energy reaches a minimum (82.6 kJ mol-1) at a ruthenium dispersion of 50%. Reaction order with respect to hydrogen decreases with the increase in H/Ru ratio, and hence attributed to a change in adsorption heat of hydrogen and an increased number of low-coordination sites. Park et al., [35] investigated bifunctional Pd-Mg/SiO2 for CO2 methanation, being motivated by the property of Pd to dissociate molecular hydrogen [35]. At 723 K, the Pd-Mg/SiO2 catalyst shows a high selectivity (>95%) to CH4 with 59% of CO2 conversion, whereas Pd supported on silica reduces CO2 primarily to CO while Mg/SiO2 alone is inactive. A bifunctional mechanism was proposed that Pd provides disassociated hydrogen to Mg carbonates to form methane, and upon desorption of methane, the carbonate is reformed by gas phase CO2 (Scheme 5.2) [35].



Scheme 5.2. Potential bifunctional model for Pd-Mg/SiO2. [Reproduced with permission from Ref. 35. Copyright 2009 Elsevier].

Yu et al., [56] prepared platinum on titania nanotubes with high surface area (187 m2 g-1), containing scrolled multi-walled titania-nanotubes uniformly dispersed with Pt nanoparticles in the mixed valence states. CO2-TPD results showed that a large amount of CO2 adsorbed on the catalyst can be ascribed to the combined effect of the tubular structure with high surface area and Pt nanoparticles with the mixed-valence. In situ FTIR study demonstrated that CH4 was the unique product and the catalyst showed high activity for CO2 methanation at low temperature (450 K). Since industrial feedstock typically contains trace amounts of sulfur compounds, Szailer et al. [57] have examined the effect of sulfur on the methanation of CO2. Interestingly, a trace amount of H2S (e.g., 22 ppm) can promote the reaction on TiO2- and CeO2-supported metals clusters (e.g., Ru, Rh, and Pd), whereas, on other supported catalysts (e.g., ZrO2- and MgO- based) or when the H2S content is high (116 ppm), the reaction rate decreases. When the support is diffused with H2S, the catalyst becomes more active, due to the formation of new active sites at interfaces between the metal and the support [57]. Most of the catalytic methanation of CO2 have been performed in fixed-bed reactors.

Application of electrochemistry in the reactor design is cost efficient and environmentally friendly to industrial processes for the minimization of waste production and toxic materials [58]. CO2 hydrogenation using YSZ solid electrolyte and Rh electrode was studied in a single chamber reactor [59]. CO and CH4 were produced at temperatures between 654 and 890 K, and the rates of CH4 and CO formation were enhanced with positive potentials (electrophobic behavior) and negative potentials (electrophilic behavior), respectively. Moreover, a monolithic electropromoted reactor (MEPR) with Rh/YSZ/Pt or Cu/TiO2/YSZ/Au cells was used to investigate the hydrogenation of CO2 at atmospheric pressure [60]. In the case of Rh/YSZ/Pt cells, both positive and negative applied potentials significantly enhance the total hydrogenation rate and the formation of CO, but the selectivity of CH4 remains below 12%. In the case of Cu/TiO2/YSZ/Au cells, selective reduction of CO2 to CH4 starts at 493 K and the selectivity of CH4 could reach ~100% at open-circuit polarization conditions at temperatures of 493-653 K [60].

* + - 1. **Reaction Mechanism**

Although the methanation of CO2 is a simple reaction, establishing the mechanistic route is a difficult task as there exist different opinions on the nature of the intermediate and the methane formation process. Reaction mechanisms proposed for CO2 methanation fall into two main categories. The first one involves the conversion of CO2 to CO prior to methanation, and the subsequent reaction follows the same mechanism as CO methanation [61-65]. While the second category involves the direct hydrogenation of CO2 to methane, without the CO intermediate formation [66, 67]. It can be noted that even for CO methanation, there is a lack of understanding on the kinetics and mechanism. It has been proposed that the rate-determining step is either the formation of the CHxO intermediate and its hydrogenation or the formation of surface carbon in CO dissociation and its interaction with hydrogen [65, 68]. Steady-state transient measurements have been employed in kinetic investigations on a Ru/TiO2 catalyst to identify reaction intermediates [64]. CO is a key intermediate and its hydrogenation leads to the formation of methane. Formates, also as intermediates for the formation of CO, are bound more strongly on the support in equilibrium with the active formate species on the interface between metal and support. A reaction mechanism (Scheme 5.3) is proposed including the formation of the formate through a carbonate species.



Scheme 5.3. Proposed reaction mechanism for CO2 methanation [Reproduced with permission from Ref. 64. Copyright 1997 Elsevier].

A surface science approach using model systems aids in understanding mechanistic aspects of reactions. Ni single crystals have been considered to be the reasonable models of practical catalysts for methanation [69, 70]. Peebles et al., [42] studied the methanation and dissociation of CO2 on Ni(100) and calculated the activation energies for the formation of CH4 and CO as 88.7 kJ mol-1 and 72.8-82.4 kJ mol-1 respectively. The activation energy and reaction rate for CO2 methanation are very close to values for CH4 formation from CO under identical reaction conditions. The results support a mechanism that CO2 is converted to CO and subsequently to carbon before hydrogenation. Using the ASED-MD (atom superposition and electron delocalization-molecular orbital) theory, Choe et al. [71] investigated the CO2 methanation on a Ni(111) surface in a detailed manner. The elementary reaction steps are listed below.

CO2ads → COads + Oads (Eq. 5.5)

COads → Cads + Oads (Eq. 5.6)

2COads → Cads + CO2gas (Eq. 5.7)

Cads + Hads → CHads (Eq. 5.8)

CHads + Hads → CH2ads (Eq. 5.9)

CH2ads + 2Hads → CH2gas (Eq. 5.10)

These elementary steps consist of two mechanisms - carbon formation and carbon methanation. For the first mechanism, the activation energies were calculated to be 1.27 eV for CO2 dissociation, 2.97 eV for the CO dissociation, and 1.93 eV for the 2CO dissociation. For the carbon methanation mechanism, following activation energies were reported: 0.72 eV for methylidyne, 0.52 eV for methylene, and 0.50 eV for methane [70]. Thus, CO dissociation is the rate-determining step. In aiming to provide clear insights into the role of Pd and MgO, Kim et al. [72] used computational and experimental methods investigating the reaction mechanism of CO2 methanation on Pd-MgO/SiO2. CO2-TPD results agree with DFT calculations that MgO initiates the reaction by binding CO2 molecules, forming an activated surface magnesium carbonate species. Pd species dissociates molecular hydrogen, essential for further hydrogenation of the carbonates and residual carbon atoms. The bifunctional reaction mechanism is consistent with the previously proposed reaction scheme (Scheme 5.2). Interestingly, it has been demonstrated that CO2 can react with H2 over Rh/γ-Al2O3 catalyst to produce methane at room temperature and atmospheric pressure with a high selectivity (99.9-100%), even in the absence of photo excitation [73]. Jacquemin et al. [74] looked into the reaction mechanism of CO2 methanation on the Rh/γ-Al2O3 catalyst to better understand this process. The dissociation of CO2 into CO and oxygen on the surface of the catalyst has been evidenced via in situ DRIFT experiments (Fig. 5.3).



Fig. 5.3. DRIFT results after adsorption of CO2 and CO and after adsorption of CO2 and reaction with hydrogen. [Reproduced with permission from Ref. 74. Copyright 2010 Elsevier]

The formation of COads was confirmed by the presence of the bands corresponding to linear Rh-CO (2048 cm-1), Rh3+-CO (2123 cm-1), and Rh-(CO)2 (2024 and 2092 cm-1). CO2 adsorbed as Rh-(CO)2 and CO associated with oxidized Rh are the most reactive species with hydrogen.

* + 1. **Synthesis of Hydrocarbons**

As fossil fuel depletion, global warming, climate change, and hikes in the price of fuels are driving scientists to investigate on commercial and environmentally friendly fuels, the process of CO2 conversion to value-added products is considered as a possible remedy to meet the requirements. In this context, it is highly desirable to develop alternative fuels from non-fossil fuel sources and processes. The products of CO2 hydrogenation such as methanol and hydrocarbons are excellent fuels for use in internal combustion engines, as they can be easily stored and transported. Further, methanol is a raw material in chemical industries. In the following sections, two different processes, namely hydrocarbon and methanol synthesis through CO2 hydrogenation are presented in detail - starting with hydrocarbon synthesis, reaction mechanism, and continues with the effect of catalyst and reactor on enhancement of product efficiency by hydrogenation of CO2. It proceeds to the second process covering reaction mechanism as well as effect of catalyst type, operating conditions and reactor type on the process improvement. A brief overview on the reactor types as the most effective component of the theoretical and experimental reported results on the process improvement is given and all the information is tabulated to provide clear understanding.

CO2 can be hydrogenated to hydrocarbons either by direct or indirect routes, e.g. via synthesis gas and/or methanol intermediate formation [75-77]. The indirect route can be either a multi-stage approach, e.g. with different reactors, or a single-stage approach, using hybrid catalysts to simultaneously perform the multi-step transformation as shown in Eqs. 5.11- 5.13.

CO2 + H2 ↔ CO + H2O ΔH573K = 38kJ mol -1  (Eq. 5. 11)

CO + 2H2 → (CH2) + H2O ΔH573K = - 166kJ mol -1  (Eq. 5. 12)

CO2 + 3H2 → (CH2) + 2H2O ΔH573K = - 128kJ mol -1 (negligible) (Eq. 5. 13)

Production of hydrocarbons from CO2 hydrogenation is essentially a modification of the Fischer-Tropsch (FT) synthesis, where CO2 is used instead of CO. CO2 hydrogenation to methane (Sabatier reaction) is also well known, but the larger consumption of H2, lower energy per volume and more difficult to store compared to oxygenated species like methanol or DME, and therefore, this route is not favorable for the conversion of carbon dioxide to fuels using H2. In general, the production of hydrocarbons compared to oxygenated forms from CO2 requires a more intensive use of resources - energy, H2, more reaction steps, etc., and thus in principle is a less favorable route for the production of fuels, though other motivations and incentives such as market needs, better infrastructure integration, etc. may justify this route. Therefore, an integrated techno-economic and life-cycle assessment is necessary to evaluate the different options, but limited data on these aspects are available in the literature. The production of light alkanes from carbon dioxide is fundamentally a modification of the Fischer-Tropsch synthesis, where CO2 is used instead of CO, and in which the catalyst composition is tailored to maximize the production of light alkanes. These products would be utilized as liquefied petroleum gas (LPG) or petrochemical feed stocks. In FT route, the relative competition between CO and CO2 is an important aspect to consider. The conversion of CO/H2, CO2/H2 and (CO + CO2)/H2 mixture using cobalt catalysts under typical FT conditions has been investigated by Zhang et al. [78, 79]. Similar catalytic activities, but different selectivity was achieved by feeding only CO or CO2. In CO hydrogenation, normal FT synthesis product distributions were observed with a factor about 0.80. In contrast, the CO2 hydrogenation products contained about 70% or more of methane as shown in Fig. 5.4. Therefore, CO2 and CO hydrogenation follows different reaction pathways. There are also differences in terms of catalyst stability. The catalyst deactivates faster by feeding CO instead of CO2 even though the H2O/ H2 ratio is at least two times larger for the conversion of CO2 [80]. However, over Fe-Al2O3-Cu-K catalyst the same hydrocarbon products were obtained in CO2 or CO hydrogenation [81]. The different behavior in Fe-and Co-based FT catalysts was explained by a different inhibition steps of methane formation and product desorption as a prerequisite for chain growth [81]. In the iron case, there is irreversible carbiding and alkali surface coverage, while in the cobalt case there is a strong reversible CO adsorption. γ-Al2O3 was observed to be the best support with iron as active site and potassium was an excellent promoter [81]. It should also be considered that for iron catalysts the active phase forms in situ (formation of iron carbide-Fe5C2) [82]. It was observed that the lattice parameters of iron and cobalt carbides change as a function of the feed composition [83]. The lattice parameters are constant in CO/H2 but decrease in CO2/H2. Furthermore, the CO/H2 reaction occurs without a preliminary reduction unlike under CO2/H2, in which it is necessary. Therefore, the effective catalysts for CO/H2 or CO2/H2 FT reactions are different. In terms of performances, Co-based catalysts form high amounts of methane, while Fe-based catalysts give better results, comparable to those feeding synthesis gas. Combining the iron-based FT catalyst with zeolites, it is possible to maximize the formation of isoalkanes. CO2 hydrogenation over Fe-Zn-Zr/HY composite catalysts [84] yields isoalkanes. Similar catalysts formed iso-butane from propylene and methanol through MTG (methanol to gasoline) reaction and iso-pentane is obtained from the reaction of C2 and C3 through the additive dimerization. In the methanol-mediated approach, CO2 and H2 react over Cu-Zn-based catalysts to produce methanol, which is subsequently transformed into other hydrocarbons such as gasoline [86, 87]. In spite of considerable efforts made in the development of composite catalysts, this approach usually yields light alkanes as major products owing to the further catalytic hydrogenation of the alkenes [88].

In the case of non-methanol-mediated process, CO2 hydrogenation proceeds via two steps RWGS reaction and FT synthesis. Cobalt catalysts are widely used in FT synthesis, owing to the high performance to cost ratio. Upon switching feeding gas from synthesis gas to the gas mixture of CO2 and H2, cobalt performs as a methanation catalyst rather than acting as an FT catalyst [78, 81, 89, 90]. Mixed Fe/Co catalysts have also exhibited low selectivity to the desired hydrocarbons [83]. Akin et al. [90] observed that products of CO2 hydrogenation contain ~70 mol% methane over Co/Al2O3 catalyst. They proposed that the conversion of CO and CO2 occurs via different reaction pathways: the former involving mainly species of C-H and O-H produced from hydrogenation, the latter involving surface-bound intermediates of H-C-O and O-H in order to better clarify the difference in product distributions of CO and CO2 hydrogenation.



Fig. 5.4. Anderson-Schulz-Flory (ASF) plots in terms of hydrocarbons selectivity during CO and CO2 hydrogenation [86].

Fig. 5.4. shows typical Anderson-Schulz-Flory (ASF) diagram in terms of selectivity of total hydrocarbons in CO and CO2 hydrogenation [91]. It is obvious that hydrogenation of CO2 does not lead to a typical ASF distribution, which differs from what takes place for CO hydrogenation. During CO2 hydrogenation a low C/H ratio is obtained due to the slow CO2 adsorption rate on the surface due to thermodynamic and chemical stability of CO2 molecules. This favors the hydrogenation of surface-adsorbed intermediates, leading to methane formation and a decrease in chain growth. Iron oxides which have been used as FT catalysts for many years are also active in both WGS and RWGS reactions [86, 92, 93]. Iron-based catalysts are attractive for the hydrocarbons synthesis due to the highly olefinic nature of the obtained products [86, 94, 95]. Iron and γ-Al2O3 can act as an active site catalyst and as best support respectively and also potassium as promoter for CO2 hydrogenation which proceeds via a two-step process - with initial reduction of CO2 to CO via the RWGS reaction followed by the conversion of CO to hydrocarbons via a FT reaction [81, 96-99]. Due to the importance of the reaction mechanism involving the facile proceeding of the reaction and catalyst deactivation, the catalyst and reactor type effect on H2/ CO2 to hydrocarbon are discussed below in detail.

* + - 1. **Reaction Mechanism**

A modified Fischer-Tropsch (H2/CO2) mechanism is presented below to validate the synthesis of hydrocarbons. The catalyst deactivation mechanism is also presented in full details to determine how the catalyst is deactivated in different stages of hydrogenation reaction which helps us to understand the reasons for the deactivation and to seek for possible solutions to mitigate the catalyst deactivation.

* + - * 1. **Modified Fischer-Tropsch mechanism**

A few reaction mechanisms for hydrogenation of carbon dioxide to hydrocarbon are postulated. Lee et al. [100] proposed a reaction mechanism as presented in Fig. 5.5.

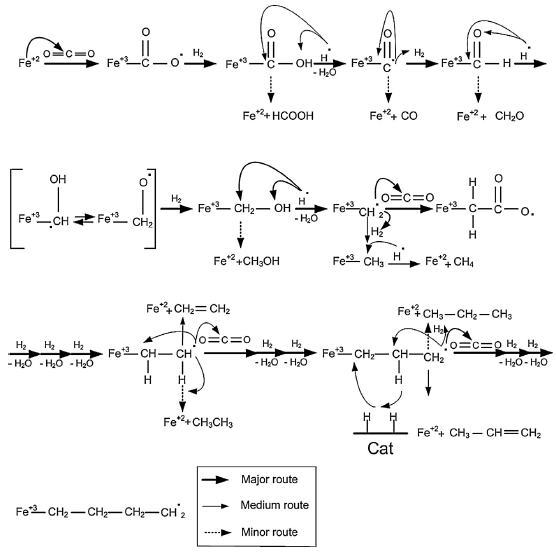


Fig. 5.5. Proposed overall reaction mechanism of CO2 hydrogenation [100]

CO2 is reduced by iron (II) followed by H radical abstraction on the catalyst surface. When the residual H attacks carbonyl C and OH, formic acid and CO are formed respectively. In the same way, Fe-CH2 radical is formed and acts as carbon-carbon propagation species. In this reaction system chain propagation is considered as a major route because higher hydrocarbon is the major product. Higher α-olefin selectivity to paraffin is attributed to less H2 uptake due to the absence of excess H2 in this reaction system and hence it is essential to moderate the hydrogen dosing during the reaction depending on the reactor configuration.

* + - * 1. **Catalyst deactivation mechanism**

Riedel et al., [82, 101] demonstrated that the steady states of hydrocarbons synthesis with iron oxides could be divided into five distinct kinetic regimes as shown in Fig. 5.6. In stage I, the reactants adsorb on the catalyst surface, predominantly carbonizing the catalyst. In stages II and III, formation of products from the RWGS reaction is dominant during the process of carbon deposition. In stage IV, the FT activity develops up to the steady state and maintains at the state of stage V. The iron phases of the reduced catalyst before the reaction consist mainly of α-Fe and Fe3O4. With time, Fe3O4 and Fe2O3 phases are consumed and a new amorphous, probably oxidic iron phase is formed, which appears to be active for the RWGS reaction. FT activity begins under the formation of iron carbide (Fe5C2) by a reaction of iron with carbon from CO dissociation. The iron-based catalysts deactivate significantly during RWGS reaction because of water formation which can cause catalyst poisoning from carbon deposit [86, 102] and hence it is crucial to remove water in situ. For example, deactivation occurs on a Fe-K/γ-Al2O3 catalyst in a packed bed reactor although the long-run activity is above 35% during the reaction [103].



Fig. 5.6. Iron-phase composition as a function of time during hydrocarbon synthesis on Fe/Al/Cu catalyst [101].

A detail reaction mechanism can be utilized to validate novel reactor configurations. By employing the membrane reactor, up to 12% can be mitigated. The stable but inactive carbide (Fe3C) is accountable for the catalyst deactivation, which is formed by Fe5C2 carburization [104]. Further, Lee et al. [104] predicted the reaction mechanism for H2/CO2 to hydrocarbon formation in order to examine the deactivation pathway of Fe-K/γ-Al2O3 catalyst by using XPS, HR-TEM, TPO and Mössbauer spectroscopy which is illustrated in Fig. 5.7. The iron-based catalysts were extensively deactivated during CO2 hydrogenation because of catalyst poisoning and carbon deposit. The characterizations of deactivated catalyst were also carried out to gain information on the deactivation pathway as a function of time and the state of the catalyst. The deactivation occurred on Fe-K/γ-Al2O3 during the reaction although the long term activity remained above 35%. The deactivation pathway differed according to reactor configuration.



Fig. 5.7. Proposed mechanism of CO2 hydrogenation over Fe-K/γ-Al2O3 catalyst [104]

As time progressed, hematite (Fe3O4) was formed after H2 reductions, and was gradually carburized to ᵪ-Fe5C3. Finally, ᵪ-Fe5C3 phase was converted to ᵪ-Fe3C, which is an inactive species for CO2 hydrogenation. The main cause for the deactivation at the inlet reactor part was phase transformation. Conversely, the main factor at the outlet reactor part was the coke deposit generated by secondary reactions.

* + - 1. **Effect of catalyst type on H2/CO2 to hydrocarbon**

The influence of catalyst type on the conversion efficiencies of H2/CO2 to hydrocarbon has been examined. The results shown in Table 5.1 indicate that four aspects of catalyst have been studied for H2/CO2 conversion to hydrocarbon formation and hence a detail discussion on these four aspects is presented below.

Table. 5.1. Summary of a few selected experimental reports on hydrogenation of CO2 to HC (C2-C4); CO2 conversion and hydrocarbons selectivity values based on the type of reactor and catalyst employed under the same experimental conditions for a few selected results are also given.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Reactor Type | Catalyst Type | | | | Operating conditions | XCO2 [%] | XCO [%] | C1 S | C2 = S | | C2 S | C3 = S | C3 S | C4 = S | C4 S | Ref. | |
| **Effect of catalyst type** | | | | | | | | | | | | | | | | | |
| Fixed-bed | Fe/SiO2 | | | T = 523-573 K, (H2/CO/CO2) = 1-3 | | 6.9 | 4.9 | 80.9 | 0 | | 13.7 | 0.12 | 4.5 | 0 | 1.3 | 81 | |
| Fixed-bed | Fe/TiO2 | | | T = 523-573 K, (H2/CO/CO2) = 1-3 | | 11.5 | 4.1 | 51.7 | 0.07 | | 16.7 | 0.57 | 14.9 | 0.51 | 8.8 | 81 | |
| Fixed-bed | Fe/Al2O3 | | | T = 523-573 K, (H2/CO/CO2) = 1-3 | | 22.8 | 2.6 | 43.2 | 0.02 | | 19.1 | 0.15 | 17.9 | 0.11 | 10.8 | 81 | |
| Fixed-bed | Fe-K/Al2O3 | | | T = 523-573 K, (H2/CO/CO2) = 1-3 | | 30.4 | 12.3 | 12.7 | 9.7 | | 1.8 | 17.0 | 2.1 | 16.9 | 0.28 | 81 | |
| Fixed-bed | Fe-K-/γ-Al2O3 FN | | | T = 500-1000 K, time | | 36.2 | 16.3 | 10.2 | 12.1 | | 2.9 | 16.2 | 4.5 | 9.2 | 1.2 | 105 | |
| Fixed-bed | Fe-K-/γ-Al2O3  FS A | | | T = 500-1000 K, time | | 14.2 | 15.3 | 16.1 | 17.5 | | 0.5 | 19.3 | 1.7 | 4.3 | 0.2 | 105 | |
| Fixed-bed | Fe-K-/γ-Al2O3  FA A | | | T = 500-1000 K, time | | 41.2 | 19.3 | 10.5 | 6.3 | | 0.3 | 6.8 | 0.8 | 11.0 | 1.2 | 105 | |
| Fixed-bed | Fe-K-/γ-Al2O3 FP | | | T = 500-1000 K, time | | 35.4 | 21.3 | 12.2 | 9.3 | | 1.8 | 14.9 | 3.3 | 10.6 | 1.3 | 105 | |
| Fixed-bed | Fe | | | P = 101 kPa | | 20.4 | 16.8 | 66.8 | NA | | 17.3 | NA | 9.4 | NA | 3.4 | 77 | |
| Fixed-bed | Mn-Fe | | | P = 101 kPa | | 22.7 | 18.7 | 55.3 | NA | | 21.6 | NA | 12.8 | NA | 5.5 | 77 | |
| Fixed-bed | K-Mn-Fe | | | P = 101 kPa | | 23.4 | 21.7 | 39.4 | NA | | 16.0 | NA | 14.3 | NA | 9.2 | 77 | |
| Fixed-bed | Fe | | | P = 1013 kPa | | 32.0 | 7.5 | 33.1 | NA | | 15.7 | NA | 15.7 | NA | 9.9 | 77 | |
| Fixed-bed | Mn-Fe | | | P = 1013 kPa | | 34.2 | 5.2 | 33.8 | NA | | 18.1 | NA | 18.1 | NA | 18.1 | 77 | |
| Fixed-bed | K-Mn-Fe | | | P = 1013 kPa | | 33.8 | 5.4 | 19.2 | NA | | 13.1 | NA | 13.1 | NA | 13.1 | 77 | |
| Fixed-bed | Fe-K-/γ-Al2O3 | | | SV = 1000-4000 ml/(gcat h) | | 51.7 | 8.0 | 7.8 | 6.2 | | 1.1 | 9.3 | 1.2 | 6.0 | 0.9 | 106 | |
| Fixed-bed | Fe-K-/La-Al2O3 | | | SV = 1000-4000 ml/(gcat h) | | 45.8 | 8.8 | 9.6 | 5.3 | | 0.9 | 7.5 | 1.0 | 5.4 | 0.9 | 106 | |
| **Effect of operating conditions** | | | | | | | | | | | | | | | | | |
| Fixed-bed | Fe-ZrO2 | | T = 573 K | | | 5.9 | 81.6 | 6.9 | | 0.6 | 10.9 | NA | NA | NA | NA | | 107 |
| Fixed-bed | Fe-ZrO2 | | T = 623 K | | | 14.1 | 17.6 | 8.5 | | 2.5 | 17.4 | NA | NA | NA | NA | | 107 |
| Fixed-bed | Fe-TiO2 | | T = 573 K | | | 3.1 | 80.3 | 10.2 | | NA | 9.5 | NA | NA | NA | NA | | 107 |
| Fixed-bed | Fe-TiO2 | | T = 623 K | | | 10.5 | 49.5 | 18.3 | | 2.2 | 32.2 | NA | NA | NA | NA | | 107 |
| Fixed-bed | Fe-K-/γ-Al2O3 | | Time on stream (h) 31 h | | | 31.33 | 6.99 | 10.69 | | C2–C4 36.29 | NA | NA | NA | NA | C5–C7 17.43 | | 108 |
| Fixed-bed | Fe-K-/γ-Al2O3 | | 850 h (deactivated catalyst) | | | 25.75 | 10.34 | 14.13 | | C2–C4 40.61 | NA | NA | NA | NA | C5–C7  13.82 | | 108 |
| Fixed-bed | Fe-K-/γ-Al2O3 | | After deactivated catalyst 37.8 h | | | 26.39 | 10.35 | 14.64 | | C2–C4 40.78 | NA | NA | NA | NA | C5–C7  12.67 | | 108 |
| Fixed-bed | Fe-K-/γ-Al2O3 | | After air-oxidation 40 h | | | 30.91 | 6.32 | 12.82 | | C2–C4 38.10 | NA | NA | NA | NA | C5–C7  14.54 | | 108 |
| **Effect of reactor type** | | | | | | | | | | | | | | | | | |
| Fixed-bed | | Fe-Cu-K-Al | | | T = 300, 325 °C | 35.6 | 9.6 | 10.9 | | 5.8 | 3.2 | 11.6 | 2.9 | 9.3 | 2.4 | | 109 |
| Fluidized-bed | | Fe-Cu-K-Al | | | T = 300, 325 °C | 48.9 | 8.8 | 12.2 | | 7.8 | 1.6 | 14.1 | 0.2 | 8.2 | 0.8 | | 109 |
| Fixed-bed | | Fe-Cu-K-Al | | | T = 250-350 °C, P = 1-4 MPa | 32.2 | 11.0 | 8.5 | | 5.1 | 1.9 | 9.4 | 3.4 | 8.0 | 3.6 | | 110 |
| Fluidized-bed | | Fe-Cu-K-Al | | | T = 250-350 °C, P = 1-4 MPa | 46.8 | 14.5 | 9.2 | | 6.2 | 2.2 | 10.0 | 1.2 | 6.7 | 1.1 | | 110 |
| Fixed-bed (single) | | Fe:K:  Al2O3 | | | Sv single = 1000 ml/(gcat h) | 40.8 | 11.1 | 7.4 | | 5.8 | 1.4 | 9.6 | 1.1 | 7.0 | 0.9 | | 100 |
| Series | | Fe:K:  Al2O3 | | | Sv series = 1000 | 68.5 | 13.7 | 10.1 | | 4.9 | 2.4 | 6.5 | 1.1 | 3.4 | 0.8 | | 100 |
| Recycle reactor-A | | Fe:K:  Al2O3 | | | SVF(A) = 1000 R = 3,SV = 40000 | 62.5 | 4.3 | 4.8 | | 3.6 | 1.1 | 5.8 | 0.8 | 4.1 | 1.0 | | 100 |
| Recycle reactor-B | | Fe:K:  Al2O3 | | | SVF(B) = 570 R = 6,SV = 4000 | 75.6 | 2.2 | 7.3 | | 3.8 | 2.2 | 7.4 | 1.2 | 3.8 | 0.8 | | 100 |
| Recycle reactor-C | | Fe:K:  Al2O3 | | | SVF(C) = 330 R = 5,SV = 2000 | 88.2 | 2.1 | 12.1 | | 2.7 | 3.3 | 4.8 | 2.2 | 3.2 | 1.3 | | 100 |
| Fixed-bed | | Fe-Cu-K-Al | | | T = 300 °C. STY = 31.8 | 35.6 | 9.6 | 10.9 | | 5.8 | 3.2 | 11.6 | 2.9 | 9.3 | 2.4 | | 111 |
| Fluidized-bed | | Fe-Cu-K-Al | | | T = 300 °C. STY = 41.8 | 46.8 | 8.2 | 9.8 | | 7.5 | 2.1 | 13.7 | 1.3 | 8.8 | 1.2 | | 111 |
| Slurry | | Fe-Cu-K-Al | | | T = 300 °C. STY = 35.2 | 39.4 | 7.6 | 8.3 | | 3.7 | 1.7 | 6.3 | 1.5 | 3.7 | 1.9 | | 111 |
| Fluidized-bed | | Fe-Cu-K-Al | | | T = 325 °C. STY = 43.7 | 48.9 | 8.8 | 12.2 | | 7.8 | 1.6 | 14.1 | 1.2 | 8.2 | 0.8 | | 111 |
| Slurry | | Fe-Cu-K-Al | | | T = 275 °C. STY = 28.9 | 32.4 | 7.4 | 5.8 | | 3.5 | 2.1 | 5.6 | 1.6 | 3.3 | 2.1 | | 111 |

* + - * 1. **Role of Active Site**

Unlike cobalt, iron as an active site is known to exhibit higher WGS activity, which makes it a less attractive choice for FT application as it will yield a notable amount of CO2 as product. However, when choosing a metal catalyst for CO2 hydrogenation, the attributes which make Fe unattractive for FT favor in the conversion of CO2 to hydrocarbon. CO2 hydrogenation over an iron catalyst has been shown to proceed via a two-step process, with initial conversion of CO2 to CO via the reverse water-gas shift reaction (RWGS) followed by chain propagation [96, 98, 112, 113] with water vapor displaying an inhibiting effect on the reaction rate [98]. Therefore, it is necessary to find a way to remove the H2O and such one way is to employ water permeable membranes within the reactor [113]. Riedel et al. [98] reported a calculated equilibrium conversion of 72%, with actual conversion levels between 46 and 53%. In general, the reported conversion levels range from 19% to 68% [114-116, 111] depending on the type of reactors, different catalysts as well as experimental conditions. It is noteworthy to mention that methane is thermodynamically the most favored HC product [98] while alkene selectivity in the C2 - C5 range of around 80% is commonly reported [81, 98, 116, 117]. Further, it is postulated that as ethane is re-adsorbed onto the catalyst’s surface and subsequently incorporated in the chain growth leading to long chain HCFT regimes, the ASF distributions deviate at the C2-products with lower than expected concentrations[118-120]. This phenomenon is, however, not apparent in ASF plots in CO2 hydrogenation regimes, with C2 products seemingly high in concentration [98, 117]. However, as with FT regimes, one can assume that either the iron magnetite phase is responsible for the water gas shift activity [121] or an amorphous oxidic iron phase [101], while the carbide phase is essential for chain growth, most likely the χ-Fe5C2 phase [122, 123]. CO2-hydrogenation over iron-based catalysts yields high percentages of alkenes, which can be easily upgraded to HC fuels as shown in Fig. 5.8 [124].

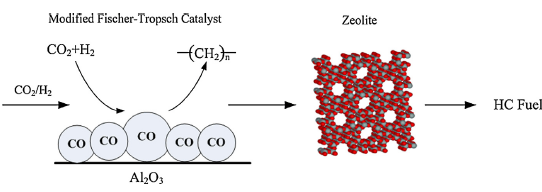


Fig. 5.8. Schematic representation of CO2 conversion to HC fuels, employing a two stage synthesis process, with CO2 initially converted to alkenes, which are then subsequently converted to HC fuel over a solid acid catalyst such as zeolites [117].

* + - * 1. **Role of Promoter**

Promoters are often added to catalysts to tailor and optimize product distribution. For CO2 conversion to HC fuels, they are employed to increase the yield of the desired hydrocarbon products. Though iron catalysts are able to convert CO2 with a much higher affinity for alkenes and long chain HC in comparison to cobalt, the undoped catalyst show high selectivity to undesired products and thus promoters are needed to tailor and optimize the synthesis yield [117]. Promoters can either act as electronic promoters or as structural promoters, or possibly as both. Structural promoters affect the formation and stabilization of the active phase of the catalyst, leading to a better dispersion of the catalyst over the support, which tends to yield higher conversion rates. Electronic promoters on the other hand may donate or withdraw electron density near the valence band of the catalyst, and thus modifying the local electron density around the surface which lead to the modification of the active site. Electronic promoters usually not only increase conversion levels, but also alter product selectivity [117]. The role of Mn has been reported to be two fold. Besides acting as a structural promoter, Mn also has an electronic effect on iron. The addition of Mn to an iron catalyst suppresses methane formation and increases the alkene/alkane ratio in FT as well as CO2 hydrogenation [116, 117] acting both as a structural and an electronic promoter [125]. It is suggested that Mn promotes catalyst reduction, the dispersion and carburization of the precursor Fe2O3-state, while increasing the surface basicity of the catalyst [126], possibly by the incorporation into the lattice of iron [114]. Over doping of the iron catalyst imparts negative effect by blocking the active sites and forming undesired products, thereby reducing CO conversion [87, 126, 127] efficiency. Copper can often replace Mn as a promoter in iron-based CO2 hydrogenation catalysts as its performance is similar to Mn in significantly enhancing the CO2 hydrogenation ability of iron. Copper, besides being a RWGS catalyst [128], has been reported to augment the reduction of the hematite particles during carburization and by increasing the dispersion of the catalytic particles [122]. When copper is reduced to its metallic form, it provides active sites for dissociative adsorbion of hydrogen [114]. The addition of potassium has a significant influence on the overall performance of the catalyst [129]. The role of potassium, both in FT as well as CO2 conversion is still not clearly understood; however, the difference among alkaline promoters is not understood clearly [114]. Potassium has been shown to act as an electronic promoter in FT rather than a structural promoter. Dry et al., [130] proposed that potassium lowers the metal work function by donating electron density to the vacant d orbital of the iron, enhancing the dissociative adsorption of CO while lowering the H2 adsorption ability. A decrease in H2 adsorption thus leads to a reduction in the hydrogenation of alkenes and therefore the alkene content increases [77, 127, 130, 131]. While for FT larger amounts of K are known to poison the iron catalyst, in CO2 hydrogenation it is beneficial to have a larger amount of K promoter [98, 127]. Addition of potassium has been demonstrated to increase CO2 conversion and decrease the methane yield [127, 132, 133]. In fact, increasing the alkene/alkane ratio almost fourfold with a shift toward longer chain HC was also observed [127]. The ASF distribution for K/Mn/Fe CO2 hydrogenation catalysts shows a high chain growth probability which is only slightly lower than with iron catalysts in FT [81, 127, 134]. Ceria is a well-known and well-documented WGS catalyst. Based on the reaction mechanism outlined below, where CO2 is initially converted to CO via the RWGS reaction before the occurrence of chain growth, ceria could be considered as an ideal promoter for iron-based CO2 hydrogenation catalysts. Perez-Alonso et al., tested unsupported Fe-Ce catalysts for hydrogenation of CO2, and the catalyst showed less activity than the unpromoted iron catalyst for chain growth but yielded a larger percentage of CO [135, 136]. Based on the product composition and by considering the reaction mechanism, it is concluded that ceria deactivates the catalyst’s hydrogenation activity by blocking the iron active sites. Based on this assumption a supported iron catalyst was tested by Perez- Alonso group, where the ceria might show preference to be deposited on the support in favor of the iron/manganese particles, which in turn would result in an improved activity. However, the results are similar to that of the unsupported catalyst with ceria showing a preference to be deposited on the surface of the particle, blocking ultimately the more important chain growth active site of the catalyst [137]. Deactivation of catalyst with time-on-stream is reported to occur via crystallite size growth and component separation, with corking of the catalyst only playing a minor role [108]. Other promoters ranging from Zn [115], Zr [138], Ru [138, 104], Mg [139] and La [140] have also been investigated but are of minor importance.

* + - * 1. **Influence of Support**

Iron-based catalysts dispersed on different supports exhibited notable variations in product distributions as presented in Table 5.1 [101]. The supports act as stabilizers preventing the sintering or Oswald ripening of catalytically active particles during the reaction. As supports, γ-Al2O3 performs best followed by silicas and titanias [81,102, 107]. γ-Al2O3 appears to hinder sintering due to strong metal support interactions, which leads to a well dispersed catalyst [141]. However it has been reported later that the improvement of the catalyst on γ-Al2O3 may be attributed to the support forming a catalytically active phase with the catalyst [62]. The improved performance of iron-based hydrogenation catalysts dispersed on γ-Al2O3 as well as the significant difference in promotion between potassium and other alkali metals in CO2 hydrogenation can be explained by this phase formation. When both γ-Al2O3 and K are used as part of the catalyst, there is a possibility for the formation of KAlH4 (potassium alanate) phase. KAlH4 is known for its reversible hydrogen sorption at moderate temperatures (523-573K) [8]. The presence of K-alanate would facilitate the reduction of the hydrogenation of surface-bound carbonaceous species and act as a H2-reservoir. This would result in higher alkene and lower methane selectivity. The alanate phase may also play some role in the activation of molecular hydrogen. It is known that K is far superior in promoting iron catalysts in comparison with Na [114]. This is in good agreement with the alanate concept, as sodium alanate is known to adsorb/desorb and activate hydrogen at much lower temperatures (around 523 K) in comparison to the equivalent potassium form [8] and is thus much less useful at the operating temperatures used in FT/CO2 hydrogenation reactors. The difference in activity (almost two fold) of the sodium and potassium promoted catalyst [114] cannot simply be ascribed to the variation in basicity of the alkali oxides, which only amounts to approximately 18% [80]. In contrast, chemisorption experiments on Fe-Al catalysts have shown that upon addition of K, CO2 adsorption increases while H2 adsorption decreases [81, 102] - an observation in good agreement with mentioned reaction mechanism of hydrogenation of CO2 to hydrocarbon based on surface basicity theory [104]. However, as the chemisorption experiments were conducted at room temperature rather than at the elevated temperatures and conditions of an FT reactor, conclusions cannot be drawn from this regarding the alanate phase. The potassium alanate model does not challenge the role K2O or KOH species may play in the catalytic cycle and their influence on surface basicity, but augments this role. It also implies the necessity to include both K and Al as part of a successful CO2 hydrogenation catalyst at operating temperatures around 573K.

* + - * 1. **Effect of Binder**

Catalytic behavior with and without binder in CO2 hydrogenation was investigated by Lee et al [105]. It was found that Fe-K/γ-Al*2*O3 with alumina binder exhibited excellent CO2 hydrogenation capability, while Fe-K/γ-Al2O3 with silica binder showed significantly lower capability compared with those of other catalysts. The product selectivity for catalysts with and without binder was compared under the same reaction conditions. The selectivity and activity of Fe-K/γ-Al2O3 with polyvinyl alcohol (PVA) binder tended to be similar to those of Fe-K/γ-Al2O3 without binder. Fe-K/γ-Al2O3 with silica binder catalyst system exhibited higher methane (16 mol %) and C2-C4 selectivity (43.5 mole %) than Fe-K/γ-Al2O3 without binder catalyst system. For Fe-K/γ-Al*2*O3 with alumina binder catalyst system, the main products were higher hydrocarbons such as C5+ hydrocarbon. This phenomenon can be explained if the structure and porosity of catalysts with alumina binder have differences in spite of the similarities of main chemical composition, indicating that the higher hydrocarbon selectivity of Fe-K/γ-Al*2*O3 with alumina binder catalyst system is increased with increase in strong acid sites. It is worth noting the need for adding binder. This binder is not generally chemically inert to the catalyst, particularly at high temperatures, and also is not catalytically inactive. Hence, binder-catalyst interactions can strongly influence the activity and selectivity in CO2 hydrogenation. The influence is mainly due to changes in catalytic acidity [105]. Finally, according to the above detailed discussions on the effects of catalyst type on H2/CO2 to hydrocarbon through careful investigation of all parameters, it can be concluded that the only parameter which enhances the percentage of CO2 conversion is the ‘promoter’ while the rest of parameters such as ‘binder’, ‘support’, and ‘active site’ marginally improve product selectivity.

* + - 1. **Effect of operating conditions on H2/CO2 to hydrocarbon**

In this section, the effect of operating conditions - three operational parameters namely, space velocity, temperature, and pressure - on H2/CO2 to hydrocarbon conversion is discussed based on the experimental results presented in Table 5.1.

* + - * 1. **Effect of space velocity**

The higher CO2 conversion accompanied by enhanced HC yield at low space velocity (high residence time) leads to the production of a considerably large amount of H2O. It is believed that the preference for oxide formation at low space velocity can be partially attributed to the oxidation of metallic iron by H2O. As shown in Table 5.1 the recycle reactor with SV = 2000 is the best one followed by a series with SV = 1000 and finally single reactor with SV = 1000. Space velocity (SV) is considered as a key parameter to increase conversion efficiency [100].

* + - * 1. **Effect of pressure**

Besides the effect of lowering space velocity, the HC distribution significantly shifted toward long-chain products with enhanced HC yield under elevated pressure and the olefin/paraffin ratio was lowered. Also since the RWGS reaction is reversible the pressure elevation should have no effect on CO2 conversion unless the CO produced by the RWGS reaction is subsequently consumed by the FT reaction. Although the FT is basically irreversible, as product molecules fewer than reactants, H2O would be produced which still unavoidably contribute to the obstruction of RWGS reaction and hence the CO2 conversion. The Mössbauer spectroscopic analysis reveals that Fe3O4 is the dominant phase on the used catalyst at high reaction pressure. Since H2O in both RWGS and FT reaction, high CO2 conversion, especially with enhanced HC yield as obtained under high pressure, may lead to a considerably high partial pressure of H2O on the catalyst bed; therefore, it is important to find ways to remove the H2O in situ.

* + - * 1. **Effect of Temperature**

Researchers observed the effect of reaction temperature on the time-dependent patterns of CO2 conversion. Conversion increased slowly with increasing reaction time since CO yield increased with temperature, and this is not surprising since CO is formed via the RWGS reaction, which is a reversible endothermic reaction. Therefore, finding a technique to prevent this thermal conflict between these reactions is crucial. However, the dependence of HC yield on temperature was not so obvious under the compromise between higher driving force in activity and larger tendency of deactivation due to inert carbon deposition. Further, the cleavage of carbon-carbon chain (cracking effect) appears to be high at high temperature, leading to higher CH4 in HC distribution. The enhancement of carburization also led to a higher olefin/paraffin ratio in HC products at higher temperature owing to the enhanced H-elimination effect in termination of carbon-carbon chain growth on a carbon-rich surface and reaction distort on Boudouard reaction which shown in Eq. 5.14; therefore, H2 concentration should be adjusted to avoid this condition.

CO + CO → C(S) + CO2  ΔRH300°C  = 173.5 kJ/mol (Eq. 5.14)

* + - 1. **Effect of reactor type and reactor design**

As mentioned in the reaction mechanisms section, two kinds of reaction (exothermic and endothermic) would occur along the single reactor. With regard to potential drawbacks in the fixed-bed reactor to solve and cover these potential drawbacks, fluidized bed and slurry reactors have been employed to increase the conversion of CO2 and obtain desirable products as they are beneficial for the removal of generated heat due to the highly exothermic nature of the reaction as shown in Fig. 5. 9 [111]. Moreover, hydrogenation of CO2 to hydrocarbons proceeded in fluidized bed and slurry reactors over Fe-Cu-Al-K catalyst yields better catalytic performance compared to a fixed-bed reactor [111]. Light olefins and heavy hydrocarbons can be selectively formed in fluidized bed reactors and slurry reactors respectively as shown in Fig. 5.10. However, it should be noted that slurry reactor is suitable for saturated hydrocarbons and high boiling products (based on Fig. 5.10).



Fig. 5.9. Axial temperature distribution of CO2 hydrogenation in the different type of reactor (Cat. = Fe-Cu-Al-K, SV = 2000 ml/(gcat h), P = 1 MPa, H2/CO2 = 3) [111].

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Fig. 5. 10. Influence of the process parameters with different type of reactor on the product distribution [111].

* + 1. **Production of Methanol**

Methanol is a common solvent, renewable fuel and a starting material in chemical industry. On industrial scale, methanol is currently produced from syngas by employing metal based catalysts. Replacing CO with CO2 in methanol synthesis is a great challenge. Methanol synthesis from atmospheric CO2 and hydrogen is considered as one of the economic ways to alleviate the global warming and to drive chemical and energy companies towards more sustainable use of resources. As an alternative feedstock, CO2 has replaced CO and is considered as an effective way for CO2 utilization in the methanol production [142].

CO2 + 3H2 → CH3OH + H2O ΔH298K = - 49.5 kJ mol-1 (Eq. 5.15)

From the thermodynamic point of view, a decrease in reaction temperature or an increase in reaction pressure could favor the synthesis of methanol. Indeed, enhanced reaction temperature (e.g., higher than 513 K) facilitates CO2 activation and subsequent methanol formation [142]. Furthermore, other byproducts are formed during the hydrogenation of CO2, such as CO, hydrocarbons, and higher alcohols [143]. Therefore, a highly selective catalyst is in need to avoid the formation of undesired byproducts for methanol synthesis. Typically, catalysts used in CO2 hydrogenation are those for methanol synthesis from CO hydrogenation. A number of investigations have addressed the effects of active components, supports, promoters, preparation methods, and surface morphology on reactivity.

* + - 1. **Limitation in Methanol Formation**

In CO2 hydrogenation to methanol processes, the reaction parts can be represented as in Equations 5. 15 (methanol formation) and 5.16 (reverse water-gas shift reaction, RWGS).

CO2 + H2 → CO + H2O (Eq. 5.16)

The formation of methanol increases with the decrease of reaction temperature and increase of pressure due to the exothermal CO2 and H2 reaction, endothermic RWGS reaction and reduction of reaction molecule number [144-147]. Further, the high reaction temperature favors the formation of undesired byproducts such as higher alcohols and hydrocarbons, which reduces the methanol selectivity [148, 149]. The low reactive, chemically inert CO2 require a reaction temperature higher than 513K to activate the CO2 molecules to form methanol [144,145,149]. In CO2 hydrogenation, the medium activation energies are actually lower for the methanol formation than those of the RWGS reaction. The large amount of water that come from both the reactions act as inhibitor on the active sites, leading to the deactivation of catalyst and subsequently reducing the consecutive step in the production of methanol [144-146]. Highly efficient catalysts are required in CO2 activation to increase methanol production and to suppress byproducts formation. The catalysts used in CO2 hydrogenation were mostly modified from COhydrogenation catalysts. To date, an efficient catalyst to activate the CO2 molecule has not been fully exploited for industrial applications due to the lack of design and technology in controlling the catalyst properties together and understanding the reaction mechanism. The heterogeneous catalytic activity of CO2 hydrogenation to methanol depends on various factors such as the metal and catalyst structures, particle size of the metal, distribution of the metal on the support, surface area of the catalysts, active sites on the catalyst, stability and long term operation, types of promoters and supporters and the growth of the metal particles [144, 146-153].

* + - 1. **Reaction Mechanism**

Owing to great complexity of methanol synthesis from CO2 hydrogenation, atomic level understanding regarding the reaction mechanism has been a long-standing challenge. Until now, the key issues in the field such as how and where CO2 is activated over the surface of the catalysts remain unclear [154]. Methanol formation is generally presumed to occur at the interface of Cu and oxides [155, 156]. That is, CO2 can adsorb on bare oxides and H2 can dissociate on Cu species [157]. However, the nature of active Cu phase at interface is still elusive. Koeppel et al. [158] found that active copper species is predominantly present as Cu0 over Cu/ ZrO2 based on X-ray diffraction (XRD) measurements. In contrast, Cu+ was proposed to be the active component for a Cu/ZnO/SiO2 catalyst employing static low-energy ion scatter experiments [159]. However, it has also been postulated that Cu metal and low valence states of Cu such as Cuδ+ and Cu+ may all affect the catalytic activity of Cu-based oxide catalysts [160-163]. Elucidation of the electronic and geometrical structures of the active site is the first step in a rational designing of a catalyst with high activity and selectivity [164]. Two classes of reaction routes to methanol have been contested in literature. One is the formate pathway, where the formation of intermediate HCOO is usually considered to be the rate determining step [165-168]. On Cu, the intermediate is a bidentate formate, the most stable adsorbed species; while on ZnO, the intermediate is a monodentate formate [169, 170]. The other path involves the formation of CO through the RWGS reaction and conventional gas-to-methanol conversion (CO + 2H2 → CH3OH) [155, 171]. The formate mechanism suggests that CO may be formed from methanol decomposition, while the RWGS mechanism can explain directly the formation of CO as the major byproduct [172, 173].

The mechanism of CO2 hydrogenation to methanol over Cu/ZnO catalyst using ab-initio molecular orbital (MO) calculation was proposed by Kakumoto and Watanabe [174], as shown in Fig. 5.11. CO2 is adsorbed on the Cu+ site. The H atom from H2 is being adsorbed on the metallic Cu and then attack the C atom in adsorbed CO2, forming the formate intermediate [174, 175]. Then, the C-O bond is broken simultaneously when H atoms attack the formate species on the C and O atoms, which then generates formaldehyde intermediate on the Cu+ site. The heterogeneous dissociation of H2 adsorbed on ZnO generates H- on the Zn sites and attacks the C atom of the formaldehyde to form the methoxy intermediate. Finally, methanol is produced when the H+ on the O atom of ZnO attacks the O atom of the methoxide [174]. The presence of Cu+ species in the catalyst led to higher methanol selectivity and lower RWGS reaction [149]. However, no promotional effect of Zn has been found for the RWGS reaction producing carbon monoxide and water [147, 174]. Further, the post-reaction surface analysis carried out by Fujitani et al. [147] by employing XPS demonstrated the formation of formate species on the Cu surface as an intermediate during methanol formation. The formate coverage linearly increased with the Zn coverage below θZn = 0.15, indicating that the formate species formation was stabilized by the Zn species [147]. At higher Zn coverage, more Zn was readily oxidized on Cu to ZnO during the reaction of hydrogenation, while Zn was partially oxidized without oxygen to ZnO or O on the surface of Cu under the reaction conditions. Thus, the Zn on Cu species was directly bound to the oxygen of the surface formate species as the active sites [147]. However, the mode of the copper presence on the surface and its interaction with the promoters are also crucial for optimizing the methanol formation [148, 149].

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Fig. 5.11. CO2 hydrogenation mechanism on Cu/ZnO catalyst proposed by ab-initio MO calculations [174]

A detailed study was carried out to identify the intermediates for methanol synthesis over Pd/β-Ga2O3 using *in situ* FT-IR spectroscopy [176]. The reaction follows the formate pathway, which proceeds through the formation of HCOO, H2COO (dioxo-methylene), CH3O (methoxy), and the final product, CH3OH as shown in Fig. 5.12.



Fig. 5.12. Reaction pathways for the methanol synthesis from CO2/H2 over a palladium/gallia catalyst [86].

The outstanding activity and selectivity of Pd/β-Ga2O3 catalyst are attributed to the efficient spillover of atomic hydrogen from Pd surface to the carbonaceous species and the moderate stability of methoxy species on Ga2O3. DFT calculations on Cu (111) and Cu29 nanoparticles indicated that the rate-determining steps are both HCOO and H2COO hydrogenation [177]. Compared to Cu (111), the superior activity of Cu nanoparticles for the synthesis of methanol is associated with the active corner sites and structural flexibility, which stabilize the key intermediates (HCOO, H2COO, and CH2O) and reduce the barrier of the rate-determining steps.

* + - 1. **Catalysts and Performances**

Although many kinds of metal-based catalysts have been investigated and examined for the methanol synthesis, Cu remains as the main active catalyst component, together with different promoters (Zn, Zr, Ce, Al, Si, V, Ti, Ga, B, Cr, etc.) [178,179]. An appropriate support not only affects the formation and stabilization of the active phase of the catalyst but is also capable of modifying the interactions between the major component and promoter. In addition, basicity and/or acidity characteristics of the catalyst are also determined by the selected support [154].

**Cu/ZnO catalysts**: Over the past few decades, Cu/ZnO catalyst has been intensively studied for CO2 hydrogenation to methanol [174, 180-182]. Copper alone is not efficient in the synthesis of methanol from CO2 [148, 149]. The preparation of Cu/ZnO catalyst by physical mixture of Cu/SiO2 and ZnO/SiO2 resulted in formation of the ZnOx on the surface of Cu particles to stabilize Cu+, which is a crucial catalytic species. Higher ZnO/SiO2 content gives a remarkable performance (three times greater) than that of Cu/SiO2 due to the role of ZnO/SiO2 in creating Cu+ and Cu0 as active species in driving the hydrogenation steps for the production of methanol [147, 181]. Moreover, the mixture was beneficial for stabilization of Cu+ sites on the Cu surface as ZnO could control the Cu+/Cu0 ratio without affecting the Cu morphology [175, 181]. Toyir et al., [149] and Choi et al., [175] proposed that the ZnO acts as a support and a dispersing agent during the impregnation process. For Cu/ZnO catalyst, the hydrogen was reported to come from the spillover of copper and subsequently involved in methanol synthesis on the supports [149].

**Multicomponent catalysts:** Although Cu/ZnO catalyst has been reported to be an active catalyst for methanol formation, the presence of well-dispersed Zn alone cannot guarantee a strong junction connecting the active species of Cu [146]. Therefore, various CO2 hydrogenation catalysts containing both Cu and Zn metal as the main components with different modifiers were developed. The metal surface areas and dispersion are generally observed to be the key components in CO2 hydrogenation over multicomponent catalysts [148, 149, 146, 153]. The addition of Ga2O3 on Cu/ZnO has a good promoting effect towards the methanol production, which achieved two times higher methanol selectivity than the respective Cu/ZnO due to the interaction at atomic scale between the metal oxide and copper, and strong promoting effect of Ga2O3 species on the catalyst activity and stability [149]. The loading of gallium-promoted copper-based catalysts onto Si and ZnO supports by impregnation and co-impregnation of methoxide was reported by Toyir et al., [148,149]. The hydrophobic silica supported catalyst offer higher surface area, pore volume and stability than that of ZnO, which could enhance the conversion and selectivity at the temperatures up to 543K due to the hydrophobic silica support which lead to highest dispersion of Ga2O3 and a better interaction between ZnO, Ga2O3 and Cu active sites [148, 149]. Toyir et al. [146] studied two categories of metal oxides which are effective in catalyst synthesis. Al2O3 or ZrO2 added on Cu/ZnO could increase the surface area and Cu particles dispersion, while Ga2O3 or Cr2O3 could increase the activity per unit copper surface area of the catalyst [148, 149, 146]. Small amount of silica added on the catalyst greatly enhanced the catalyst stability up to 500h by suppressing the metal crystallization by preventing agglomeration of Cu and ZnO metal by silica, which partially covered the surface of metal particles in the catalyst during the initial deactivation [146, 183]. Sloczynksi et al., [184] reported that Au and Cu had a similar and better distribution than Ag and their surface areas decreased when the metal contents increased. In the case of Cu and Au, the addition of large amounts of CuO and AuO led to the formation of large pore diameter of catalysts in contrast with Ag loading [184]. This could be attributed to the formation of large Ag crystallites that eliminate the porous structure of catalyst. However, the introduction of Cu exhibited higher catalytic activity than the catalyst containing Ag and Au because of the synergetic effect between the Cu and ZnO or ZrO2 [184]. The presence of Cu+ favors the hydrogenation of CO2 due to strong stabilization effect of Cu+ ions on the surface of ZnO or/and ZrO2 supports compared to the catalyst containing Ag+ and Au+ ions, which becomes unstable at the reaction temperature [184]. In contrast to the transition metal, metallic Cu or metal on group IB showed an exceptional activity because of their low ability in activating the dissociative adsorption of hydrogen. Noble metals with ideal low-index and large crystal size do not form an enduring bonding with atomic hydrogen [184]. The addition of vanadium could enhance the dispersion of supported CuO species and form a new phase over Cu-V binary oxide supported on γ-Al2O3 catalyst to assist the hydrogenation of CO2 [185]. Sloczynski et al., [186] studied the effect of various metal oxides added to Cu/ZnO/ZrO2 catalyst for CO2 hydrogenation to methanol. They observed that the catalyst synthesized by co-precipitation of mixed carbonates for Cu/ZnO/ZrO2 catalyst gave small CuO crystallites compared to the catalyst prepared by complexing with citric acid. This is due to the fundamental mechanism, in which the size of CuO crystallites has already been generated during the precipitation stage. Thereafter, the growth of CuO crystallites is hindered during the calcination stage according to the separation space between ZnO and ZrO2 particles. On the other hand, the unlimited growth of CuO crystallites via complexing citric acid had been formed during the calcination, reduction and operation steps in the reactor, leading to larger crystallites growth from the smaller ones. Small metal crystallites are preferred due to their role in metal dispersed phase stabilization on the surface of the support [186]. Similarly, Toyir et al., [149] reported that when Ga2O3 was added to metal based catalyst MnO and B2O3 addition improved the initial CuO dispersion during the synthesis of catalyst, the sintering of CuO occurred during the reaction run. The intermediate properties are shown by the addition of Y and Gd, while a very negative dispersion effect on both the Cu and CuO is presented by In metal [186]. The H-reduction of YBA2Cu3O7 at 523 K was favorable in the synthesis of methanol because of orthorhombic to tetragonal structure of YBA2Cu3O7 catalyst [187]. In tetragonal YBA2Cu3O7, only Cu2+ and Cu+ exist with no metallic Cu0. During the H-reduction of YBA2Cu3O7, there were oxygen vacancies, which act as a platform for electron trap in the re-oxidation of Cu+ to Cu2+. The redox reaction between the Cu+ to Cu2+ might play an important role in the synthesis of methanol through CO2 hydrogenation [187]. The improved catalyst structural properties via reverse co-precipitation under ultrasound irradiation have been proposed by Arena et al., [188]. High dispersion of Cu-ZnO/ZrO2 catalyst with large surface area and exposure to active Cu phase was successfully synthesized. By reverse co-precipitation method, simultaneous precipitation of Cu2+, Zn2+ and ZrO2+ cations which act as active sites can be obtained through a slow drop-wise addition of the precursor solution to the precipitating agent. The texture, morphology and reactivity of the catalysts were found to be influenced by the irradiation energy of ultrasound during catalyst preparation [188]. Further, an intimate mixing of nano-sized oxide during the synthesis of Cu/ZnO/ZrO2 appear to hinder the formation of controlled crystalline phase aiding good dispersion of metal nanoparticles on the surface of the catalyst [189]. The strong Cu metal interaction with ZnO and ZrO2 promotes the metal dispersion and stabilization of Cuδ+ sites at the metal/oxides interface, which also influences the redox properties and reactivity of Cu/ZnO/ZrO2 catalyst system. The presence of Cu0, Cuδ+ and Lewis acid sites on the Cu/ZnO/ ZrO2 catalyst also led to the activation of H2, CO2 and CO during the reaction [189]. The effect of reduction temperature of Pd-CeO2 on the activity and selectivity for CO2 hydrogenation has been studied by Shen et al. [190]. They found that the reduction temperature influenced both the structural properties and the catalytic behavior of Pd-CeO2 catalyst. At the reduction temperature of 773K, the overall conversion of CO2 was reduced and the product selectivity has significantly changed. This was because during high temperature, the palladium surface was greatly changed due to the reduction of ceria species between CeO2 and Ce2O3 as well as the increase in size of palladium particles. The decrease in CO2 conversion was significant due to the weak interaction between the Pd and ceria support which was caused by the significant Pd particles growth, together with sintering of ceria as support. At high temperature treatment, the Ce3+ species act as active sites for dissociation of CO2 to form carbon monoxide and subsequently decreased production of methanol [190]. Synthesis of ZnO/Al2O3 from mixtures of ZnO and ZnAl2O4 has been carried out by Park et al., [191]. They reported that the presence of large particle size of ZnO in ZnO/Al2O3 synthesis from high composition ratio of Zn and Al could give high activity in CO2 hydrogenation. However, the parent ZnAl2O4 showed a highly stable performance with no deactivation for 240h compared to ZnO/Al2O3. The deactivation was strongly related to the agglomeration of ZnO during the reduction treatment at 1123K, which hindered the ZnO reduction [191].

**Table 5.2.** Summary of a few representative experimental reports on hydrogenation of CO2 to methanol (CO2 conversion) and methanol selectivity values based on the reactor type for a few selected results are also given.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Catalyst** | **Type of Reactor** | **T °(C); P (MPa)** | **CO2 conversion (%)** | **Methanol selectivity (%)** | **[Ref]** |
| **Effect of catalyst type** | | | | | |
| Cu/Zn/Ga/SiO2 | Fixed-bed | T = 270; P = 2 | 5.6 | 99.5 | 148 |
| Cu/Ga/ZnO | Fixed-bed | T = 270; P = 2 | 6 | 88 | 149 |
| Cu/ZrO2 | Fixed-bed | T = 240; P = 7.6 | 6.3 | 48.8 | 160 |
| Cu/Ga/ZrO2 | Fixed-bed | T = 250; P = 2 | 13.7 | 75.5 | 161 |
| Cu/B/ZrO2 | Fixed-bed | T = 250; P = 2 | 15.8 | 67.2 | 161 |
| Cu/B/Cr, Zr, Th/ZrO2 | Fixed-bed | T = 170; P = 5 | 25.9 | 72.9 | 192 |
| Cu/Zn/Ga/ZrO2 | Fixed-bed | T = 250; P = 4-8 | n/a | 75 | 186 |
| Ag/Zn/ZrO2 | Fixed-bed | T = 220; P = 8 | 2.0 | 97 | 184 |
| Au/Zn/ZrO2 | Fixed-bed | T = 220; P = 8 | 1.5 | 100 | 186 |
| Cu/Zn/ZrO2 | Fixed-bed | T = 220; P = 2 | 12 | 71.1 | 152 |
| Cu/Zn/Al/ZrO2 | Fixed-bed | T = 240; P = 2 | 18.7 | 47.2 | 193 |
| Pd/Zn/CNTs | Fixed-bed | T = 250; P = 2 | 6.3 | 99.6 | 194 |
| Ga2O3-Pd/SiO2 | Fixed-bed | T = 260; P = 3 | n/a | 70 | 176 |
| LaCr0.5Cu0.5O3 | Fixed-bed | T = 250; P = 2 | 10.4 | 90.8 | 195 |
| **Effect of operating conditions** | | | | | |
| Cu/Zn/ZrO2 | Fixed-bed | T = 250; P = 2 | 19.4 | 29.3 | 196 |
| Cu/Zn/ZrO2 | Fixed-bed | T = 240; P = 2 | 17 | 56.2 | 194 |
| Cu/Zn/ZrO2 | Fixed-bed | T = 220; P = 8 | 21 | 68 | 186 |
| **Effect of reactor type** | | | | | |
| Cu/ZnO/ZrO2/Ga2O3 | Recycle Reactor  (CAMERE Process)\* | T = 600; P = 2;  R = 4 | 61.81 | 89 | 191 |
| Cu/ZnO/ZrO2/Ga2O3 | Fixed-bed  (direct process) | T = 600; P = 2,  R = 0 | 16.04 | 79 | 191 |

\* CAMERE process has been developed to form methanol from CO2 via a reverse-water-gas-shift reaction

As demonstrated in Table 5.2, from the data derived from various experimental works, the reactor type appears to impact the CO2 conversion efficiency significantly than effects of catalyst type and operating conditions.

* + - 1. **Addition of Precursors**

The characteristics of precursors used in catalyst preparation can control the conditions of co-precipitation and influence the ultimate property of the catalyst [148]. For instance, the activity of Cu/ZnO catalyst for methanol formation depended on the precursor structure. Toyir et al., [148] reported that the presence of precursors like methoxide or acetylacetonate salts in the preparation of SiO2 or ZrO supported catalyst during impregnation could enhance the catalytic performance in CO2 hydrogenation to methanol. The presence of metallic precursors could determine the final characteristic and give a higher dispersion of metal in catalyst. In the stage prior to the impregnation, the interaction between the precursor and support could be improved and after the calcinations step, the catalysts have only the supported mixed oxides without any precursor anions. Cu/ZnO catalysts were prepared by the co-precipitates of zincian malachite and aurichalciteas hydroxy carbonate precursors as reported by Fujita et al. [151]. At low heating rates, a very small crystallite of CuO was generated in the presence of aurichalcite and no effect was found on the catalyst synthesized from zinc-malachite. Positive effects of aurichalcite precursor have also been found by Fujitani and Nakamura [147], which exhibited an excellent catalytic activity with 7.56% of methanol yield due to the automatic mixing of Cu and Zn in the compound. Guo et al., [153] prepared CuO-ZnO-ZrO2 catalyst via urea-nitrate combustion method, and it exhibited favorable characteristics such as small grain size, high surface area and low reduction temperature. The presence of urea in the combustion process might distribute some heat, which renders the rapid quenching effect forming smaller CuO particles and more favorable interaction between copper species, ZnO and ZrO2. The increase of urea content leads to the increase of partial transformation of t-ZrO2 to m-ZrO2 supported catalyst resulting in improved methanol selectivity from CO2 hydrogenation [152, 153]. Raudaskoski et al., [150] observed that the activity of Cu catalysts support on m-ZrO2 for methanol synthesis from CO2 and H2 was 4.5 times greater than that of t-ZrO2. The higher rate of methanol synthesis over the Cu/m-ZrO2 is attributed to the higher active intermediates concentration on the catalysts [150]. Guo et al., [152] have synthesized CuO-ZnO-ZrO2 catalysts by glycine-nitrate combustion, which is reported as a simple, fast and effective preparation method. The amount of glycine added greatly influenced the combustion process and the catalyst properties due to the role of glycine as a fuel in the combustion reaction and has significant effects on the formation of zirconia phase. The catalyst content of 50% glycine-nitrate exhibited an optimum activity of 16% and 10% of CO2 conversion and methanol yield, respectively. The CuO-ZnO-ZrO2 catalyst synthesized by glycine-nitrate combustion [152] appears to be more effective than urea-nitrate combustion method [153] for CO2 hydrogenation to methanol. This observation is attributed to the presence of metal nitrate and glycine in the combustion process that act as an oxidant and fuel, respectively compared to the urea alone, which only acts as a fuel. In the combustion synthesis process, a thermal redox reaction occurred between an oxidant and fuel and their characteristics were strongly depended on the choice of the fuel [152,197, 198].

* + - 1. **Water as an Exhibitor**

The poor performance of CO2 hydrogenation catalyst is mainly due to the presence of water during the CO2 hydrogenation reaction. During the methanol formation via CO2 hydrogenation, CO act as the CO2 source and scavenger of oxygen atoms from water molecules, which then act as inhibitor of the active metal sites [188, 189]. Sloczynksi et al., [186] found that the addition or total replacement of Al2O3 by ZrO2 to Cu/ZnO/Al2O3 could increase the methanol yield due to the direct decrease of H2O adsorption on the catalysts. It is mainly due to the poor specific functionality and hydrophilic character of alumina, which show a notable positive effect of water towards active site stability. The formation of dimethyl ether (DME), produced from methanol dehydration at high temperature, appears to be limited during the RWGS [148]. The presence of water during methanol synthesis accelerates the crystal growth of metal oxide and lead to the deactivation of the catalyst and non-adsorption of CO2 [151, 183]. Nonetheless, high concentration of CO during the reaction produce only small amount of water that prohibit the crystallization of catalyst [183]. Based on thermodynamics, the increase of CO2 concentration in the feed gas could lead to an increase in the yield of water and a decrease in the yield of methanol [150,183].

* + - 1. **Reactor Design**

As shown in Table 5. 2, the summary of some experimental reports on H2/CO2 to methanol, CO2 conversion is usually low using traditional fixed-bed tubular reactors and even various catalyst types have been investigated; however, CO2 conversion is notably high in recycled reactor since this reactor type mitigates the impacts of thermal conflicts along the reactor. Moreover, the effects of operating conditions have been investigated in the fixed-bed reactor with the same catalyst type (Cu/Zn/ZrO2) which shows higher CO2 conversion and product selectivity at lower temperature and higher pressure which is still lower than the result obtained from recycle reactor. Therefore, the results present in this table indicate the notable influence of reactor type on enhancement of CO2 conversion to methanol.

Novel reactor configurations are proposed, which employ dual-type membrane in the reactor consist of water perm-selective membrane in first fixed-bed reactor and a H2 perm-selective in second fluidized bed reactor as shown in **Figs. 5. 13** and **5.14** with complete configuration and their elemental volume in detail, respectively.



Fig. 5.13. Schematic diagram of dual-type perm-selective related to water and hydrogen.



Fig. 5.14. Schematic diagrams of elemental volume dual-type perm-selective membrane reactors.

Fig. 5.13 is a dual-type membrane reactor including fluidized-bed and fixed-bed reactors, in which both reactors are permeable. The shell sides of second reactor and vertical tubes of first reactor are filled with catalysts. At first, the feed (CO2 and H2) pass through the tubes (where there is no catalyst) of second reactor from upper side. The walls of these tubes is H2 perm-selective to regulate the stoichiometry and to prevent from wasting hydrogen and to direct the addition of hydrogen to the outlet gas from first reactor selectively in order to shift the chemical equilibrium towards the product side. Thus, the processes of heat and mass transfer take place simultaneously on both sides and hydrogen permeation arising from partial hydrogen pressure gradient can advance the product yield. The preheated feed (CO2/H2) gas is then fed to the tubes of the first reactor which are water perm-selective as the walls are coated by the hydroxy sodalite (H-SOD) membrane layer in the water-cooled reactor initiated by the catalyst. Therefore, water permeates from the shell to the side of the tube. In this stage, feed (H2/CO2) gas is converted to CO according to RWGS reaction; hydrocarbon synthesis reactions are exothermic with the result that the cooling water in the shell side of first reactor discharges the heat of the reactions. The outlet gas (CO) from the first reactor, leaves the first reactor and enters the bottom of the second reactor (bottom up direction through the second reactor), in counter-current mode with the tube feed (H2/CO2). The chemical reactions continue on the catalyst surface in the second reactor and the generated heat is removed by CO2 and H2 as feed in tubes. Thus, the temperature of outlet gas from first reactor is continuously reduced through the reaction path in the second reactor. The reaction is complete in the second reactor and finally the product can be removed from downstream of the second reactor [199]. The purpose of this proposed reactor including water and hydrogen perm-selective membranes for first and second reactor respectively is to achieve higher conversion of CO2 to CO; CO would finally proceed to FT hydrocarbons synthesis (C2-C4) based on Schulz Anderson Flory distribution.

It is emphasized that the reactor type is most influential among the other factors such as catalyst type and operating conditions in accordance with the results of Table 5. 1. Rahimpour et al., [200, 201] investigated hydrogenation of CO2 for methanol and the GTL (gas-to-liquid) process by comparing three different reactor types under similar conditions. They concluded that conventional reactor is the least efficient reactor. From their theoretical study, they also derive that the dual-type reactor being H2O perm-selective in the first reactor is better than conventional reactors while the dual-type reactor which is H2O and H2 per-selective in both first and second reactor respectively is the best by showing the highest efficiency in terms of methanol and gasoline production. Further, they notified that hydrogenation of CO2 to methanol is a better fit with the reactor configuration than the GTL process as the percentage of reactant conversion was higher for hydrogenation of CO2 to methanol in comparison with GTL [200-202]. A dual type membrane reactor was theoretically developed by Rahimpour et al., [203-205] for Fisher-Tropsch synthesis which favored the temperature profile along the reactor tube length and enhance the activity and lifetime of the catalyst by discharging the produced water through a water perm-selective membrane in the first reactor [113, 206].

* + 1. **Synthesis of Dimethyl Ether**

Dimethyl ether is a potential substitute for diesel due to its better combustion performances (i.e., high cetane number ([cetane](https://en.wikipedia.org/wiki/Cetane) number is an inverse function of a ignition delay of a fuel, and the time period between the start of injection and the first identifiable pressure increase during combustion of the fuel), low emissions of NOx, and near-zero smoke) [207]. DME can be produced via two ways; from CO2 hydrogenation in a two-step process (methanol synthesis on a metallic catalyst and subsequent dehydration of methanol on an acid catalyst) or in a single-step process using a bifunctional catalyst which could perform these two steps simultaneously [208-212]. The main merit of the single-step process on a bifunctional catalyst is the lower thermodynamic limitation than methanol synthesis.

* + - 1. **Hybrid oxide-based catalysts**

The first step in DME synthesis is methanol formation in which a Cu-based catalyst is commonly used. The subsequent step is the dehydration of methanol for DME synthesis, which is catalyzed by acidic catalysts such as γ-Al2O3, HZSM-5, and NaHZSM-5 [213]. Representative catalytic systems for the synthesis of DME are summarized in **Table 5. 3.**

Table 5.3. Catalytic systems for the synthesis of DME by hydrogenation of CO2

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Catalysts | T °C | CO2 conversion (%) | DME Yield (%) | Ref. |
| Cu/Zn/Al+HZSM-5 | 250 | Not Available | 12.5 | 216 |
| Cu/Ti/Zr+HZSM-5 | 250 | 15.6 | 7.4 | 217 |
| Cu/Zn/Al/Zr+HZSM-5 | 250 | 30.9 | 21.2 | 218 |
| Cu/Zn/Al+NaHZSM-5 | 275 | 35 | 26 | 222 |
| Cu/Mo+HZSM-5 | 240 | 12.3 | 9.5 | 224 |
| Pd/Cu/Zn/Al/Zr+HZSM-5 | 200 | 18.6 | 13.7 | 225 |

Selection of suitable acidic support is of importance. Jun et al., [214] claimed that NaY with weak acid sites was inferior in producing DME. Nevertheless, CuNaY is an excellent dehydration catalyst due to the presence of a considerable number of acid sites with moderate strength. In contrast to CO hydrogenation, more water is produced in CO2 hydrogenation from the RWGS reaction and methanol synthesis. However, the formed water decreased the activity of γ-Al2O3 due to high adsorption capacity of water on acid sites [215]. Since HZSM-5 zeolite is not sensitive to the concentration of water, it can possibly be incorporated as a component in the bifunctional catalyst [216-220]. Notably, HZSM-5 zeolite is also active for the transformation of DME into hydrocarbons (with ethane and propylene as primary products), even at high Si/Al ratios [221]. These hydrocarbons partially evolve to form coke that could block the pores of zeolite causing deactivation. A suitable concentration of Na moderates the number and strength of Brönsted acid sites in HZSM-5 zeolite, and prevents the formation of hydrocarbons from DME [222, 223]. For Cu-Zn-Al/NaHZSM-5 catalysts, there is no irreversible deactivation observed [215]. The catalysts can be used uninterruptedly as long as the reaction temperature is well controlled below 573K in order to avoid the sintering of CuO nanoparticles [215]. Addition of promoters to Cu-based catalysts leads to an increase in yield of DME. For example, the addition of Ga2O3 and Cr2O3 increases DME selectivity significantly over a Cu/ZnO catalyst [214]. Qi et al. found that a small amount of MoO3 addition can enhance the catalytic activity [224]. The presence of Mo not only produces new adsorption sites but also enhances binding of adsorbate on the catalyst surface. To increase catalytic reactivity of DME synthesis at low temperature, palladium is added to Cu-Zn-Al-Zr/HZSM-5 catalysts [225]. The addition of Pd significantly improves DME production and retards CO formation, probably due to the spillover of hydrogen from Pd0 to the neighboring sites [225].

**5.1.5.2. Theoretical Studies**

A kinetic model has been proposed for the synthesis of DME in a single reaction step on Cu-Zn-Al/γ-Al2O3 bifunctional catalysts [209]; the kinetic parameters were calculated involving the synthesis of methanol, dehydration of DME, and hydrocarbons formation. The kinetic model ideally fits the experimental results for an isothermal fixed bed reactor for a wide range of operating conditions. The model incorporates the role of water in the reaction system as an inhibitor in the steps of methanol and hydrocarbons synthesis [209]. Though it is generally presumed that DME synthesis is determined by the kinetics rather than thermodynamics, a comprehensive thermodynamic analysis on this process is necessary to fully understand the intrinsic characteristics [226,227]. In this direction, detailed results of thermodynamic calculations are available in terms of equilibrium conversions of CO2 for DME synthesis [228, 229]. For any feed composition, the equilibrium yields of DME increase with higher pressures but decrease with higher temperatures.

* + 1. **Synthesis of Higher Alcohols**

Higher alcohols are preferable to methanol as products of CO2 hydrogenation from viewpoint of safe transport and good compatibility to gasoline [3]. Direct synthesis of higher alcohols from CO2 could be regarded as a combination of the RWGS reaction and the subsequent formation of higher alcohols from syngas [3]. Therefore, a catalyst that is active for both reactions under similar conditions is desired for the overall reaction, for example, Fe-based and Rh-based catalysts [230-236]. Catalysts for the formation of ethanol require active centers for promoting partial reduction of CO2 to CO, C-C bond formation, and OH group insertion [234,236]. Fe-based FT catalysts mixed with Cu-based catalysts execute the functions of partial reduction of CO2 to CO and formation of ethanol [234, 236]. Addition of small amounts of Pd and Ga can assist to sustain the optimal redox state during the reaction, and promote ethanol synthesis. Further improvement is expected through incorporation of basic compounds, such as potassium carbonate, with the polyfunctional composite catalyst leading to suppression of methane formation [236]. For example, Arakawa et al., [237, 238] reported that doping K2CO3 on a Cu/Fe/ZnO catalyst increased the selectivity of ethanol from ~6% to ~20% at 573K and 7 MPa. An alternate route for improving the yield of ethanol from CO2 is through the conversion of syngas into ethanol along with methane as another main product over Rh/SiO2 catalyst [231]. The addition of various metal oxides to the catalysts could improve the CO2 conversion and selectivity towards the formation of alcohols [231]. The addition of Li to Rh/SiO2 yields an ethanol selectivity of 15.5% and a CO2 conversion of 7.0%. In situ FTIR analysis reveals that CO2 is hydrogenated to ethanol via CO intermediate, the amount of which is increased by increasing Li loading [231]. A plausible mechanism of ethanol formation is shown in Scheme 5.4.



Scheme 5.4. Plausible reaction mechanism for CO2 hydrogenation to ethanol. [Reproduced with permission from ref. 231. Copyright 1996 Elsevier.]

With a 5 wt% Rh-Fe/SiO2 catalyst, a CO2 conversion of 26.7% and an ethanol selectivity of 16% were obtained at 533K [233]. Based on results of XPS and in-situ FTIR, it is concluded that Fe3+ changes the electronic states of Rh, and the presence of Fe0 promotes methanation and prevents formation of methanol, ethanol, and CO [233]. The promoting effect of anionic Se is realized by modifying the electronic states of active sites of Rh/SiO2 or by the direct coordination of Se to surface intermediate species [239, 240]. Kurakata et al. used Rh10Se/TiO2 catalyst for CO2 hydrogenation in a closed circulating reaction system at a fairly low pressure, and reported that the selectivity of ethanol could reach as high as 83% [230, 235]. The mechanism proposed for ethanol synthesis on Rh10Se/TiO2 is depicted in Fig.5.15 [232, 235].



Fig.5.15. Proposed mechanism for ethanol synthesis from CO2 hydrogenation on a Rh10Se/TiO2 catalyst. [Reproduced with permission from Ref. 3. Copyright 2009 Elsevier.]

CHx,ads species on rhodium reacts with COy,ads to form acetate, which is subsequently hydrogenated to ethanol on Rh sites. The reaction of CO and H2 proceeds fairly slowly and the products distribution is entirely different from that of CO2 hydrogenation on Rh10Se/TiO2 catalyst, suggesting that ethanol synthesis does not occur via CO over the catalyst [230]. Additionally, a multi-step method for utilizing CO2 via the RWGS reaction as a source of CO was introduced by Tominaga et al., in hydroformylation reaction [241]. Hydroformylation with CO2 proceeds in two steps - CO2 is first converted to CO, which further involves in hydroformylation of the substrate (Scheme 5.5).



Scheme 5.5. Formation of alcohols from alkenes by hydroformylation with CO2. [Reproduced with permission from Ref. 246. Copyright 2009 Elsevier.]

Ruthenium carbonyls, particularly multinuclear ruthenium clusters are active for the process since they are capable of catalyzing both the steps (i.e., the RWGS reaction and the subsequent hydroformylation) [241-246]. A potential side reaction - hydrogenation of alkene - could be inhibited by adding an alkali metal or alkaline earth halide or by using ionic liquid as the solvent. In the latter case, ionic liquid acts as both promoter and solvent, and the yield of heptanol could reach 82% [245].

* + 1. **Synthesis of dimethyl carbonate (DMC)**

Dimethyl carbonate (DMC) is a non-toxic, biodegradable and environmentally benign compound and it is widely used in industry for the production of polycarbonate, polyurethane and other chemicals [144, 247, 248]. It is also an ideal additive to gasoline or fuel oil for transportation due to its high oxygen content (53%) and octane number [248-250]. Commercially, the production of DMC is carried out through three processes: (i) direct synthesis of DMC from CO2 and methanol; (ii) synthesis of DMC from CO2, methanol and epoxides; (iii) synthesis of DMC from CO2 and acetals or ortho-ester [251]. DMC produced via the reaction of methanol and toxic phosgene is subsequently improved by non-phosgene route of carboxylation of methanol [248]. However, the process is hazardous because of the use of a highly flammable reactant mixture and toxic chemicals.

* + - 1. **Direct synthesis of DMC from CO2 and methanol**

The direct synthesis of DMC from methanol and CO2 has attracted considerable attention as one of the options to overcome the global warming and also for the development of carbon resources [144, 248]. It is challenging to find high performance catalyst for the production of DMC due to the high thermodynamic stability of CO2 and catalyst deactivation [144, 248, 249].

2 CH3OH + CO2 → (CH3O)2CO + H2O (Eq. 5.17)

Various types of heterogeneous catalysts were developed for the production of DMC via CO2 and methanol. ZrO2 catalysts have unique properties and are effective for production of DMC from methanol and CO2 [144]. Tomishige et al. [252] reported that the neighboring acidic and basic sites on ZrO2 act as active sites in the formation of DMC through the TPD results of CO2 and NH3 co-adsorption. The formation mechanism of DMC from methanol and CO2 over ZrO2 catalyst using in situ infrared spectroscopy has been investigated by Jung and Bell [253] and is shown in **Fig. 5.16.** The presence of Brönsted basic hydroxyl group (Zr-OH) and coordinately unsaturated Zr4+O2− on the ZrO2 were effective for the production of DMC from CO2 and methanol feedstock [253].

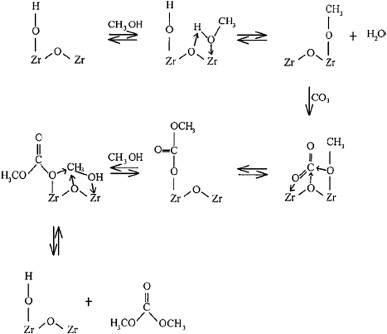


Fig. 5.16. Mechanism for the formation of DMC from CH3OH and CO2 over ZrO2 [253].

Modified ZrO2 based catalysts were examined with the aim to enhance the catalytic activity in the reaction. Ikeda et al., [254] added phosphoric acid (H3PO4) to ZrO2 for DMC synthesis, and observed that the acid-base bifunctional properties of H3PO4/ZrO2 and catalyst calcination temperature were the two parameters which influenced the catalytic activity. Tomishige et al. [255] reported a similar observation on the effect of calcination temperature on the CeO2-ZrO2 catalyst, in which higher the calcination temperature, larger the catalyst crystal size and higher the catalytic activity for DMC formation. The calcination temperature however did not influence the tetragonal and the bulk structure of the binary CeO2-ZrO2 catalyst.

Bian et al. [[256]](http://www.sciencedirect.com/science/article/pii/S1364032112002705#bib83) found that the activation of CH3OH and CO2 was high with increase in reaction temperature. The DMC yield decreased notably when the reaction temperature increased more than the optimum value due to the decreased CO2 adsorption on the catalyst surface. Tomishige et al., [257] carried out further investigation on CeO2-ZrO2 catalyst with the addition of 2,2-dimethoxy propane (DMP) for DMC synthesis and found that an appropriate amount of DMP was effective for water removal in the reaction system enhancing the DMC yield due to the established equilibrium between DMP and water [257]. Jiang et al. [258] reported the effective synthesis of DMC over Keggin unit, 12-tungstophosphoric acid/zirconia (H3PW12O40/ZrO2). The activities of catalysts prepared through sol-gel method under mild condition increased linearly with an increase of H3PW12O40 content on catalyst up to 50 mg. The characteristic weak Brönsted acid sites in the H3PW12O40/ZrO2 increased the effectiveness of the catalyst for nearly nine times than ZrO2 in methanol activation [258].

The performance of metal oxide catalysts in the production of DMC from CO2 and methanol was reported by La and Song [259]. The catalytic effectiveness of metal oxides has been observed in the order of Ce0.1Ti0.9O2 > CexTi1−xO2 (x=0.2-0.8) > ZrO2 > CeO2 > TiO2. The stabilization of crystalline phase of Ce0.1Ti0.9O2 could enhance the activity performance of the catalyst. The addition of H3PW12O40 on Ce0.1Ti0.9O2 shown to exhibit the highest catalytic performance compared to that of H3PW12O40/ZrO2 and Ce0.1Ti0.9O2 due to the Brönsted acid and base sites of H3PW12O40/Ce0.1Ti0.9O2 catalyst as deduced from the results of NH3 and CO2-TPD for H3PW12O40 and CexTi1−xO2, respectively [259, 260]. The supported bimetallic catalysts could allow for systematic altering of the size, electronic structure, absorption characteristics, reducibility and deactivation behavior of a catalyst [261, 262]. Other heterogeneous catalysts such as Ni-Cu/MoSiO and Ni-Cu/VSiO catalysts were also effective in DMC synthesis directly from CO2 and methanol [263]. Appropriate surface sites of catalyst is important for obtaining good reaction rates of about 15% of CH3OH conversion and over 85% of DMC selectivity. Further, the metallic site M (Ni-Cu alloy), Lewis acid site Mn+ (Mo6+ or V5+) and Lewis base site M-O (Mo-O or V-O) on the catalysts surface and the changes in their *d*-electron density play an important role in facilitating the activation of CO2 and CH3OH molecules [263]. The effect of Cu-Ni/VSO catalyst in synthesis of DMC from CO2 and CH3OH was studied by Wu et al. [264], and they observed that the catalysts crystallinity was influenced by the reduction process and the increase in the crystallinity could enhance the DMC yield. Graphite supported Cu-Ni bimetallic catalyst appear to show high activity, selectivity and stability towards DMC synthesis [249]. High catalytic activity of Cu-Ni/graphite has been attributed to the unique structure of graphite, moderate Cu-Ni-graphite interactions, and synergetic effects of metal Cu, Ni and Cu-Ni alloy on the CH3OH and CO2 activation; a reaction mechanism has also been discussed [249].

Poor mechanical stability, limited thermal stability, and low surface area of SiO2, Al2O3, ZrO2 and TiO2 as supports have led Fan et al. [265] to design catalyst based-mesoporous silica for synthesis of DMC. Mesoporous silica is considered as a suitable catalyst support because of large surface areas, high thermal stability, well-defined uniform mesopores, and surface modification behavior. Immobilization of organo tin compound of (MeO)2ClSi(CH2)3SnCl3 on the SBA-15 and SBA-16 mesoporous silicas was also reported by Fan et al. [265]. In their studies, four methods were used for removing the surfactants in the synthesis of mesoporous silicas: (i) calcination at 550 °C (mesocal); (ii) Soxhlet extraction with a solution of HCl in ethanol (MesoHCl-EtOH); (iii) Soxhlet extraction with a solution of pyridine (Py) in ethanol (MesoPy-EtOH) and (iv) refluxed in H2O2 aqueous solution (MesoH2O2), where Meso was referred to as mesoporous silicas. The surfactants removal methods influenced the surface area, -OH groups surface concentration, amount of grafted organo tin compound and catalyst activity. The catalysts activity for direct synthesis of DMC from CO2 and CH3OH was in the order of Sn/SBA-15HCl-EtOH > Sn/SBA-15Py-EtOH > Sn/SBA-15cal > Sn/SBA-15H2O2. However, the concrete reason on how the preparation methods could affect the catalyst performance has not been clearly explained in their paper.

Cai et al. [266] studied the use of K2CO3, KOH and CH3OK basic catalyst with the emphasis on thermodynamics. As limited temperature and pressure conditions can only favor the reaction, careful nesting of coupling reaction over those catalysts was essential to increase the yield of DMC [266]. The effect of V-doped activated carbon (AC) supported Cu-Ni bimetal catalysts have been investigated by Bian et al. [262]. The addition of 3 wt% of V on Cu-Ni/AC enhanced the CH3OH conversion by 1.2 times than the respective Cu-Ni/AC due to the uniform particle size (10-30 nm), well dispersed active metals on activated carbon surface (AC), and formation of new phases between the Cu-Ni and V promoter [262] . A novel photo-assisted synthetic process was used by Wang et al., [267] in the preparation of copper modified (Ni, V, O) semiconductor complex catalysts. The presence of UV light and irradiation during the catalytic reaction could reduce the reaction pressure to 0.1 MPa and enhance the activity with the increase of DMC yield up to 63%. The presence of UV irradiation or photocatalysis for reaction was more effective due to the additional energy supply, which assisted the C-O bond cleavage of the ·CO2− anion radical [267].

The use of carbon nanotubes (CNTs) as a catalyst support has been exploited due to high surface area, high capacity of hydrogen uptake and superior electronic conductivity compared to graphite and activated carbon [256]. Effective and novel catalyst utilization was realized by Bian et al. [256] on CNTs supported Cu-Ni bimetal for direct synthesis of DMC from CO2 and methanol with 4.3% of CH3OH conversion and 85.0% of DMC selectivity at the optimum reaction conditions. This was due to the synergetic effect of metal Cu and Ni alloy, the interaction between metal and MWCNTs, unique structure and character of MWCNTs, and homogeneously dispersed active metal particles on the MWCNTs surface [256]. Interestingly, Cu-Ni alloy phase was partially evolved during the calcination and activation step of catalyst [256].

The activity data of various heterogeneous catalysts for direct synthesis of DMC from CO2 and methanol are presented in Table 5.4. Due to the limitations in reaction thermodynamics, most of the catalysts have low catalytic activity despite the prolonged reaction time up to 12 h at respective reaction conditions. Most of the catalysts operating at higher reaction temperature demonstrated low yield of DMC because of the DMC decomposition. The design of appropriate catalyst is crucial for the reaction because of the methanol and CO2 activation which occurs via the adsorption onto the catalyst.

Table 5.4. Various heterogeneous catalysts for direct synthesis of DMC from CO2 and methanol

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Catalyst | Reaction Condition | | | | Reaction Results | | Ref. |
| Calcination temperature (°C) | Pressure (MPa) | Temp (°C) | Time (h) | Methanol conversion (%) | DMC yield (%)/  Mmol (a) |  |
| Cu-Ni/graphite | 600 | 1.2 | 105 | 3 | 10.13 | 0.91 | 249 |
| H3PO4/ZrO2 | 400 | 5 | 130 | 2 | - | 0.63 | 254 |
| CeO2–ZrO2 | 1000 | - | 110 | 2 | - | 0.7(a) | 255 |
| Cu–Ni/MWCNTs | - | 1.2 | 120 | 3 | 4.3 | 3.74 | 256 |
| CeO2–ZrO2 | 1000 | - | 110 | 4 | - | 1.4 (a) | 257 |
| H3PW12O40/ZrO2 | 300 | 4 | 100 | 3.5 | - | 2.8(a) | 258 |
| ZrO2 | 300 | 5 | 170 | 12 | - | 0.4(a) | 259 |
| TiO2 | 300 | 5 | 170 | 12 | - | 0.1(a) | 259 |
| CeO2 | 300 | 5 | 170 | 12 | - | 0.3(a) | 259 |
| H3PW12O40/ZrO2 | 300 | 5 | 170 | 12 | - | 3.6(a) | 259 |
| Ce0.1Ti0.9O2 | 300 | 5 | 170 | 12 | - | 1(a) | 259 |
| H3PW12O40/Ce0.1Ti0.9O2 | 300 | 5 | 170 | 12 | - | 5(a) | 259 |
| Cu–Ni/AC | 500 | 1.2 | 110 | 3 | 6.44 | 5.62 | 262 |
| V–Cu–Ni/AC | 500 | 1.2 | 110 | 3 | 7.76 | 6.98 | 262 |
| Ni–Cu/MoSiO | 450 | 0.1 | 140 | - | 16.37 | 14.16 | 263 |
| Ni–Cu/VSiO | 450 | 0.1 | 140 | - | 14.54 | 12.77 | 263 |
| Cu–Ni/VSO | 450 | 0.6 | 140 | - | - | 6(a) | 264 |
| Sn/SBA-15cal | - | 18.2 | 180 | 10 | - | 0.22 | 265 |
| Sn/SBA-15HCl-EtOH | - | 18.2 | 180 | 10 | - | 0.41 | 265 |
| Sn/SBA-15H2O2 | - | 18.2 | 180 | 10 | - | 0.01 | 265 |
| Sn/SBA-15Py-EtOH | - | 18.2 | 180 | 10 | - | 0.34 | 265 |
| Sn/SBA-16HCl-EtOH | - | 18.2 | 180 | 10 | - | 0.22 | 265 |
| K2CO3 | - | 7.3 | 80 | 6 | - | 4.1 | 266 |
| KOH | - | 2.0 | 80 | 6 | - | 8.5 | 266 |
| CH3OK |  | 2.0 | 80 | 6 | - | 14.1 | 266 |
| Cu (Ni, V, O) semiconductor | 450 | 0.1 | 130 | Na | 4.04 | 6.5 | 267 |

* + - 1. **Synthesis of DMC from CO2, methanol, and epoxides**

Epoxide compounds such as ethylene oxide, propylene oxide or styrene oxide can be used for the synthesis of DMC with reaction of CO2 and methanol [251, 268]. The reaction occurs in two steps: (i) cycloaddtion of epoxide to CO2 to form cyclic carbonate (ii) transesterification of cyclic carbonate with methanol to DMC and glycol **Fig. 5.17.** The study on various basic metal oxides as catalysts has been carried out by Bhanage et al. [268]. Among which, MgO was found to be effective for both reactions due to the large numbers of basic sites. Both strong and moderate basic sites were efficiently active for the epoxides and CO2 reaction. Moderate basic sites are required for subsequent reaction of cyclic carbonates with methanol to form DMC [268]. The catalytic performance of KOH supported on various solid base catalysts has been evaluated by Li et al. [269] for the synthesis of DMC. Among these catalysts, KOH supported on 4A molecular sieve exhibited the highest activity and it could be recycled for nearly eight times. Under the optimized condition, propylene oxide was converted completely to yield 16.8% of DMC. Due to an increase in yield of propylene carbonate while methanol was introduced in the reaction system, it is presumed that methanol acts as raw material and promoter for the synthesis of DMC. Cui et al., [270] employed high pressure CO2 as the reaction medium for the synthesis of DMC from ethylene carbonate (EC) and methanol over the K2CO3 catalyst. The DMC selectivity was enhanced about two times by pressurizing the reaction with supercritical CO2, the ethylene carbonate conversion was still decreased due to the high pressure CO2 which makes the ethylene carbonate compound stable and inhibit the formation of by-products and undesired reactions [270].

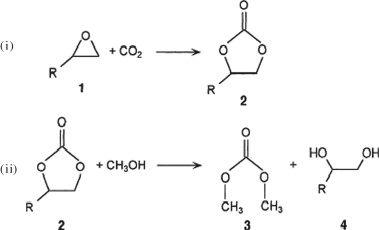


Fig. 5. 17. Reaction step for synthesis of DMC: (i) Cycloaddition of CO2 to epoxides; (ii) Trans esterification of methanol with cyclic carbonate: 1: epoxides; 2: cyclic carbonate; 3: DMC; 4: glycol [251, 268].

This reaction requires high energy consumption and high investment and production costs, due to the separation of intermediate cyclic carbonates [251]. A new method has been developed for one-pot synthesis of DMC from CO2, methanol and epoxides as shown in **Fig. 5.18** [251, 268]. There are some reports on one-pot system in synthesis of DMC, which have limitations due to the formation of major by-products such as 1-methoxy-2-propanol and 2-methoxy-1-propanol.

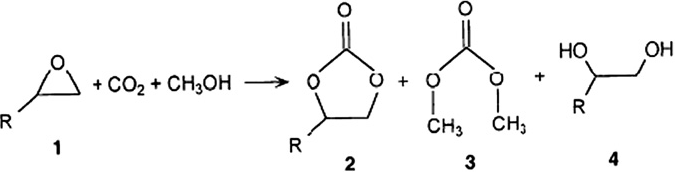


Fig. 5. 18. One-pot synthesis of DMC from CO2, methanol, and epoxides.1: epoxides; 2: cyclic carbonate; 3: DMC; 4: glycol [251, 268].

### Chen et al. [271] carried out this reaction over the ionic liquid, [1-butyl-3-methylimidazolium tetrafluoroborate](https://www.google.com/url?sa=t&rct=j&q=&esrc=s&source=web&cd=2&cad=rja&uact=8&ved=0ahUKEwj5ruH-n8fKAhUBWo4KHZMrDzwQFggkMAE&url=http%3A%2F%2Fwww.chemicalbook.com%2FChemicalProductProperty_EN_CB1381191.htm&usg=AFQjCNHPIRZ7iXfusfHPhQfrf0FeUAqEDw&sig2=OZaLk8YVe9sBK916QaTxqg) [bmim]BF4 and CH3ONa. An optimum amount of [bmim]BF4 ionic liquid and CH3ONa showed good catalytic activity yielding 67.6% of DMC which was higher than other similar reaction systems due to the synergetic effect between the two components and ionic liquids properties itself which acted as acid or base catalyst and a suitable reaction medium [271]. Chang et al. [272] observed that KI/ZnO and K2CO3-KI/ZnO catalysts after calcinations were highly active and selective for synthesis of DMC. Complete conversion of epoxides with less than 0.2% of by-products was achieved with K2CO3-KI/ZnO and the catalyst could be reused for nearly four times due to the presence of stronger basic sites on the surface of K2CO3-KI/ZnO enhancing the activity of the catalyst. These researchers also reported on the activity of KI supported on CaO, MgO and ZnO and the performance of catalysts was in the order of KI/ZnO > KI/MgO > KI/CaO, while the basic sites strength of supports followed in the order of CaO > MgO > ZnO [272]. A possible reaction mechanism was also proposed in their study [272].

### Table 5.5 presents various heterogeneous catalysts which are employed for the synthesis of DMC from CO2, methanol, and epoxides. Although this route is possible for the synthesis of DMC, no good results were obtained because of the alcoholysis of the epoxide that impact the formation of DMC. It is challenging to design the effective catalyst with both strong and moderate basic sites to catalyze the reaction to form DMC.

Table 5.5. Various heterogeneous catalysts investigated for synthesis of DMC from CO2, methanol, and epoxides

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Catalyst | Reaction condition | | | Reaction results | | | Ref. |
| Pressure (MPa) | Temp (°C) | Time (h) | Epoxide conversion (%) | Cyclic carbonate conversion (%) | DMC yield (%) |  |
| MgO | 8 | 150 | 4 | 81.9[a](http://www.sciencedirect.com/science/article/pii/S1364032112002705#tbl5fna) | 66.1 | 66.1 | 268 |
| MgO | 8 | 150 | 4 | 34.9[b](http://www.sciencedirect.com/science/article/pii/S1364032112002705#tbl5fnb) | 28.0 | 28.0 | 268 |
| MgO | 8 | 150 | 4 | 92.3[c](http://www.sciencedirect.com/science/article/pii/S1364032112002705#tbl5fnc) | 66.4 | 14.9 | 268 |
| CaO | 8 | 150 | 4 | 9.9[b](http://www.sciencedirect.com/science/article/pii/S1364032112002705#tbl5fnb) | 25.6 | 25.6 | 268 |
| ZnO | 8 | 150 | 4 | 9.4[b](http://www.sciencedirect.com/science/article/pii/S1364032112002705#tbl5fnb) | 23.0 | 23.0 | 268 |
| ZrO2 | 8 | 150 | 4 | 21.5[b](http://www.sciencedirect.com/science/article/pii/S1364032112002705#tbl5fnb) | 11.8 | 11.8 | 268 |
| La2O3 | 8 | 150 | 4 | 72.6[b](http://www.sciencedirect.com/science/article/pii/S1364032112002705#tbl5fnb) | 7.1 | 7.1 | 268 |
| CeO2 | 8 | 150 | 4 | 22.7[b](http://www.sciencedirect.com/science/article/pii/S1364032112002705#tbl5fnb) | 32.8 | 32.4 | 268 |
| Al2O3 | 8 | 150 | 4 | 100[b](http://www.sciencedirect.com/science/article/pii/S1364032112002705#tbl5fnb) | 4.2 | 4.2 | 268 |
| K2CO3 | 8 | 150 | 4 | 11.3[b](http://www.sciencedirect.com/science/article/pii/S1364032112002705#tbl5fnb) | 61.6 | 40.4 | 268 |
| KOH/4A molecular sieve | 3 | 180 | 6 | 100[b](http://www.sciencedirect.com/science/article/pii/S1364032112002705#tbl5fnb) | 58[b](http://www.sciencedirect.com/science/article/pii/S1364032112002705#tbl5fnb) | 16.8 | 269 |
| KOH/Al2O3 | 3 | 180 | 6 | Na | 49[b](http://www.sciencedirect.com/science/article/pii/S1364032112002705#tbl5fnb) | 13.0 | 269 |
| KOH/Hβ | 3 | 180 | 6 | Na | 52[b](http://www.sciencedirect.com/science/article/pii/S1364032112002705#tbl5fnb) | 13.0 | 269 |
| KOH/X | 3 | 180 | 6 | Na | 52[b](http://www.sciencedirect.com/science/article/pii/S1364032112002705#tbl5fnb) | 15.0 | 269 |
| K2CO3 | 5.5 | 140 | 1.5 | Na | 47.9[a](http://www.sciencedirect.com/science/article/pii/S1364032112002705#tbl5fna) | 47.0 | [270](http://www.sciencedirect.com/science/article/pii/S1364032112002705#bib97) |
| [bmim]BF4/CH3ONa | 4 | 150 | 5 | 95.0[b](http://www.sciencedirect.com/science/article/pii/S1364032112002705#tbl5fnb) | Na | 67.6 | [271](http://www.sciencedirect.com/science/article/pii/S1364032112002705#bib98) |
| KI/ZnO | 16.5 | 150 | 4 | 98.6[a](http://www.sciencedirect.com/science/article/pii/S1364032112002705#tbl5fna) | Na | 57.9 | 272 |
| KI/ZnO | 16.5 | 150 | 4 | 99.6[b](http://www.sciencedirect.com/science/article/pii/S1364032112002705#tbl5fnb) | Na | 36.8 | 272 |
| K2CO3-KI/ZnO | 16.5 | 150 | 4 | 98.0[a](http://www.sciencedirect.com/science/article/pii/S1364032112002705#tbl5fna) | Na | 63.2 | 272 |
| K2CO3-KI/ZnO | 16.5 | 150 | 4 | 98.7[b](http://www.sciencedirect.com/science/article/pii/S1364032112002705#tbl5fnb) | Na | 43.4 | 272 |
| KI/MgO | 16.5 | 150 | 4 | 96.7[a](http://www.sciencedirect.com/science/article/pii/S1364032112002705#tbl5fna) | Na | 43.8 | 272 |
| KI/MgO | 16.5 | 150 | 4 | 98.7[b](http://www.sciencedirect.com/science/article/pii/S1364032112002705#tbl5fnb) | na | 25.8 | 272 |
| KI/CaO | 16.5 | 150 | 4 | 97.4[a](http://www.sciencedirect.com/science/article/pii/S1364032112002705#tbl5fna) | Na | 36.1 | 272 |

a  Ethylene carbonate; b  Propylene carbonate; c Styrene carbonate

* + - 1. **Synthesis of DMC from CO2, acetals or ortho-ester**

There are a few reports on the heterogeneous catalysts employed in the synthesis of DMC from CO2 and acetal or ortho-ester. Acetal or ortho-ester while used as starting materials can act as dehydrated derivative, and can avoid the negative effect of deactivation of catalysts by water in the reaction system [251, 273-275]. Polymer-supported iodide in the presence of trimethyl orthoesters was found to be an effective catalyst [274]. Sakakura et al. [273] reported that the addition of 2,2-dimethoxypropane in the reaction system assist to overcome the thermodynamic limitation, exhibiting a steady increase in DMC yield during the long reaction time up to 100 h. An increase in CO2 pressure up to 200 MPa enhanced the DMC yield and selectivity up to 90% and 100%, respectively due to an increased CO2 density at high pressures [273]. An addition of small amount of acidic co-catalysts to Bu2SnO or Ti(O-i-Pr)4 catalysts accelerated the yield of DMC [275]. The obtained DMC yield was only 17% over Bu2SnO without acidic co-catalysts, while the addition of p-toluene sulfonic acid increased the DMC yield up to 20%. The yield of DMC increased two fold in the presence of ammonium triflates such as [Ph2NH2]OTf and [C6F5NH3]OTf. Further, the addition of conventional Brönsted acid co-catalysts (HCl, H2SO4 and H3PO4) and ammonium chloride co-catalyst ((Ph2NH2)Cl and Bu4NCl ) in the reaction system showed no significant effect in the DMC yield. Addition of [Ph2NH2]OTf as co-catalyst to Ti(O-i-Pr)4 improved the DMC yield to nearly five times as compared to Ti(O-i-Pr)4 [275]. The high catalytic activities are related to the affinity to CO2 and relatively strong acidities of co-catalysts [275]. It should be noted that the reaction depends strongly on the CO2 pressure and needs to be operated at very high pressures up to 200 Mpa to obtain an optimum yield of DMC. Table 5.6 summarizes various heterogeneous catalysts used in the synthesis of DMC from CO2 and acetal or ortho-ester.

Table 5.6 Various heterogeneous catalysts used in the synthesis of DMC from CO2 and acetal or ortho-ester

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Catalyst | Co-catalyst | Acetal/ortho-ester | Reaction conditions | | | DMC yield (%) | Ref. |
| Pressure (MPa) | Temp (°C) | Time (h) |
| Bu2Sn(OMe)2 | Na | 2,2-dimethoxypropane | 30 | 180 | 24 | 14 | [[273]](http://www.sciencedirect.com/science/article/pii/S1364032112002705#bib100) |
| Polymer-supported iodide | Na | Trimethylorthoesters | 200 | 150 | 6 | 90 | [[274]](http://www.sciencedirect.com/science/article/pii/S1364032112002705#bib101) |
| Bu2SnO | Na | 2,2-dimethoxypropane | 30 | 180 | 24 | 17 | [[275]](http://www.sciencedirect.com/science/article/pii/S1364032112002705#bib102) |
| Bu2SnO | CH3-C6H4-SO3H | 2,2-dimethoxypropane | 30 | 180 | 24 | 20 | [[275]](http://www.sciencedirect.com/science/article/pii/S1364032112002705#bib102) |
| Bu2SnO | [Ph2NH2]OTf | 2,2-dimethoxypropane | 30 | 180 | 24 | 40 | [[275]](http://www.sciencedirect.com/science/article/pii/S1364032112002705#bib102) |
| Bu2SnO | [C6F5NH3]OTf | 2,2-dimethoxypropane | 30 | 180 | 24 | 40 | [[275]](http://www.sciencedirect.com/science/article/pii/S1364032112002705#bib102) |
| Ti(O-i-Pr)4 | Na | 2,2-dimethoxypropane | 30 | 180 | 24 | 5 | [[275]](http://www.sciencedirect.com/science/article/pii/S1364032112002705#bib102) |
| Ti(O-i-Pr)4 | [Ph2NH2]OTf | 2,2-dimethoxypropane | 30 | 180 | 24 | 25 | [[275]](http://www.sciencedirect.com/science/article/pii/S1364032112002705#bib102) |

* + 1. **Concluding Remarks and Perspectives**

CO2 being a renewable and environmentally friendly source of carbon, conversions of CO2 to fuels and chemicals offer opportunities to mitigate the increasing CO2 buildup in the atmosphere. As discussed in this chapter, hydrogenation of CO2 is a feasible and powerful process in this regard. However, the high chemical stability of CO2 and unfavourable thermodynamics are to be taken into consideration. To eliminate the limitations on the conversion and selectivity, various technical directions and specific research approaches on rational design of catalysts, reactor optimization, and exploration of reaction mechanisms have been attempted.

Both homogenous and heterogeneous catalysts play crucial roles in the hydrogenation of CO2. Homogeneous catalysts (e.g., Ru-, Rh-, and Ir-based catalysts) are efficient for the formation of formic acid and formates. The reactions can be accelerated by the addition of solvents such as water, supercritical CO2, and ionic liquids. However, the need for expensive catalyst, high operating pressure, and the tedious procedures involved for catalyst separation and recycling make these processes unattractive for commercial applications. Therefore, researchers have paid increasing attention to immobilize homogenous catalysts to combine the efficient activity with the properties of separation and recyclability. Heterogeneous catalysts (e.g., Fe-, Cu-, and Ni-based catalysts) are attractive due to practical reasons for industrial applications compared to homogeneous catalysts. The catalyst with larger surface area, ultrafine particle, and higher metal dispersion can usually possess higher activity and selectivity, and durability in the hydrogenation of CO2. However, these heterogeneous catalysts often suffer from low yield and poor selectivity due to fast kinetics of the C-H bond formation. Further, preparation methods have considerable influences on the nature of the catalysts (such as BET surface area, particle size, metal dispersion, etc.), leading to the disparities of the catalytic performance. Therefore, in order to make CO2 hydrogenation economically feasible, significant improvements in new catalytic systems with rational design and molecular simulations would be necessary. Even though a large number of investigations have been done with experimental observations and theoretical analyses, mechanisms of CO2 hydrogenation are still in infancy. For example, fundamental understanding regarding the role of added solvent at molecular level in the homogeneous systems is unclear. In heterogeneous reaction, the prevalent consensus is that the active site is provided by the synergy between the primary catalyst and the support or the promoter. Nevertheless, the nature of the active sites and interactions among active components, support, and promoter as well as reaction mechanisms are still elusive, even for the synthesis of formic acid, the first step of the hydrogenation. For both homogenous and heterogeneous catalysts, the primary focus of the mechanisms for CO2 hydrogenation is on how and where CO2 is activated and interacts with hydrogen and/or hydroxyl species under different reaction conditions. Surface science approaches coupled with molecular simulations would bridge the gap between the macroscopic characteristics (e.g., kinetics) of practical catalysts and molecular understanding of the reaction.

Utilizations of CO2 as solvent and reactant by the industries amount to only 0.5 wt% (~128 Mt y-1) of the total anthropogenic CO2 emissions every year in the atmosphere. Candidly, chemical utilizations of CO2 do not necessarily aid to mitigate the greenhouse effect considering energy input and carbon circulation. However, if CO2 could be chemically transformed to fuels, it would be helpful to circulate carbon to alleviate the greenhouse effect. Particularly, production of fuels that can be easily stored and transported is preferable. Commercially, methanol is produced from synthesis gas, mainly containing CO and H2 along with a small amount of CO2 (~6 Mt y-1) as the additive. Therefore, the utilization of CO2-enriched synthesis gas mixtures for CO2 hydrogenation would be a potential process to chemical industries. From scientific standpoint, the grand challenge is to the develop catalysts with inexpensive metals such as iron and copper compounds which can also be active in mild conditions. To reduce energy consumption, the introduction of electrochemical catalysis and solar energy with reactors not only alter the reaction equilibrium but also supplies hydrogen from water in situ. Moreover, efficient perm-selective membranes can be employed to isolate the by-product water from the reaction systems which deactivates catalysts and inhibits reaction rate. It is yet another challenge to look into the efficient hydrogenation of CO32- or HCO3- in detail, considering the availability and handling. The future R&D efforts should certainly focus on the rational design of highly active catalyst and integral process to satisfy the economic development and sustainable utilization of carbon sources.