



## **Recent advances in hydrogenation of CO<sub>2</sub> into hydrocarbons via methanol intermediate over heterogeneous catalysts**

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## MINI REVIEW

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[View Journal](#) | [View Issue](#)Cite this: *Catal. Sci. Technol.*, 2021, 11, 1665Recent advances in hydrogenation of CO<sub>2</sub> into hydrocarbons via methanol intermediate over heterogeneous catalystsPoonam Sharma, Joby Sebastian, Sreetama Ghosh,  
Derek Creaser and Louise Olsson \*

The efficient conversion of CO<sub>2</sub> to hydrocarbons offers a way to replace the dependency on fossil fuels and mitigate the accumulation of surplus CO<sub>2</sub> in the atmosphere that causes global warming. Therefore, various efforts have been made in recent years to convert CO<sub>2</sub> to fuels and value-added chemicals. In this review, the direct and indirect hydrogenation of CO<sub>2</sub> to hydrocarbons via methanol as an intermediate is spotlighted. We discuss the most recent approaches in the direct hydrogenation of CO<sub>2</sub> into hydrocarbons via the methanol route wherein catalyst design, catalyst performance, and the reaction mechanism of CO<sub>2</sub> hydrogenation are discussed in detail. As a comparison, various studies related to CO<sub>2</sub> to methanol on transition metals and metal oxide-based catalysts and methanol to hydrocarbons are also provided, and the performance of various zeolite catalysts in H<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>O rich environments is discussed during the conversion of methanol to hydrocarbons. In addition, a detailed analysis of the performance and mechanisms of the CO<sub>2</sub> hydrogenation reactions is summarized based on different kinetic modeling studies. The challenges remaining in this field are analyzed and future directions associated with direct synthesis of hydrocarbons from CO<sub>2</sub> are outlined.

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## 1. Introduction

Global warming and dwindling fossil fuels have been a huge and growing recent concern for the human community. The excessive use of fossil fuels increases the emissions of CO<sub>2</sub> into the atmosphere and contributes to global warming.<sup>1–3</sup> Therefore, the conversion of CO<sub>2</sub> to value-added products is a very attractive method to use a non-toxic, renewable and abundant source of carbon<sup>4</sup> (Fig. 1). The synthesis of electrofuels also offers the possibility to produce carbon-based fuels from CO<sub>2</sub> and H<sub>2</sub>O using renewable electricity as the primary source of energy.<sup>5</sup> There are two main sources of CO<sub>2</sub> emissions: 1) biogenic sources and 2) fossil sources. Biogenic emissions are from either natural or human harvesting, combustion, fermentation and decomposition of biomaterials. It involves carbon that is already in the biosphere and is thus part of the natural carbon cycle. Fossil carbon is derived from largely human driven combustion and processing of fossil resources, like natural gas, coal, and petroleum, and involves an unsustainable transfer of carbon that has been stored in the earth's crust for hundreds of millions of years into the biosphere.<sup>6,7</sup>

Carbon capture is the main technology to obtain CO<sub>2</sub> from different sources before and after its release into the atmosphere. The captured CO<sub>2</sub> can thereafter be either stored, *i.e.* carbon capture and storage (CCS), or utilized further in carbon capture and utilization (CCU). Pre-combustion, post-combustion, and oxyfuel combustion are the three main CO<sub>2</sub> capture systems related to different combustion processes.<sup>8,9</sup> Out of them, the post-combustion technology offers a way to capture CO<sub>2</sub> from flue gases that come from the combustion of fossil fuels. There are many separation technologies such as wet scrubbing, dry

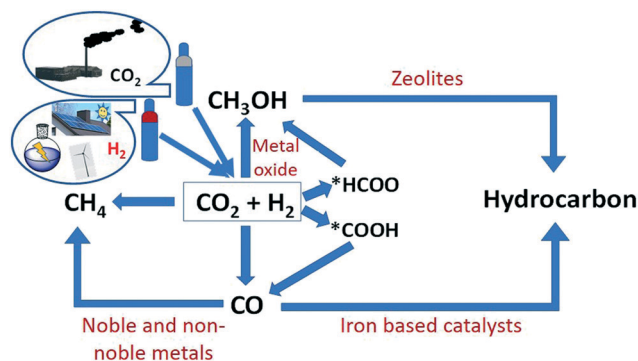


Fig. 1 Pictorial representation of regeneration of CO<sub>2</sub> to value-added products via hydrogenation.

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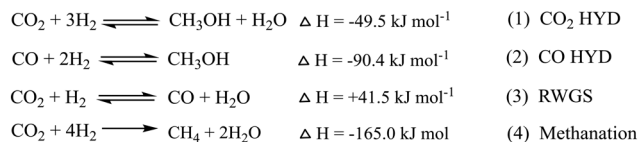
regenerable adsorption, membrane separation, cryogenic distillation, pressure and temperature swing adsorption that can be used to isolate CO<sub>2</sub> from flue gases.<sup>8</sup> CCS could face many challenges concerning transportation and storage of CO<sub>2</sub>, as there is a possibility for leakage and contamination of groundwater if geological storage is used.<sup>10</sup>

The utilization of CO<sub>2</sub> after capturing is an attractive way to mitigate CO<sub>2</sub> emissions. There are several processes where CO<sub>2</sub> can be utilized such as enhanced oil recovery,<sup>11</sup> mineralization,<sup>12</sup> and conversion into value-added chemicals and fuels.<sup>13</sup> However, CCU needs a large amount of energy for the conversion of CO<sub>2</sub> due to its kinetic inertness and thermodynamic stability, but it could function as a part of the sustainable natural carbon cycle in the biosphere, if the cost of the produced materials is equal to the cost of their production as well as possible offset costs for emissions while reducing the excess CO<sub>2</sub> emitted into the atmosphere.<sup>14</sup> The second main reagent for CO<sub>2</sub> transformation is hydrogen. Hydrogen itself is a renewable source of energy if it is produced from water splitting and using electricity from resources like wind, hydro and solar at low cost<sup>15</sup> but its handling, storage, and transportation are challenging, considering its explosiveness and low-energy density. It is therefore a large advantage to use hydrogen for the reduction of CO<sub>2</sub> and in this way to store energy in the form of chemicals and fuels, which are easier to store and transport. Therefore, the current focus of this review is the production of chemicals like CH<sub>3</sub>OH (methanol) and value-added hydrocarbons such as lower olefins, gasoline, aromatics and petroleum gas from the hydrogenation (HYD) of CO<sub>2</sub>.

The hydrocarbon synthesis could be possible *via* direct and indirect routes (Scheme 1).<sup>16</sup>

1. Indirect CO<sub>2</sub> hydrogenation to hydrocarbons
2. Direct CO<sub>2</sub> hydrogenation to hydrocarbons

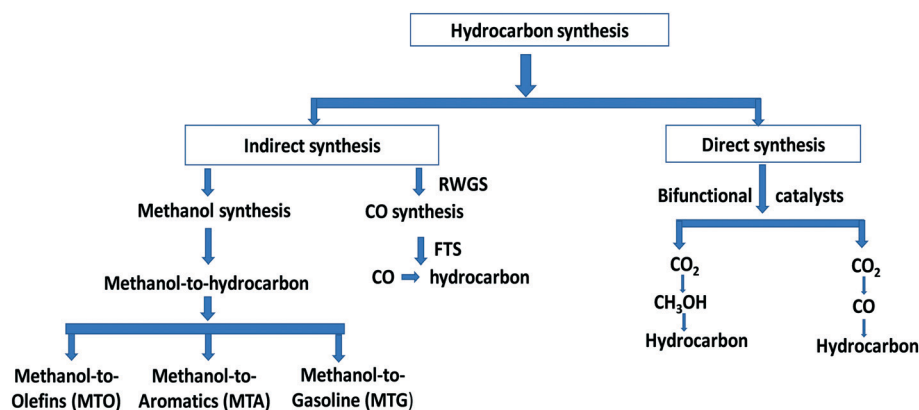
There are two main routes in indirect synthesis of hydrocarbons from CO<sub>2</sub> which are (i) synthesis of CH<sub>3</sub>OH and subsequent transformation into hydrocarbons (olefins, gasolines, aromatics, alkanes, and so on) in different stages and (ii) synthesis of CO *via* reverse water gas shift (RWGS) and then formation of hydrocarbons using a modified Fischer–Tropsch synthesis (FTS) process based on two reactor



Scheme 2 Possible reaction between CO/CO<sub>2</sub> and H<sub>2</sub>.

stages. Hydrocarbons can be synthesized by a direct route which could be more economically favourable and environmentally benign compared to indirect routes.<sup>17,18</sup> The direct route also includes two routes: (i) hydrocarbon synthesis over bifunctional catalysts in which CO<sub>2</sub> is first hydrogenated into CH<sub>3</sub>OH and then hydrocarbon, and (ii) reduction of CO<sub>2</sub> to CO *via* the RWGS reaction followed by hydrogenation of CO to hydrocarbons *via* FTS. There are various possible reactions between CO/CO<sub>2</sub> and H<sub>2</sub> (Scheme 2), which could occur during CO/CO<sub>2</sub> hydrogenation.

Some reviews have explored the catalytic hydrogenation of CO<sub>2</sub> including various factors related to catalyst activity, selectivity and conversion of CO<sub>2</sub>.<sup>19–21</sup> These reviews mainly focus on various aspects of CO<sub>2</sub> hydrogenation over noble and non-noble metal catalysts.<sup>19–25</sup> In this review, the objective is to focus on recent advances in CO<sub>2</sub> hydrogenation to hydrocarbons *via* methanol as an intermediate. In recent studies, CO<sub>2</sub> hydrogenation over bifunctional catalysts was found to be an efficient method to synthesize hydrocarbons. In addition, metal and metal oxide-based catalysts have been developed for the synthesis of CH<sub>3</sub>OH and hydrocarbons directly from CO<sub>2</sub> reduction. Thus, this review includes these recent studies where hydrocarbons are synthesized directly from CO<sub>2</sub> in a single step combining CO<sub>2</sub> to methanol, and methanol to hydrocarbons reaction steps. The mechanisms, catalyst preparation methods, and proximity effects are discussed based on results from *in situ* experiments and DFT studies over bifunctional catalysts to understand the one-step process for the synthesis of hydrocarbons. To gain a flavor of how each process performs separately, detailed studies of CO<sub>2</sub> to methanol and methanol to hydrocarbons are also discussed in this review. More specifically, for the



Scheme 1 A schematic overview of hydrocarbon synthesis.



methanol to hydrocarbons process, we review the process from the perspective of the CO<sub>2</sub> to hydrocarbons process itself. Thus, the performance of catalysts in the presence of H<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>O (the reactants and byproducts of the direct conversion of CO<sub>2</sub> to hydrocarbons process) is discussed in detail. Furthermore, this section also incorporates a review of the methanol to hydrocarbons process, reaction mechanism based on experimental evidence, shape selectivity, catalyst deactivation, and regeneration pathways for a better understanding of the direct conversion of CO<sub>2</sub> to hydrocarbons process discussed in detail in the following section. In addition, this review also provides an outline of various aspects like catalyst synthesis, catalytic activity and reaction mechanisms from experiments, DFT calculations, and a kinetic modeling section discussing the reaction kinetics for the conversion of CO<sub>2</sub> to methanol and methanol to hydrocarbons using advanced heterogeneous catalysts.

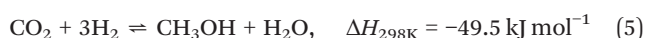
Thus, this review consists of four major sections which cover (1) CO<sub>2</sub> to methanol, (2) methanol to hydrocarbons, (3) CO<sub>2</sub> to hydrocarbons, and (4) kinetic modeling.

## 2. Indirect CO<sub>2</sub> hydrogenation

A variety of chemicals such as CH<sub>3</sub>OH, dimethyl ether (DME), formic acid, ethanol, and hydrocarbons like methane, liquid fuels, aromatics and lower olefins are the products of CO<sub>2</sub> hydrogenation. There are many reports and reviews on the synthesis of these products from CO<sub>2</sub>.<sup>24,26</sup> For example, Yang *et al.* reported the catalytic hydrogenation of CO<sub>2</sub> to value-added hydrocarbons.<sup>20</sup> Recently, Li *et al.* reviewed the recent advances in CO<sub>2</sub> hydrogenation to CH<sub>4</sub> and C<sub>2+</sub> hydrocarbons over Ni, Co, Ru, Ir, Fe and Rh catalysts and discussed the metal-support interaction, effect of metal particle size, process integration, reaction mechanism, and catalyst deactivation during CO<sub>2</sub> hydrogenation.<sup>27</sup> This review section covers the indirect route of CO<sub>2</sub> hydrogenation into hydrocarbons which includes (1) CO<sub>2</sub> hydrogenation to CH<sub>3</sub>-OH and (2) CH<sub>3</sub>OH to hydrocarbons (MTH). A detailed study of catalyst performance and reaction mechanisms is discussed below.

### 2.1 CO<sub>2</sub> hydrogenation to CH<sub>3</sub>OH

This section gives an overview of the various reports on CH<sub>3</sub>-OH synthesis (Table 1). Methanol has been synthesized by heterogeneous and homogeneous catalysis, as well as electrochemical and photocatalytic processes.<sup>28–34</sup> In earlier studies, syngas was the main source for the production of CH<sub>3</sub>OH as it can be produced from various sources such as biomass, natural gas, coal, and wastes, but in recent studies, CO<sub>2</sub> transformation into value added chemicals is found to be an important theme to use surplus CO<sub>2</sub> present in the environment. The main chemical reactions include direct CO<sub>2</sub> hydrogenation to CH<sub>3</sub>OH according to:



and the competing RWGS reaction:



From the above chemical reaction, it can be seen that CH<sub>3</sub>OH synthesis from CO<sub>2</sub> and the direction of the reaction depends upon temperature, pressure and reactant ratio as the CO<sub>2</sub> hydrogenation to CH<sub>3</sub>OH reaction is exothermic (eqn (5)), whereas the competitive RWGS reaction is endothermic (eqn (6)). Generally, a lower reaction temperature and higher reaction pressure favor the synthesis of CH<sub>3</sub>OH. However, a high reaction temperature is helpful for CO<sub>2</sub> activation whereas the lower temperature is thermodynamically favorable for CH<sub>3</sub>OH formation and this condition may create a kinetic limitation for the reaction. Under the reaction conditions, there are other competing reactions that occur in addition to RWGS that can produce many side products like methane, formaldehyde, and formic acid.<sup>32</sup> The water vapor and other side products inhibit the reaction and may cause catalyst deactivation.<sup>35–37</sup> To avoid the formation of side products and increase the stability of the catalyst, an efficient catalyst system is required.

Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts have been used and studied for the synthesis of CH<sub>3</sub>OH from syngas at the industrial scale while at the laboratory scale, the Cu–ZnO system with various support materials has been studied extensively for CH<sub>3</sub>OH synthesis.<sup>38–40</sup> A number of research groups have developed a wide variety of heterogeneous catalysts for the synthesis of CH<sub>3</sub>OH from CO<sub>2</sub> hydrogenation. There are various reports in which Cu, Pd, Ag and Pt have been used as active catalysts and as promoters, and oxygen-deficient materials like In<sub>2</sub>O<sub>3</sub> have been employed as active catalysts.<sup>41–44</sup>

**2.1.1 Transition metal-based catalysts for methanol synthesis.** Numerous reports and reviews based on transition-metal-catalyzed CH<sub>3</sub>OH synthesis have been published as shown in Table 1.<sup>22,23,25,45</sup> Transition metals have been used for CO<sub>2</sub> hydrogenation due to their considerable activity and selectivity. Most of the studies have employed Cu-based systems, such as Cu–ZnO-based composites, that have demonstrated good activity for CH<sub>3</sub>OH synthesis. In these studies, Al<sub>2</sub>O<sub>3</sub> (alumina) and ZrO<sub>2</sub> (zirconia) have appeared as the most popular support materials.<sup>46–48</sup> Other than Cu, Pd-based catalysts with Ga<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub> and SiO<sub>2</sub> as supports have been screened for CH<sub>3</sub>OH synthesis.<sup>49–51</sup> Bimetallic combinations like Co–Cu, Ni–Ga, Au–Cu, and Pd–Cu have been tested for CH<sub>3</sub>OH synthesis from CO<sub>2</sub> hydrogenation.<sup>52–56</sup>

At the industrial scale, BASF was the first to produce CH<sub>3</sub>OH from syngas.<sup>57,58</sup> The Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst, which was developed by ICI (Imperial Chemical Industries), allowed for industrial operation under milder reaction conditions.<sup>59–61</sup> In many reports, Cu has been used as an active catalyst and later it was modified with other metals and non-metal promoters. Activity and selectivity for CO<sub>2</sub> hydrogenation over Cu alone were not enough for large scale CH<sub>3</sub>OH synthesis; thus appropriate changes were made to increase the activity and selectivity of catalysts.<sup>62,63</sup> No doubt, the achievable activity and



**Table 1** Catalytic performance of transition metal-based catalysts in CO<sub>2</sub> hydrogenation to CH<sub>3</sub>OH

Catalysts	<i>P</i> (MPa)	Preparation method	<i>T</i> (K)	GHSV (h <sup>-1</sup> )	CO <sub>2</sub> conv. (%)	CH <sub>3</sub> OH select. (%)	Ref.
Cu/ZrO <sub>2</sub>	1.7	Co-precipitation	493	—	6.0	67.0	46
Cu–ZnO	5	Co-precipitation	523	—	11.7	36.1	51
Cu/ZnO/Al <sub>2</sub> O <sub>3</sub>	4.9	Co-precipitation	523	—	19.7	48.1	47
Cu/ZrO <sub>2</sub>	1.7	Sequential precipitation	623	—	6.9	70.0	48
Cu/ZrO <sub>2</sub>	2	Deposition–precipitation	513	5400	6.3	48.8	64
Cu/Zn/Ga/SiO <sub>2</sub>	2	Co-precipitation	543	—	5.6	99.5	83
Cu/Ga/ZnO	2	Co-precipitation	543	—	6.0	88.0	84
Cu/YDC/γ-Al <sub>2</sub> O <sub>3</sub>	3	Co-precipitation	523	—	na	78.6	87
Cu/ZnO/ZnO	2	Gel co-precipitation	513	7200	17.3	32.4	88
Cu–ZnO–ZrO <sub>2</sub>	8	Co-precipitation	493	3300	21.0	68.0	81
Mn–Cu/Zn/ZrO <sub>2</sub>	10	Thermal decomposition	553	3400	16.0	91.0	85
Cu/Ga/ZrO <sub>2</sub>	2	Deposition–precipitation	523	2500	13.7	75.5	86
Cu/B/ZrO <sub>2</sub>	2	Deposition–precipitation	523	2500	15.8	67.2	86
Cu/Zn/Ga/ZrO <sub>2</sub>	8	Co-precipitation	523	3300	na	75.0	55
Cu/Zn/Al/ZrO <sub>2</sub>	4	Co-precipitation	513	9742	18.7	47.2	89
Cu–ZnO–Al <sub>2</sub> O <sub>3</sub>	5	Co-precipitation	443	—	14.3	54.8	90
Cu–ZnO–ZrO <sub>2</sub>	1.0–3.0	Co-precipitation	473	8800	5.8	55.2	91
Cu–ZnO–ZrO <sub>2</sub>	3	Co-precipitation	503	—	15.2	35.1	82
Cu/Zn/ZrO <sub>2</sub>	3	Co-precipitation	523	—	19.4	29.3	82
Cu/Zn/ZrO <sub>2</sub>	3	Urea–nitrate combustion	513	3600	17.0	56.2	92
Cu/Zn/ZrO <sub>2</sub>	3	Glycine–nitrate combustion	493	3600	12.0	71.1	93
Cu/plate ZnO/Al <sub>2</sub> O <sub>3</sub>	4.5	Precipitation	543	—	10.9	72.7	69
Cu/Ga <sub>2</sub> O <sub>3</sub> /ZrO <sub>2</sub>	3	Ion exchange/impregnation	523	20 000	1.3	74.0	54
Cu/Al <sub>2</sub> O <sub>3</sub>	95	Impregnation	553	11 900–25 000	30.0	80.0	78
Cu–ZnO–ZrO <sub>2</sub>	4	Co-precipitation	513	4000	na	na	94
Cu–ZnO–Al <sub>2</sub> O <sub>3</sub>	36	Co-precipitation	533	10 471	65.8	77.3	79
Cu/ZnO/Al <sub>2</sub> O <sub>3</sub>	3	Co-precipitation	503	—	18.3	43.0	80
Cu/ZnO/ZrO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	3	Co-precipitation	503	—	23.2	60.3	80
Cu–ZnO–ZrO <sub>2</sub>	3	Co-precipitation	513	3600	12.1	54.1	95
Cu–ZnO–ZrO <sub>2</sub>	5	Co-precipitation	553	10 000	23.0	33.0	96
Cu/ZrO <sub>2</sub>	3	Impregnation	553	—	12.0	32.0	97
Cu/ZrO <sub>2</sub>	0.1	Deposition–precipitation	493	—	0.53	19.8	98
Cu–ZnO–ZrO <sub>2</sub>	5	Co-precipitation	553	10 000	21.0	34.0	99
Cu–ZnO–Al <sub>2</sub> O <sub>3</sub>	44.2	Co-precipitation	553	10 000	65.3	91.9	77
Cu–ZnO–ZrO <sub>2</sub>	3.9	Co-precipitation	473	7800	3.9	70.0	100
Pd/SiO <sub>2</sub>	0.95	Incipient wetness	548	—	0.8	9.5	49
Pd/CeO <sub>2</sub>	3	Impregnation	533	—	5.2	84.7	50
Pd/SiO <sub>2</sub>	5	Co-precipitation	523	—	0.05	100	51
Pd/Ga <sub>2</sub> O <sub>3</sub>	5	Co-precipitation	523	—	19.6	51.5	51
PdZn/h-CNTs	3	Impregnation	523	1800	na	99.6	101
Pd/β-Ga <sub>2</sub> O <sub>3</sub>	3	Incipient impregnation	523	—	0.9	52.0	102
PdGa/(β-Ga <sub>2</sub> O <sub>3</sub> )	0.7	Incipient wetness impregnation	523	—	≤1	5.2	103
Pd/plate Ga <sub>2</sub> O <sub>3</sub>	5	Deposition	523	—	17.3	51.6	104
PdGa/(rod-Ga <sub>2</sub> O <sub>3</sub> )	5	Impregnation	523	—	11.0	41.3	105
Pd–Cu/SiO <sub>2</sub>	4.1	Impregnation	573	3600	6.6	34.0	52
Pd/ZnO	2	Sol-immobilization	523	—	10.7	60.0	106
PdZnAl/hydrotalcite	3	Co-precipitation	523	—	0.6	60.0	107
Au/ZnO/ZrO <sub>2</sub>	8	Co-precipitation	493	3300	1.5	100	81
Au/Cu–ZnO–Al <sub>2</sub> O <sub>3</sub>	1–6	Co-precipitation	533	7000–13 200	28.0	55.0	56
Au/ZnO	0.5	Deposition–precipitation	493	—	0.2	56.2	108
Au/ZnO	0.5	Deposition–precipitation	513	—	1.0	70.0	109
Ni <sub>5</sub> Ga <sub>3</sub> /SiO <sub>2</sub>	1	Impregnation	483	6000	na	na	110
PtW/SiO <sub>2</sub>	3	Impregnation	473	—	2.6	92.2	111
Re/ZrO <sub>2</sub>	1	Impregnation	433	—	na	73.2	112
Rh/TiO <sub>2</sub>	1	Impregnation	513	2400	na	60.7	113
Rh/SiO <sub>2</sub>	5	Impregnation	473	—	0.5	6.8	114
Rh/TiO <sub>2</sub>	2	Incipient wetness impregnation	543	3000–6000	7.9	0.8	53
Rh–Fe/TiO <sub>2</sub>	2	Incipient wetness impregnation	543	3000–6000	9.2	1.2	53
Ag/ZnO/ZrO <sub>2</sub>	8	Co-precipitation	493	3300	2.0	97.0	81
La–Zr–Cu–ZnO	5	Sol–gel	523	3600	13.0	52.5	115

na = not available.

selectivity depend on other factors as well like the catalyst composition, catalyst preparation method and reaction

conditions which also affect the surface structure of the catalyst.<sup>64</sup> ZnO has been found to be most preferably combined





with Cu, as it facilitates the dispersion and stability of the active Cu sites by providing a close contact between itself and the Cu phase.<sup>23,25,65</sup> The interface between Cu and ZnO plays a crucial role in preparing a highly active catalyst and it can be optimized by various factors like temperature, hydrogen partial pressure, and heating rate.<sup>66,67</sup> In addition, the exposed phase of ZnO which is in contact with Cu regulates the catalytic activity of the Cu/ZnO system.<sup>68,69</sup> Lei *et al.* studied the morphology effect of ZnO and found that the (002) face of ZnO gave good results in CH<sub>3</sub>OH synthesis due to its higher concentration of oxygen vacancies.<sup>68</sup> Several efforts have been made to increase the activity of the Cu/ZnO system by fabricating new structures of the catalyst like a core-shell design of Cu-ZnO, graphitic-like ZnO and nano-alloy layers of Cu-Zn.<sup>66,67,70,71</sup> Further, Cu/ZnO-based catalysts have been modified with promoters and stabilizers to increase the activity and stability.<sup>72,73</sup> Later, it has been reported that the addition of Al<sub>2</sub>O<sub>3</sub> increases the stabilization of the Cu active site.<sup>74</sup> Another method to increase activity is to focus on the synthesis process. The conventional synthesis process for Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> is co-precipitation in which the synthesis of hydroxycarbonates of Cu, Zn and Al<sub>2</sub>O<sub>3</sub> is a crucial stage. This stage can alter the surface area of Cu and the interaction between ZnO and Cu that are the important factors to define/change the activity of the catalysts.<sup>29,75</sup> The synthesis of the hydroxycarbonates can be controlled by pH, temperature and precipitate washing.<sup>76</sup>

Gaikwad *et al.* studied the effect of pressure, temperature, and GHSV (gas hourly space velocity) on CO<sub>2</sub> hydrogenation to CH<sub>3</sub>OH over a commercial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst.<sup>77</sup> Excellent results were observed at 44.2 MPa with a low GHSV in the range of 533–553 K (Table 1). In this study, the authors achieved the highest CH<sub>3</sub>OH selectivity compared to the other Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>-based studies mentioned in Table 1 along with high CO<sub>2</sub> conversion. Cu/Al<sub>2</sub>O<sub>3</sub> has also been screened for CH<sub>3</sub>OH synthesis at 95 MPa to get a higher product yield and CO<sub>2</sub> conversion.<sup>78</sup> Tidona *et al.* reported a higher space-time yield at 95 MPa compared to 3 MPa.<sup>78</sup> In both studies, it can be noted though that the extreme pressures which are thermodynamically favorable played an important role in obtaining higher conversion and selectivity rather than the catalyst performance. To get higher CH<sub>3</sub>OH selectivity, Bansode and Urakawa reported the effect of high H<sub>2</sub> partial pressure by decreasing the molar ratio of CO<sub>2</sub>/H<sub>2</sub> from 1:3 to 1:10 and they found good CH<sub>3</sub>OH selectivity and CO<sub>2</sub> conversion with excess CO<sub>2</sub>.<sup>79</sup> Li *et al.* doped Zr into commercial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts and studied the activity, stability and poisoning effect of water on the active sites of the catalysts.<sup>80</sup> The authors found excellent performance for the Zr-doped catalyst compared to the commercial catalyst with excellent tolerance for water vapor. Considering the positive effect of Zr in CO<sub>2</sub> hydrogenation, Al<sub>2</sub>O<sub>3</sub> has been replaced with ZrO<sub>2</sub> in recent years. Słoczyński *et al.* synthesized a series of catalysts in which crystalline ZnO and amorphous ZrO<sub>2</sub> were co-precipitated with Cu, Ag, and Au.<sup>81</sup> The Cu-containing ZnO/ZrO<sub>2</sub> catalyst exhibited higher activity than Ag and Au. The effect of suspension ageing on a co-precipitated Cu/ZnO/ZrO<sub>2</sub> catalyst

was studied by Raudaskoski *et al.* and as a result, they found higher CO<sub>2</sub> conversion and selectivity to CH<sub>3</sub>OH with increasing ageing time. With a longer ageing time, a fine crystallite structure of the catalyst was obtained with a high surface area and less sodium content as Na<sub>2</sub>CO<sub>3</sub> was used as the precipitating agent. The longer ageing time also helped in the reduction of Cu.<sup>82</sup>

In addition, different modifiers are used to increase the activity and stability of the Cu-based system. Toyir *et al.* prepared a Ga-promoted Cu-based system in which SiO<sub>2</sub> and ZnO were used as supports. The hydrophilic nature of SiO<sub>2</sub> along with smaller particles of Ga<sub>2</sub>O<sub>3</sub> enhanced the catalytic activity. The hydrophilic support increased the dispersion of the catalyst whereas the small Ga<sub>2</sub>O<sub>3</sub> particles favor the formation of Cu<sup>+</sup>.<sup>83</sup> Further, the same group studied the influence of metallic precursors on the catalytic performance of the Ga-promoted Cu-based system and found that the use of methanolic solutions of methoxide-acetic acid precursors in the Ga-promoted catalyst preparation played a key role in obtaining a high performance catalyst in CO<sub>2</sub> hydrogenation to CH<sub>3</sub>OH.<sup>84</sup> Lachowska and Skrzypek investigated the effect of Mn as a promoter on Cu/Zn/Zr systems.<sup>85</sup> Later from the same group, Słoczyński *et al.* studied the effect of metal and metal oxides (Mn, B, In, Ga, Gd, Y, and Mg oxides) on the stability and activity of Cu/ZnO/ZrO<sub>2</sub> systems.<sup>55</sup> Among the various oxides, the Ga<sub>2</sub>O<sub>3</sub> additive with the catalyst gave the highest CH<sub>3</sub>OH selectivity. Liu *et al.* prepared Cu/Ga<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> and CuO/B<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> catalysts and in this study, they discussed the effect of the nanocrystalline Zr size on the catalytic performance.<sup>86</sup> It was observed that the nanocrystalline Zr changed various properties of the catalyst such as the electronic structure and the interaction between the metal and support, leading to more corner defects, facile reduction, and more oxygen vacancies on the surface, and all these changes were found to be beneficial for CH<sub>3</sub>OH synthesis. Fornero *et al.* synthesized Cu-GaO<sub>x</sub>/ZrO<sub>2</sub> catalysts and observed higher CH<sub>3</sub>OH selectivity with a high Ga/Cu atomic ratio.<sup>54</sup> Besides Cu, other transition metals have been used for CH<sub>3</sub>OH synthesis. In the literature, Pd-based catalysts are the most commonly studied for hydrogenation of CO<sub>2</sub> to CH<sub>3</sub>OH after Cu. Erdöhelyi *et al.* reported various Pd-based catalysts supported on SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and MgO and concentrated on the surface species during the reaction.<sup>49</sup> It was observed that the dispersion of Pd plays an important role in controlling the direction of the CO<sub>2</sub> + H<sub>2</sub> reaction. Pd catalysts supported on CeO<sub>2</sub>, SiO<sub>2</sub>, Ga<sub>2</sub>O<sub>3</sub> and carbon nanotubes (CNTs) were used for CH<sub>3</sub>OH synthesis.<sup>50,51</sup> Bahruji *et al.* prepared Pd/ZnO catalysts by different methods and screened them for hydrogenation of CO<sub>2</sub>. Their study includes the structure-activity relationship and they found the PdZn alloy to be the active site, where a high surface area, smaller alloy size, and less metallic Pd surface are favorable conditions to increase the selectivity for CH<sub>3</sub>OH.<sup>106</sup> Liang *et al.* developed PdZn alloys supported on multiwalled CNT catalysts for CH<sub>3</sub>OH synthesis where CNTs function as a promoter and catalyst support.<sup>101</sup> Pd-ZnO/CNT



catalysts were successful in providing a micro-environment with a higher concentration of active H-adspecies at the surface, whereas herringbone-type CNTs helped in the promotion of the catalysts.

Collins *et al.* studied Ga<sub>2</sub>O<sub>3</sub> supported Pd catalysts and explained the function of Ga<sub>2</sub>O<sub>3</sub> and Pd.<sup>102</sup> It is proposed in this catalytic system that gallium oxide provides a surface for adsorption of CO<sub>2</sub> as carbonate species and Pd dissociates the hydrogen molecule to hydrogen atoms that spillover to the oxide surface converting the adsorbed carbonate to formate species. Further, the same function and interaction between Pd and Ga were identified using quasi-*in situ* transmission electron microscopy by the same group.<sup>103</sup> The effect of the shape of Ga<sub>2</sub>O<sub>3</sub> on interactions was explained by Zhou *et al.*, where the (002) surface of Ga<sub>2</sub>O<sub>3</sub> was found to be highly unstable, which readily provided more O-defect sites and electrons in the conduction band than other surfaces. It gave higher metal dispersion that led to the formation of PdGa<sub>x</sub> which was found to be more active for CH<sub>3</sub>OH production.<sup>104,105</sup> In another metal series, Ni, Rh, Re, and Pt have been used for CH<sub>3</sub>OH selectivity as they have higher activity towards the hydrogenation reaction.<sup>53,112,113</sup> Studt *et al.* explored the activity of Ni-based alloys (NiGa, Ni<sub>3</sub>Ga and Ni<sub>5</sub>Ga<sub>3</sub>) for hydrogenation of CO<sub>2</sub> at ambient pressure.<sup>110</sup> Importantly, these alloys were superior to the Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst due to their ability to reduce the RWGS activity and favor CH<sub>3</sub>OH production.<sup>116,117</sup> The structure effect of the alloys on the reaction was studied by Sharafutdinov *et al.*,<sup>118</sup> where a series of Ni–Ga catalysts were prepared with different compositions. Later, the catalysts were screened, and it was found that the reactivity depended on the catalysts' intermediate phase, particle size or structure. The Ni<sub>5</sub>Ga<sub>3</sub> composition was found to be more active for CH<sub>3</sub>OH selectivity among the various compositions.<sup>110</sup>

Many studies have reported the high reactivity of Au and Ag towards CH<sub>3</sub>OH selectivity.<sup>81,108,119</sup> Hartadi *et al.* studied the pressure and CO effect over Au/ZnO catalysts and observed that high temperature and pressure inhibit the activity of the RWGS reaction and improve the product selectivity, whereas an increase in the CO concentration decreases the formation of CH<sub>3</sub>OH.<sup>119</sup> Słoczyński *et al.* prepared Au and Ag-based catalysts with a support composition of 3ZnO–ZrO<sub>2</sub> and studied the morphology, surface composition and activity of the catalysts for CH<sub>3</sub>OH synthesis from CO<sub>2</sub>.<sup>81</sup> In the Au–Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> system, the hydrogen spillover on the Au–Cu surface reduced the reaction selectivity towards CO.<sup>56</sup> Hartadi *et al.* reported about various Au supported catalysts (Au/Al<sub>2</sub>O<sub>3</sub>, Au/ZnO, Au/TiO<sub>2</sub>, and Au/ZrO<sub>2</sub>) and studied their activity for CH<sub>3</sub>OH synthesis.<sup>108</sup> The Au/ZnO system was found to be more selective for CH<sub>3</sub>OH synthesis and the authors extended this study to examine the effect of the catalyst size, total pressure, support, and influence of CO on the reaction activity.<sup>119</sup>

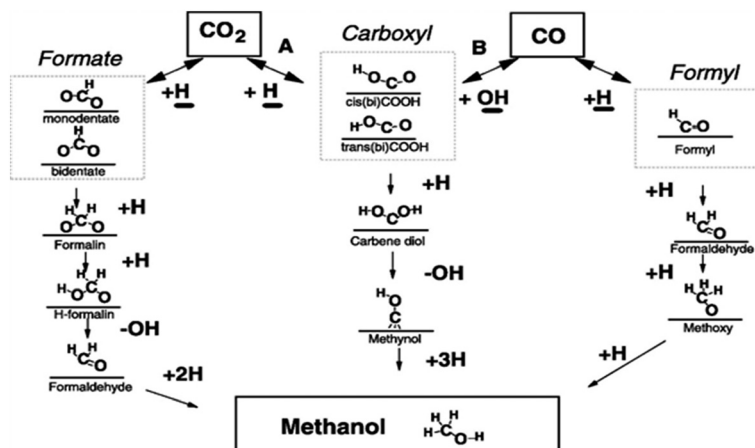
Frauenheim and Xiao reported first principles calculations for CO<sub>2</sub> hydrogenation on the ZnO supported Ag (111) monolayer.<sup>120</sup> The CO<sub>2</sub> adsorption on the pristine and

stretched surface of Ag (111) was weak and the ZnO support increased the binding ability of CO<sub>2</sub> and catalytic activity due to a strong metal–support interaction. Furthermore, the phase diagram for the Ag-doped ZnO surface was investigated under hydrogen and oxygen atmospheres and found stable in a hydrogen atmosphere. Also, the Zn impurities do not affect the reactivity for CO<sub>2</sub> adsorption and reduction.

**2.1.1.1 Reaction intermediates and mechanism over Cu-based systems.** Since many reports are based on Cu-based systems, the reaction mechanism has been more explored on Cu-containing catalysts by means of experiments, analytical techniques, and DFT calculations.<sup>89,121–124</sup> Many studies have reported two key intermediates formed during the synthesis of CH<sub>3</sub>OH.<sup>125,126</sup> Some research groups found the formate (HCOO\*) intermediate<sup>127,128</sup> whereas others the hydrocarboxyl species (COOH\*) on the surface of the catalysts. These intermediate species divide the mechanism into two routes: (1) formate route and (2) hydrocarboxyl route.<sup>129,130</sup> Scheme 3 below illustrates different possible reaction intermediates and steps during the hydrogenation of CO and CO<sub>2</sub> into CH<sub>3</sub>OH over Cu.<sup>131</sup> Here, we will only elaborate on the intermediates that formed during CO<sub>2</sub> hydrogenation. Nakatsuji and Hu explained the formation of formate on Cu (100) and Zn/Cu (100) surfaces employing *ab initio* calculations and found that CO<sub>2</sub> reacts with surface hydrogen to form formate *via* either a Langmuir–Hinshelwood (LH) or an Eley–Rideal (ER) mechanism.<sup>132</sup> In the formate route, first CO<sub>2</sub> reacts with atomic hydrogen to form HCOO\*. Further, this species again hydrogenates to HCOOH\* (ref. 63) which is further hydrogenated making H<sub>2</sub>-COOH\* followed by cleavage into H<sub>2</sub>CO\* and \*OH. Further, the subsequent hydrogenation of this species forms H<sub>3</sub>COH. In the above route, the first atomic hydrogen attached with carbon (HCOO\*) and the second hydrogen has two ways to attach: (A) it could attach again to carbon and form H<sub>2</sub>COO\* (ref. 40) and (B) it could bind with oxygen to make HCOOH\* (ref. 133) which further could take hydrogen on the carbon atom whereas H<sub>2</sub>COO\* could take hydrogen on the oxygen atom before cleavage. Larmier *et al.* determined the surface intermediates on the surface of Cu–ZrO<sub>2</sub> using kinetics, *in situ* IR, NMR, and DFT.<sup>121</sup> The combined results showed the formation of the HCOO\* intermediate and the Cu–ZrO<sub>2</sub> interface plays a crucial role in converting HCOO\* to CH<sub>3</sub>OH. Kattel *et al.* identified the same intermediate by kinetic Monte Carlo simulations, DFT, and X-ray photoemission spectroscopy (XPS) on the Cu–ZnO synergic interface.<sup>129</sup>

The second route favors the first attachment of atomic hydrogen with an oxygen of the CO<sub>2</sub> molecule rather than carbon to form \*COOH. Further, the second atomic hydrogen also binds with the second oxygen of CO<sub>2</sub> followed by the formation of \*OH and \*COH. Then the third, fourth and fifth hydrogen atoms bond with carbon to finally yield CH<sub>3</sub>OH.<sup>126</sup> In this route, there is one more possibility for successive hydrogenation. In this possible alternative, \*COOH (*cis*-COOH) first dissociates into CO and OH and a further hydrogen atom binds with carbon to form methoxy which





**Scheme 3** Mechanistic pathways for conversion of CO and CO<sub>2</sub> to CH<sub>3</sub>OH over Cu. Reprinted from *J. Catal.*, 298, Y. Yang, C. A. Mims, D. Mei, C. H. Peden and C. T. Campbell, Mechanistic studies of methanol synthesis over Cu from CO/CO<sub>2</sub>/H<sub>2</sub>/H<sub>2</sub>O mixtures: the source of C in methanol and the role of water, page no. 10–17, Copyright (2013), with permission from Elsevier.

then forms CH<sub>3</sub>OH by the addition of hydrogen with oxygen. This intermediate was observed on Cu (111) and proposed based on a DFT study. The authors claimed based on their DFT calculations that CO<sub>2</sub> hydrogenation to methanol on Cu (111) *via* the hydrocarboxyl (*trans*-COOH) intermediate is kinetically more favorable than formate in the presence of H<sub>2</sub>O *via* a unique hydrogen transfer mechanism. It was reported that the formate intermediate on Cu (111) is not feasible due to the high activation barriers for some of the elementary steps.<sup>126</sup>

Instead of the above two intermediates, Grabow *et al.* presented a model for CH<sub>3</sub>OH synthesis that includes reaction intermediates such as hydroxymethoxy (CH<sub>3</sub>O<sub>2</sub>) and formic acid (HCOOH) on a commercial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst.<sup>133</sup>

**2.1.2 Metal and metal oxide-based catalysts for methanol synthesis.** Most of the studies reported so far are on noble and non-noble metal systems.<sup>129,134–136</sup> Recently, oxide-based catalysts have been investigated for CO<sub>2</sub> hydrogenation apart from transition metal-based catalysts (Table 2). Oxide-based catalysts have different active sites than traditional metal catalysts with different reaction mechanisms. Recently, In<sub>2</sub>O<sub>3</sub>

was found to be a highly reported oxide for CH<sub>3</sub>OH synthesis. The activity of In<sub>2</sub>O<sub>3</sub> was studied for the RWGS reaction.<sup>137–139</sup> Moreover, some studies theoretically demonstrated the activity of In<sub>2</sub>O<sub>3</sub> towards CH<sub>3</sub>OH synthesis.<sup>140,141</sup> Sun *et al.* confirmed the previous theoretical studies and demonstrated with micro-kinetic modeling that the formation rate of CH<sub>3</sub>OH increases with increasing reaction pressure.<sup>44</sup> Martin *et al.* synthesized ZrO<sub>2</sub> supported In<sub>2</sub>O<sub>3</sub> which was found to be more stable (1000 h on stream) and more selective for CH<sub>3</sub>OH synthesis (100% selectivity) than a reference Cu–ZnO–Al<sub>2</sub>O<sub>3</sub> catalyst.<sup>142</sup> In addition, oxygen vacancies in In<sub>2</sub>O<sub>3</sub> are considered to be active sites and the number of vacancies can be regulated by CO feeding and due to effective electronic interaction with the ZrO<sub>2</sub> support. Recently, In<sub>x</sub>/ZrO<sub>2</sub> (*x* = 0.1–5 wt%) catalysts were screened for CH<sub>3</sub>OH under industrially relevant conditions and a highly tunable selectivity for CH<sub>3</sub>OH in CO<sub>2</sub> hydrogenation was observed.<sup>143</sup> With a loading of 2.5–5 wt.% of In, the catalysts have shown 70–80% CH<sub>3</sub>OH selectivity between 523 and 553 K, whereas 0.1% loading of In exhibited a CO selectivity of up to 80%. It is observed that the

**Table 2** Catalytic performance of oxide-based catalysts in CO<sub>2</sub> hydrogenation to CH<sub>3</sub>OH

Catalysts	Preparation method	<i>T</i> (K)	<i>P</i> (MPa)	GHSV (h <sup>−1</sup> )	CO <sub>2</sub> conv. (%)	CH <sub>3</sub> OH select. (%)	Ref.
In <sub>2</sub> O <sub>3</sub>	Calcination	543/603	4	15 000	1.1/7.1	54.9/39.7	44
In <sub>2</sub> O <sub>3</sub> /ZrO <sub>2</sub>	Impregnation	573	5	16 000	5.2	99.8	142
ZnO–ZrO <sub>2</sub>	Co-precipitation	588	5	24 000	>10	91.0	147
Pd/In <sub>2</sub> O <sub>3</sub>	Incipient wetness impregnation	573	5	>21 000	>20	>70	146
Pd–P/In <sub>2</sub> O <sub>3</sub>	Impregnation	498/573	5	—	3/20	6.01/27.81	146
In <sub>5</sub> /ZrO <sub>2</sub>	Impregnation	553	5	24 000	na	60.0	143
Cu–In–Zr–O	Co-precipitation	523	2.5	18 000	1.48	79.7	148
Ga <sub>0.4</sub> In <sub>2</sub> –xO <sub>3</sub>	Co-precipitation	593	3	—	12.5	26.4	149
In : Pd (2 : 1)/SiO <sub>2</sub>	Incipient wetness impregnation	573	5	—	na	61.0	150
Pd–In <sub>2</sub> O <sub>3</sub>	Co-precipitation	553	5	—	na	78.0	151
Pt/In <sub>2</sub> O <sub>3</sub>	Impregnation	303	0.1	—	37.0	62.6	152
Pd/In <sub>2</sub> O <sub>3</sub> /SBA-15	Wetness impregnation	533	4	—	12.6	83.9	153

na = not available.





distribution of products depends on the interfacial structure of  $\text{ZrO}_2$  and  $\text{In}_2\text{O}_3$ .

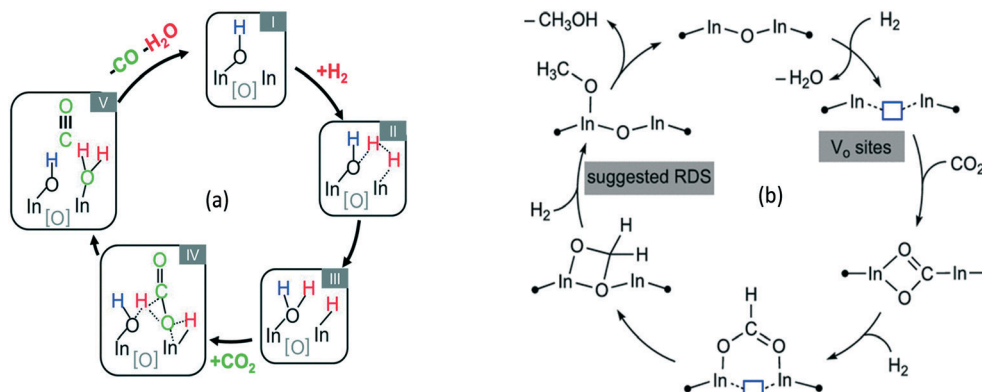
Luo *et al.* developed a porous 3D hierarchical indium-based catalyst for selective  $\text{CO}_2$  reduction *via* electrodeposition and they showed that it exhibits an extremely high  $\text{HCOO}^-$  production rate and excellent selectivity with high stability.<sup>144</sup> The reduction of  $\text{CO}_2$  to formate is explained by DFT calculations. In this study, Pd/In-nano particles (NP) having different compositions were screened in the liquid phase hydrogenation of  $\text{CO}_2$  and they were found to have higher  $\text{CH}_3\text{OH}$  synthesis activity than  $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ , Pd (0) and  $\text{In}_2\text{O}_3$ . Microkinetic modeling and DFT calculations were conducted to examine the reaction mechanism on the  $\text{Pd}_4/\text{In}_2\text{O}_3$  catalyst.<sup>145</sup> They found that the strong interaction between  $\text{In}_2\text{O}_3$  and Pd occurs during reduction and forms bimetallic species that change the nature of interfacial sites which were found detrimental to  $\text{CH}_3\text{OH}$  synthesis. Later, Rui *et al.* used a Pd loaded  $\text{In}_2\text{O}_3$  catalyst for  $\text{CH}_3\text{OH}$  synthesis in which they used a Pd-peptide composite to prevent the formation of Pd-In bimetallic species during mixing with  $\text{In}_2\text{O}_3$ .<sup>146</sup> The peptide templates bond to Pd ions through electrostatic interaction between peptide sites (negative charge) and  $\text{Pd}^{2+}$ , which control the facet and size of catalysts under mild conditions. After confinement of Pd NPs on  $\text{In}_2\text{O}_3$ , the peptide composite was removed by thermal treatment. Recently, Frei *et al.* reported a different method to stop the formation of Pd-In bimetallic species, in which the Pd clusters were anchored on the  $\text{In}_2\text{O}_3$  lattice by coprecipitation and stabilized by Pd atoms which were embedded into the  $\text{In}_2\text{O}_3$  matrix.<sup>151</sup> This preparation method helped to modify the electronic properties of the catalyst which increased the formation and dispersion of Pd atoms. The  $\text{CH}_3\text{OH}$  formation rate on this catalyst was found to be higher than Pd-P/ $\text{In}_2\text{O}_3$ .<sup>146</sup> García-Trenco *et al.* prepared unsupported PdIn (Pd:In = 1:1) intermetallic nanoparticles using a thermal decomposition method for liquid phase  $\text{CH}_3\text{OH}$  synthesis under the reaction conditions of 5 MPa at 483 K with a ratio of 3:1 of  $\text{H}_2$ : $\text{CO}_2$ .<sup>42</sup> The catalyst exhibited around 70% higher  $\text{CH}_3\text{OH}$  rates and higher stability than the conventional  $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$  catalyst. Recently, the promotional effect of Pd on the  $\text{In}_2\text{O}_3$  catalyst was investigated using *in situ* X-ray spectroscopy, microkinetic modeling, and *ex situ* characterization.<sup>150</sup> Silica ( $\text{SiO}_2$ ) supported catalysts were prepared and tested for  $\text{CH}_3\text{OH}$  synthesis by varying In: Pd ratios on  $\text{SiO}_2$  (0:1, 1:0, 1:1, 2:1, 1:2). Out of the various catalysts, the In: Pd catalyst having a 1:2 ratio on  $\text{SiO}_2$  showed the highest activity and selectivity towards  $\text{CH}_3\text{OH}$ . It was observed from characterization that the catalyst has an  $\text{In}_2\text{O}_3$  phase and In-Pd intermetallic compounds gave the highest  $\text{CH}_3\text{OH}$  formation. Further, DFT and experimental results suggested that the active phases were formed due to the synergistic interaction between the  $\text{In}_2\text{O}_3$  phase and a bimetallic In-Pd particle.

The authors found a similar composition-activity behavior in the case of In-Ni systems.<sup>150</sup> Recently, Men *et al.* prepared Pt NP incorporating  $\text{In}_2\text{O}_3$  catalysts for  $\text{CH}_3\text{OH}$  synthesis using a dielectric barrier discharge plasma reactor.<sup>152</sup> The

catalyst presented good activity and selectivity to  $\text{CH}_3\text{OH}$  at 303 K and 0.1 MPa. A composition of Cu-In-Zr-O was reported by Yao *et al.* to act as a bifunctional catalyst, where defective  $\text{In}_2\text{O}_3$  adsorbs  $\text{CO}_2$  and Cu-sites adsorb and provide active hydrogen to adjacently adsorbed  $\text{CO}_2$ .<sup>148</sup> Commercial  $\text{CH}_3\text{OH}$  synthesis occurs in a temperature range of 473–533 K but recently, Akkharaphattawon *et al.* reported  $\text{CH}_3\text{OH}$  synthesis over  $\text{Ga}_x\text{In}_{1-x}\text{O}_3$  at a higher temperature range (593–673 K).<sup>149</sup> Fan's group reported various multiple-metal catalysts including  $\text{In}_2\text{O}_3$ , like Ni-In-Al/ $\text{SiO}_2$  and La-Ni-In-Al/ $\text{SiO}_2$  for the synthesis of  $\text{CH}_3\text{OH}$  at low-pressure.<sup>154,155</sup> Wang *et al.* synthesized a  $\text{ZnO}-\text{ZrO}_2$  catalyst for  $\text{CH}_3\text{OH}$  synthesis which showed good  $\text{CH}_3\text{OH}$  selectivity and sulfur resistance.<sup>147</sup> In addition, the high  $\text{CH}_3\text{OH}$  selectivity was due to the synergetic effect between Zr and Zn sites.

**2.1.2.1 Reaction intermediates and mechanism over oxide-based catalysts.** Before methanol synthesis,  $\text{In}_2\text{O}_3$  and its composites have been studied for  $\text{CH}_3\text{OH}$  steam reforming, dehydrogenation of propane<sup>156</sup> and other chemical transformations.<sup>157–159</sup> In this section, a plausible reaction mechanism based on DFT and *in situ* infrared Fourier transform spectroscopy DRIFT studies over In-based catalysts is discussed. Ghuman *et al.* investigated the role of surface hydroxy groups and oxygen vacancies in the photochemical and thermal reduction of  $\text{CO}_2$  to CO on In-based catalysts (Fig. 2a).<sup>160</sup> The kinetic study, *in situ* spectroscopy, and DFT calculations showed that the oxygen vacancies and hydroxy groups both assist the RWGS reaction (Fig. 2a). The activation energy estimated for the RWGS reaction was 86  $\text{kJ mol}^{-1}$  for photochemical reduction whereas it was 107  $\text{kJ mol}^{-1}$  for thermal reduction. This study has opened a way to understand the surface conditions that can increase the activity of the catalyst towards the RWGS reaction, which is a concurrent reaction in the case of  $\text{CH}_3\text{OH}$  synthesis. A similar activity towards the RWGS reaction was reported by other groups.<sup>137,138,161</sup> Ye *et al.* investigated the adsorption and hydrogenation of  $\text{CO}_2$  on the (110) surface of  $\text{In}_2\text{O}_3$  *via* DFT calculations.<sup>140</sup> Later, the same group found that the oxygen vacancy on the surface of  $\text{In}_2\text{O}_3$  could act as an active site for  $\text{CH}_3\text{OH}$  synthesis *via* computational modeling.<sup>141</sup> A mechanism was proposed from various reports as shown in Fig. 2b by Tsoukalou *et al.*,<sup>162</sup> in which oxygen vacancies termed as  $\text{V}_\text{o}$  sites were formed on the  $\text{In}_2\text{O}_3$  surface. The presence of  $\text{V}_\text{o}$  sites was verified by various experiments based on electron paramagnetic resonance spectroscopy (EPR), X-ray photoelectron spectroscopy (XPS), and temperature-programmed desorption ( $\text{CO}_2$ -TPD) of  $\text{In}_2\text{O}_3$ -based catalysts.<sup>140–142,159</sup> These  $\text{V}_\text{o}$  sites assisted  $\text{CO}_2$  hydrogenation and activation by stabilizing the  $\text{HCOO}^*$ ,  $\text{H}_2\text{COO}^*$  and  $\text{H}_2\text{CO}^*$  species and the hydrogenation of  $\text{H}_2\text{CO}^*$  was found to be the rate determining step. It was observed that these sites could be recovered during hydrogenation of  $\text{CO}_2$ . Later, Sun *et al.* experimentally confirmed the activity of  $\text{In}_2\text{O}_3$  and reported 54.9%  $\text{CH}_3\text{OH}$  selectivity at 543 K.<sup>44</sup> It was observed that  $\text{CO}_2$  conversion increases and  $\text{CH}_3\text{OH}$  selectivity decreases with rising

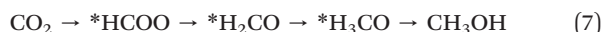




**Fig. 2** A proposed mechanism for (a) the  $\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$  reaction on  $\text{In}_2\text{O}_{3-x}(\text{OH})_y$ . Reproduced from ref. 160 with permission from the Royal Society of Chemistry. (b) The hydrogenation of  $\text{CO}_2$  to  $\text{CH}_3\text{OH}$  on  $\text{V}_0$  sites of  $\text{In}_2\text{O}_3$ . Reprinted (adapted) with permission from A. Tsoukalou, P. M. Abdala, D. Stoian, X. Huang, M.-G. Willinger, A. Fedorov and C. R. Müller, *J. Am. Chem. Soc.*, 2019, **141**, 13497–13505. Copyright (2019) American Chemical Society.

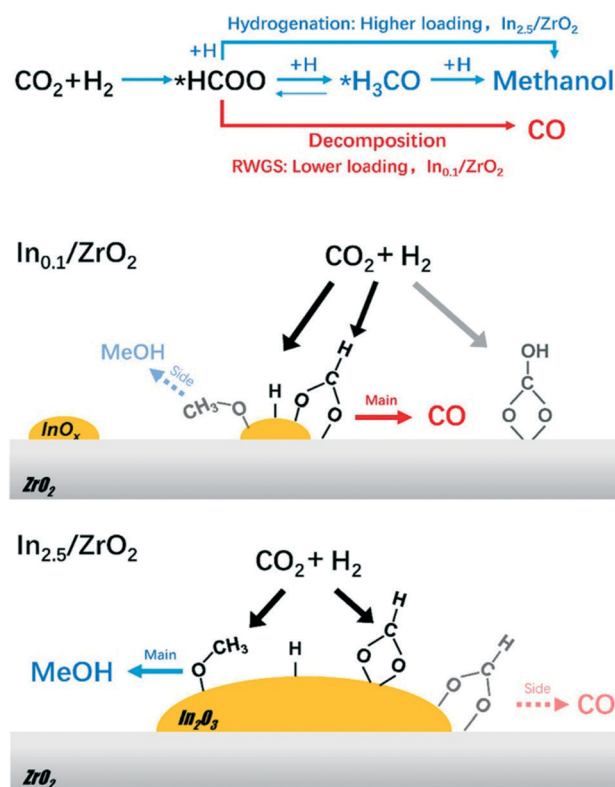
temperature. Oxygen vacancies were found to be the active sites which were generated using thermal treatment or diluted hydrogen by the Pérez-Ramírez group.<sup>142</sup> It was reported that thermally-induced oxygen vacancies had a higher  $\text{CH}_3\text{OH}$  space time yield (STY) than  $\text{H}_2$ -induced vacancies and it was found that hydrogen treatment reduced the surface area of  $\text{In}_2\text{O}_3$ . In addition, operando diffuse reflectance (DRIFTS) showed that adsorbed  $\text{CO}_2$  bridges with two In-atoms around thermally induced oxygen vacancies and hydrogenated intermediates formed thereof. The  $\text{CH}_3\text{OH}$  selectivity was also increased by Cu addition to  $\text{In}_2\text{O}_3$  where it was proposed that Cu helped to generate atomic hydrogen which was transferred to  $\text{CO}_2$  adsorbed on the surface of  $\text{In}_2\text{O}_3$ .<sup>148</sup> In some reports, oxygen vacancy formation was increased by  $\text{CO}$  co-feeding and introducing Pd nanoparticles.<sup>142,145,146</sup> Recently, a few reports discussed the positive synergetic effect between Pd and In for  $\text{CH}_3\text{OH}$  synthesis.<sup>42,150</sup> The adsorption, reactivity of hydrogen, defect formation, and bonding on different  $\text{In}_2\text{O}_3$  samples were studied and as a result, the surface reduction, bonding of hydrogen, and formation of oxygen vacancies were observed after exposure to hydrogen at 573 K.<sup>163</sup>

A DFT study proposed a mechanism for  $\text{CO}_2$  hydrogenation on  $\text{In}_2\text{O}_3$  where oxygen vacancies were created on the indium surface which aided the heterolytic cleavage of hydrogen. Further, the hydrogen atom was transferred to chemisorbed  $\text{CO}_2$  to start the hydrogenation and formation of various intermediates. According to this study, the route for  $\text{CH}_3\text{OH}$  synthesis on  $\text{In}_2\text{O}_3$  is shown below:<sup>140,141</sup> (eqn (7))



The proposed intermediates were  $* \text{HCOO}$ ,  $* \text{H}_2\text{COO}$  and  $* \text{H}_3\text{CO}$ . The stability of the intermediates was explained based on a kinetic study. Chen *et al.* reported the stability and bonding strength of these intermediate species on the  $\text{In}_x/\text{ZrO}_2$  catalyst system during  $\text{CO}_2$  hydrogenation and how the loading of In affects the product selectivity.<sup>143</sup> Fig. 3 shows that  $\text{CH}_3\text{OH}$  was

the main product in the case of 2.5 wt% loading of In on  $\text{ZrO}_2$  while 0.1 wt% In loading gave  $\text{CO}$  as the main product. The authors found *via* a DRIFTS study that among the various intermediates,  $* \text{HCOO}$  was the most abundant and stable with low loading of In on  $\text{ZrO}_2$  ( $\text{In}_{0.1}/\text{ZrO}_2$ ).  $* \text{HCOO}$  formed on the In- $\text{ZrO}_2$  interfaces and further hydrogenation was difficult due to the lack of active dissociated  $\text{H}_2$  from  $\text{In}_{0.1}$ , which led to



**Fig. 3**  $\text{CO}_2$  hydrogenation pathways and schematic-structure-performance relationships over  $\text{In}_x/\text{ZrO}_2$ . Reprinted (adapted) with permission from T.-y. Chen, C. Cao, T.-b. Chen, X. Ding, H. Huang, L. Shen, X. Cao, M. Zhu, J. Xu and J. Gao, *ACS Catal.*, 2019, **9**, 8785–8797. Copyright (2019) American Chemical Society.



subsequent decomposition to CO. Meanwhile with 2.5 and 5 wt% In loading, stepwise hydrogenation of the  $^*\text{HCOO}$  intermediate occurred forming  $^*\text{H}_3\text{CO}$ , and leading to  $\text{CH}_3\text{OH}$  on the catalyst. In addition, the STY of  $\text{CH}_3\text{OH}$  and CO varies with the loading percentage of In over  $\text{ZrO}_2$ . Apart from the conventional theory that oxygen vacancies are the most active sites for methanol synthesis on  $\text{In}_2\text{O}_3$ , Posada-Borbón and Grönbeck showed that oxygen vacancies may have only a minor role in facilitating  $\text{CO}_2$  adsorption.<sup>164</sup> Instead, they have proposed that under reaction conditions the surface of  $\text{In}_2\text{O}_3$  (110) is hydroxylated by either  $\text{H}_2$  or water adsorption and largely vacancy free and as a result it is this hydroxylated surface that plays a significant role in methanol synthesis for  $\text{CO}_2$  activation.

## 2.2 Methanol to hydrocarbons (MTH)

One of the earliest discoveries of the conversion of methanol to hydrocarbons (MTH) was reported by Mobil researchers in the late 1970s.<sup>165,166</sup> A zeolite-based catalyst (ZSM-5) was used for the reaction. This was then followed by the second oil crisis in 1979 which initiated extensive and systematic

research on the conversion of methanol to hydrocarbon-range product molecules, eventually leading to the commissioning of a methanol to gasoline (MTG) plant by 1985 in New Zealand (14 500 barrels per day).<sup>166,167</sup> Methanol can also be utilized as the starting chemical for the synthesis of light olefins (methanol to olefins, MTO process), branched alkanes, aromatics (methanol to aromatics, MTA process), *etc.*, generally designated as the methanol to hydrocarbons (MTH) process. The choice of a given product depends largely on the selection of catalyst and the operating conditions, usually in the temperature range of 623 to 773 K and atmospheric pressure. The selectivity to olefins increases with a decrease in pressure (kinetic effect) and an increase in temperature (partly thermodynamic). The conventional starting material for methanol is coal and natural gas; however, nowadays sustainable resources like biomass and  $\text{CO}_2$  are of increasing interest. Since the MTH process is a mature field of research, many excellent reviews are available in the literature covering the various aspects of the process including fundamental understanding, catalysts, structures, *etc.*<sup>168–173</sup> Here we attempt to provide a description of the

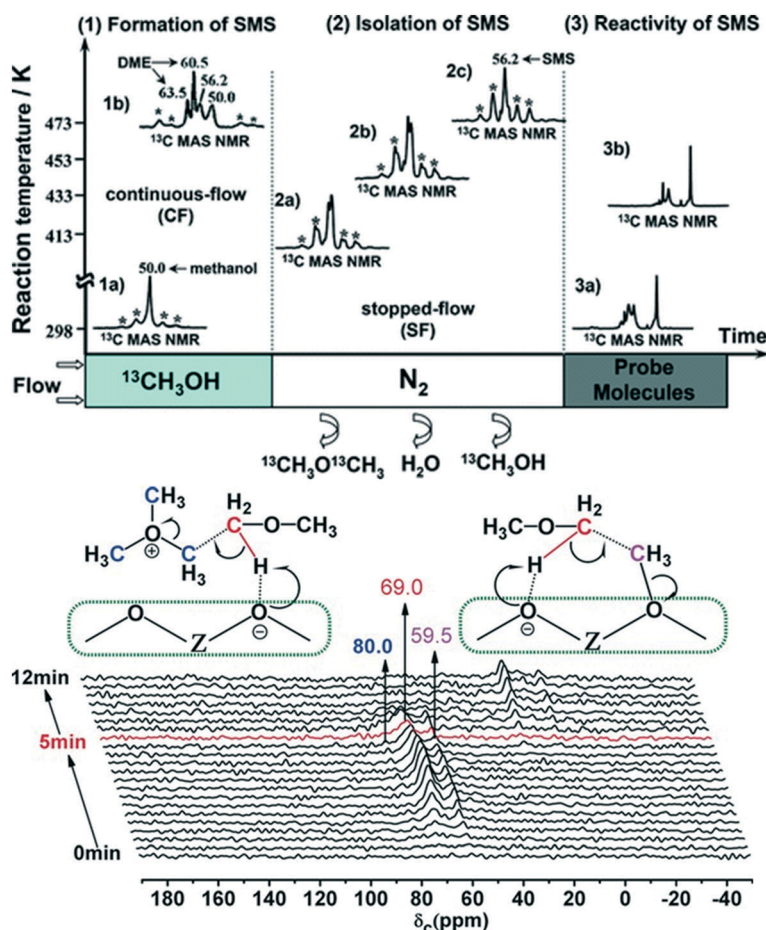


Fig. 4 Experimental evidence for surface methoxy species in different reaction environments (top panel), reprinted (adapted) with permission from W. Wang and M. Hunger, *Acc. Chem. Res.*, 2008, **41**, 895–904, Copyright (2008) American Chemical Society, and the first C–C bond formation route involving the trimethoxy oxonium species (bottom panel), Copyright (2017) Wiley, used with permission from X. Wu, S. Xu, W. Zhang, J. Huang, J. Li, B. Yu, Y. Wei and Z. Liu, Direct mechanism of the first carbon–carbon bond formation in the methanol-to-hydrocarbons process, *Angew. Chem. Int. Ed.*, 2017, **56**, 9039–9043, Wiley. 55, 15840–15845, Wiley.





MTH process in the context of the direct conversion of CO<sub>2</sub> to hydrocarbons (CTH process, both direct and indirect) as it represents an intermediate and final step of the CTH process itself. Therefore, in this section, we limit our focus to an introduction to the reaction mechanism of the MTH process as a preamble solely based on experimental evidence, shape selectivity of zeolites in the MTH reaction, and performance of catalysts and their deactivation trends in the presence of CO<sub>2</sub>, H<sub>2</sub> and H<sub>2</sub>O as these molecules are involved in the CTH process. Moreover, a brief guide to the various approaches to regenerate the deactivated catalysts is also presented.

**2.2.1 Mechanism of methanol to hydrocarbons.** The reaction mechanism of the MTH process is highly complex. Researchers have reported more than 20 different pathways since its discovery.<sup>168,169</sup> Here, we discuss a few selected literature reports providing theoretical and experimental evidence for the presence of transient reaction intermediates involved in the first C–C bond formation from methanol, and the successive formation of higher hydrocarbons.

**2.2.1.1 Experimental evidence for the first C–C bond formation mechanism.** Brønsted acid sites on the zeolite catalyst are the active sites for the MTH process. The reaction initiates by the adsorption of methanol on these acid sites generating the surface methoxy species. The presence of these surface methoxy species has now been experimentally verified with the help of *in situ* MAS NMR spectroscopy (Fig. 4).<sup>174,175</sup> The next step is the generation of trimethyl oxonium ions. These can be generated by the reaction of surface methoxy species/methanol with dimethyl ether, formed *via* the dehydration of two methanol molecules at the Brønsted acid sites. Wu *et al.*,<sup>176</sup> with the help of the *in situ* solid-state <sup>13</sup>C MAS NMR spectroscopic technique, identified the presence of trimethoxy oxonium species on the catalyst surface (Fig. 4 (bottom panel)). Both the surface methoxy species and trimethoxy oxonium species can act as potential methylating agents *via* the carbene ylide mechanism. They can methylate dimethyl ether with the help of the Lewis acidic surface oxygen atom of the zeolite framework to generate the first C–C bond, *i.e.*, a surface adsorbed methoxyethane (Fig. 4 (bottom panel)). The methoxyethane's further transformation through the elimination of methanol generates the first C–C bond containing the ethene molecule. The surface methoxy species and trimethyl oxonium ion can also methylate methanol to form a surface adsorbed ethanol molecule, which upon further dehydration can also generate the ethene molecule.<sup>176</sup>

According to Li *et al.*,<sup>177</sup> the mechanism of the first C–C bond formation over SAPO-34 occurs through the formation of the methoxymethyl cation intermediate (<sup>+</sup>CH<sub>2</sub>OCH<sub>3</sub>). The cation intermediate is formed from surface methoxy species and dimethyl ether. The methoxymethyl cation then reacts with another molecule of dimethyl ether or methanol to form 1,2-dimethoxyethane and 2-methoxyethanol, respectively, the compounds containing the first C–C bonds. The formation of the methyl cation was both theoretically and experimentally verified (Fig. 5).<sup>177</sup>

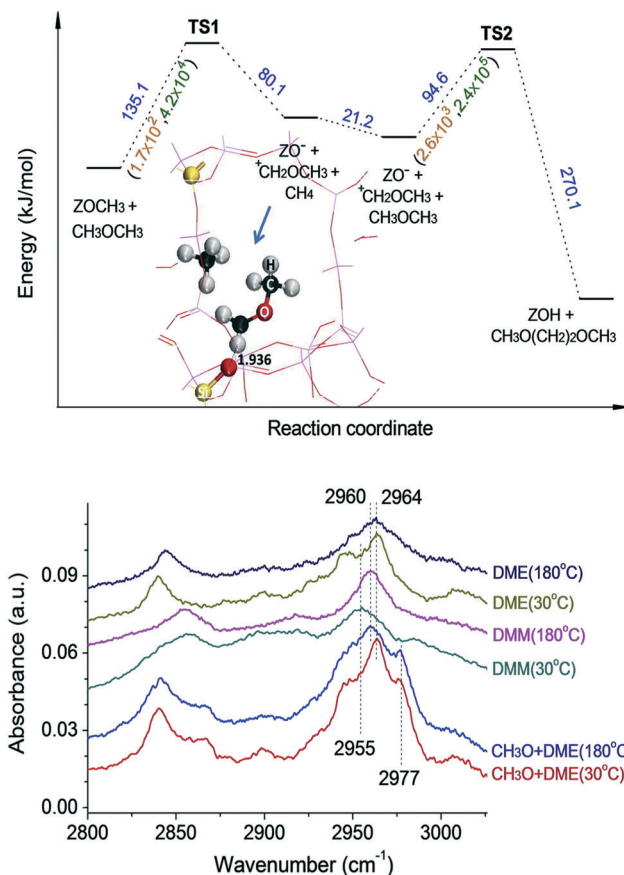


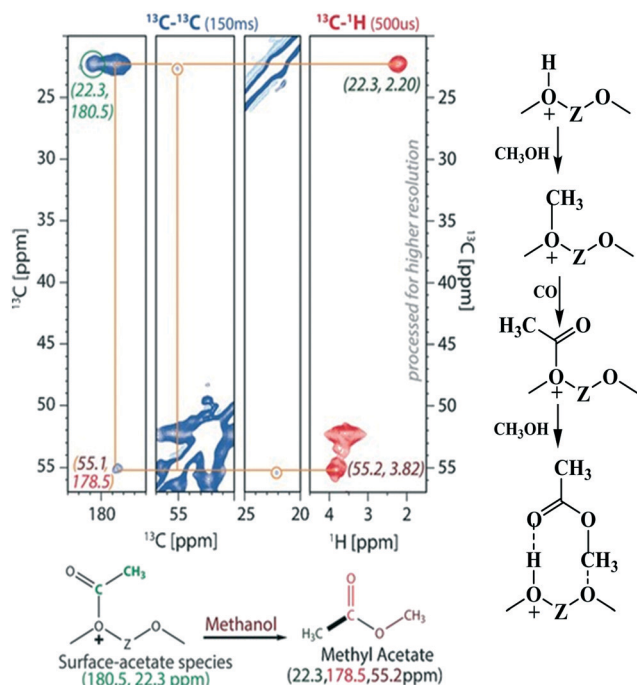
Fig. 5 Theoretical (top panel) and experimental (bottom panel) evidence for the methoxymethyl cation route, the band at 2960 cm<sup>-1</sup> is assigned to the CH<sub>2</sub> group in CH<sub>3</sub>OCH<sub>2</sub>O-zeolite, DME = dimethyl ether, CH<sub>3</sub>O = surface methoxy species, DMM = dimethoxymethane. This article was published in *Journal of Catalysis*, J. Li, Z. Wei, Y. Chen, B. Jing, Y. He, M. Dong, H. Jiao, X. Li, Z. Qin, J. Wang, and W. Fan, A route to form initial hydrocarbon pool species in methanol conversion to olefins over zeolites, *J. Catal.*, 2014, **317**, 277–283, Copyright Elsevier (2014).

Chowdhury *et al.*<sup>178</sup> presented experimental (MAS NMR) evidence for the involvement of acetate species in the first C–C bond formation over the SAPO-34 catalyst. In the proposed mechanism, the surface methoxy species undergo carbonylation (CO being derived *via* the decomposition of methanol) to form a surface-bound acetate species (the first C–C bond) which upon addition of a methanol molecule generates a surface adsorbed methyl acetate species (Fig. 6).<sup>178</sup>

**2.2.1.2 Dual (arene and alkene) cycle mechanism – the hydrocarbon pool (HCP) mechanism.** The dual cycle mechanism deals with the formation of reaction products (selectivity) after the first C–C bond formation. According to Dessau *et al.*,<sup>179</sup> various aliphatic and aromatic hydrocarbons in the MTH reaction can be considered to generate through the consecutive methylation by methanol as shown in Fig. 7 (top left panel). In principle, ethylene is methylated to form propylene. Further methylation of propylene yields butylene and the process carries on generating higher







**Fig. 6** Experimental evidence for the acetate route and the reaction pathway for the first C–C bond formation involving acetate species, Copyright (2016) Wiley, used with permission from A. D. Chowdhury, K. Houben, G. T. Whiting, M. Mokhtar, A. M. Asiri, S. A. Al-Thabaiti, S. N. Basahel, M. Baldus and B. M. Weckhuysen, Initial carbon–carbon bond formation during the early stages of the methanol-to-olefin process proven by zeolite-trapped acetate and methyl acetate, *Angew. Chem., Int. Ed.*, 2016, **55**, 15840–15845, Wiley.

hydrocarbons. Cyclization of the  $\text{C}_6$  alkenes and further methylation produces various substituted aromatics.

Dahl *et al.*<sup>180</sup> used  $^{13}\text{C}$  labeled methanol and  $^{12}\text{C}$  labeled ethene over a SAPO-34 catalyst to verify the probable routes to higher hydrocarbon formation. The authors considered two mechanistic pathways; the first one was the previously suggested consecutive methylation path, and the second one was the “hydrocarbon pool” (HCP) type mechanism. The HCP is a pool of adsorbates having many characteristics similar to ordinary coke, represented as  $(\text{CH}_x)_n$  with  $0 < x < 2$ . In the latter mechanism, methanol is continuously added to the pool of  $(\text{CH}_x)_n$  species, causing their growth. The  $(\text{CH}_x)_n$  species also undergo splitting/cracking to generate the product molecules (Fig. 7, top right panel). According to the experimental results ( $^{13}\text{C}$  and  $^{12}\text{C}$ ), only a minor part of propylene was formed from ethene and methanol, indicating that the HCP mechanism is more prevalent than the consecutive mechanism.

Arstad *et al.*<sup>181</sup> also supported the HCP mechanism, suggesting that the reaction proceeds through penta- and hexamethyl benzene intermediates (the hydrocarbon pool).  $^{13}\text{C}$  labelled methanol and detailed analysis of the trapped molecules inside the SAPO-34 catalyst were used to verify the reaction route. In the early stages of the reaction, methylated benzenes were formed inside the large cavities of SAPO-34. Because of their large molecular size, they could not diffuse through the small pore openings, hence

undergoing cracking to form smaller hydrocarbons such as ethylene and propylene – called the aromatic or arene cycle.<sup>181</sup> In addition, higher alkenes are formed *via* the methylation of lower alkenes and their interconversions (methylation, water-assisted hydrogen transfer, alkyl transition, and olefin liberation) – called the alkene or olefin cycle.<sup>182</sup> In short, the olefins meet with methylation and cracking in the alkene cycle, and the aromatics meet with methylation and dealkylation in the aromatic cycle. These two cycles are interconnected by the dealkylation of aromatics to olefins and dehydrocyclization of olefins to aromatics.<sup>183</sup> Among these steps, the methylation step is regarded as the most difficult step and hence the rate-determining step of the entire process.

**2.2.1.3 Control over arene versus alkene cycles.** There are various factors that influence which cycle operates for product generation. For instance, the position of Al in the zeolite can control the alkene and aromatic cycles. Kim *et al.*<sup>184</sup> reported a larger amount of Al in the straight channels of their hierarchical mesoporous ZSM-5 than in the microporous ZSM-5. Free energy calculations showed that over the hierarchical ZSM-5, olefins were generated mainly through the alkene cycle (largely propylene) whereas, on the microporous ZSM-5, both alkene and aromatic cycles contributed almost equally to the olefins (both ethylene and propylene) (Fig. 7, bottom panel).

The pore diameter of the zeolites also influences the alkene and aromatic cycles. For instance, small-pore zeolites like SSZ-13 and SSZ-39 having large cages follow the aromatic cycle, only permitting the effusion of small hydrocarbons in the range of  $\text{C}_2$ – $\text{C}_4$ . In contrast, the medium and large-pore zeolites, FER and BEA, respectively, favor the concurrent propagation of both the olefin cycle and the aromatic cycle, also favoring the effusion of  $\text{C}_4^+$  hydrocarbons through their pore mouth.<sup>185</sup>

Over time, the olefin and aromatic cycles start to produce polycyclic compounds that no longer serve as reaction intermediates for the generation of hydrocarbons but stay as spectators (a nonactive hydrocarbon pool). With reaction time, they polymerize to form macromolecules that block the accessibility of reactant molecules to the active sites. This situation, which is unavoidable, leads to the deactivation of the catalyst.

**2.2.1.4 Effect of zeolite topology on product selectivity.** A small pore zeolite, SAPO-34 (CHA topology) having ellipsoidal cavities ( $10.4 \times 12.0 \text{ \AA}$ ) interconnected *via* narrow 8-membered ring apertures ( $3.8 \times 3.8 \text{ \AA}$ ), allows only the effusion of small chain molecules. The large cavities in it cause the HCP mechanism (arene cycle) to prevail, permitting only small molecules to escape through the pore aperture at the same time retaining the bulky reaction intermediates (the hydrocarbon pool). Therefore, it gives high selectivities to smaller olefins for instance ethylene and propylene. The effect of cavity sizes with the same ring apertures has also been reported. Bhawe *et al.*<sup>186</sup> chose zeolites with LEV, CHA, and AFX topologies for this investigation. These zeolites have different cavity sizes ( $\text{LEV} < \text{CHA} < \text{AFX}$ ) with the same



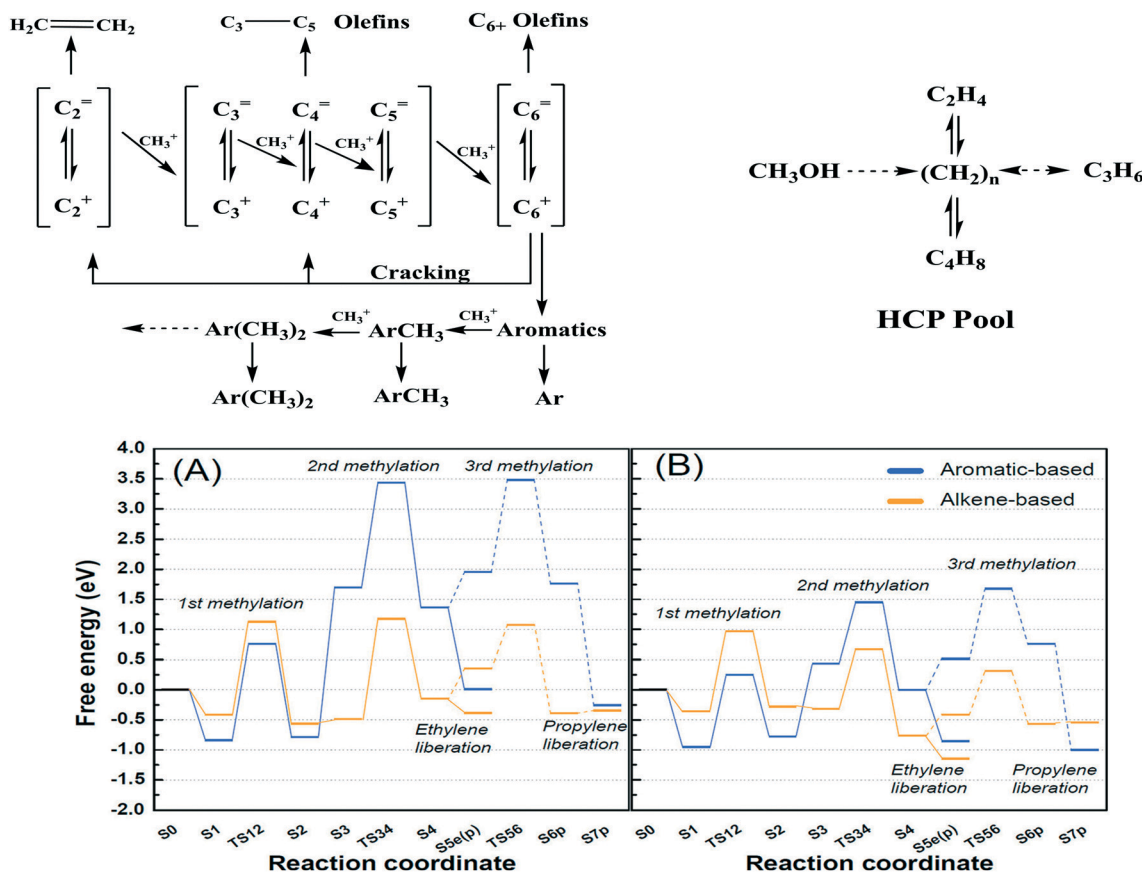


Fig. 7 Top left panel: Consecutive methylation scheme for higher hydrocarbons, this article was published in *Journal of Catalysis*, R. Dessau and R. LaPierre, On the mechanism of methanol conversion to hydrocarbons over HZSM-5, 1982, **78**, 136–141, Copyright Elsevier (1982). Top right panel: The HCP pathway, this article was published in *Journal of Catalysis*, I. M. Dahl and S. Kolboe, On the reaction mechanism for hydrocarbon formation from methanol over SAPO-34: I. Isotopic labeling studies of the co-reaction of ethene and methanol, *J. Catal.*, 1994, **149**, 458–464, Copyright Elsevier (1994). Bottom panel: Free energies of alkene- and aromatics-based MTO reactions at Al atoms situated at the straight channel – alpha position (A), and those situated at the channel intersection – beta position (B) of ZSM-5 zeolite,<sup>169</sup> reprinted (adapted) with permission from S. Kim, G. Park, M. H. Woo, G. Kwak and S. K. Kim, *ACS Catal.*, 2019, **9**, 2880–2892, Copyright (2019) American Chemical Society.

8-membered ring apertures. It was found that the ethylene selectivity decreased with increased cavity size. However, the

CHA topology gave higher selectivity to propylene than AFX. The AFX material showed the lowest carbon yield. An

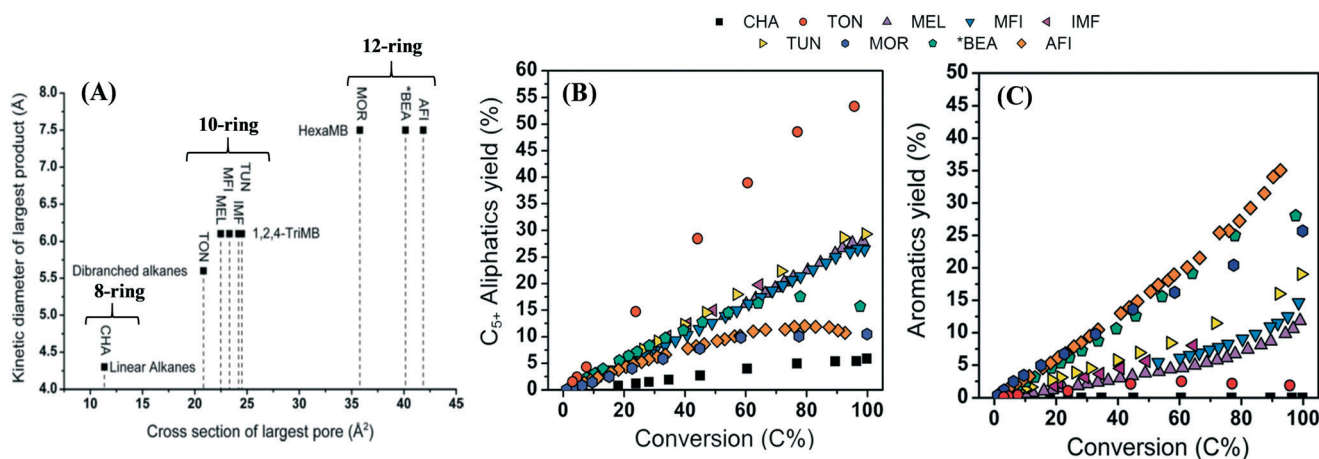


Fig. 8 (A) Cross-section of the largest pore of zeolites versus kinetic diameter of the largest product. (B) C<sub>5</sub><sup>+</sup> aliphatics yield over various zeolites as a function of conversion, 423 K, *P* (methanol) = 0.01 MPa. (C) Aromatics yield over various zeolites as a function of conversion, 423 K, *P* (methanol) = 0.01 MPa,<sup>174</sup> Bleken, S. Svelle, K. P. Lillerud and U. Olsbye, *Catalysis*, 2014, **26**, 179–217, reproduced by permission of The Royal Society of Chemistry.

increase in cavity dimension leads to the formation of larger polyaromatics *via* successive methylation, which no longer serve as active intermediates in the HCP mechanism, but leads rather to deactivation of the catalyst by polymerization to coke.<sup>187</sup> An intermediate cavity size appeared to be ideal for high olefin selectivity.<sup>186</sup>

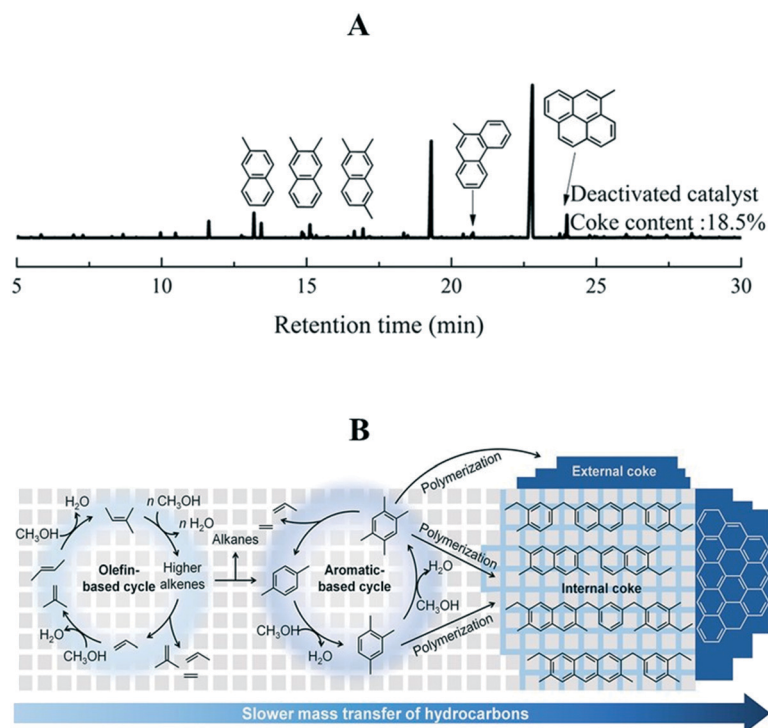
On the other hand, a medium pore zeolite, ZSM-5 (MFI topology) with channel dimensions  $5.3 \times 5.6$  Å (straight) and  $5.1 \times 5.5$  Å (sinusoidal) having 10-membered ring apertures, can allow the effusion of larger molecules. Therefore, it can yield both lower olefins and gasoline range olefins.<sup>188</sup>

The large pore zeolite BEA ( $7.7 \times 6.6$  Å, 12-membered ring aperture) can give products ranging from  $C_2$  alkanes/alkenes to  $C_{12}$  aromatics. This induces a limitation to the selectivity. Therefore, 12-ring aperture zeolites show little or no product shape selectivity in the MTH reaction.<sup>189</sup>

Fig. 8 shows a relation between the largest pore cross-section of zeolite *versus* the kinetic diameter of the largest hydrocarbon product, and the product distribution at various conversions. Zeolites with an 8-membered ring aperture give only linear alkanes during the reaction. If the ring aperture size is made up of 10-membered rings, the zeolite can give branched alkanes and/or aromatics. A further increase in the aperture size to 12-membered rings could produce heavily methylated benzenes. Bulky polymethyl benzene favors the formation of propene and butene, rather than ethene. The situation becomes more complex if the cavity size and the

dimensionality of the pore system are taken into consideration.<sup>169,189</sup>

**2.2.2 Effect of reaction environments and catalyst composition on deactivation.** The main reason for the deactivation of zeolites during the MTH reaction is coke (polycyclic aromatic compounds) deposition. Fig. 9A shows the composition of occluded organic species in a deactivated SAPO-34 catalyst. These compounds are thus considered to be the precursors for coke formation. The catalytic or non-catalytic transformation (oligomerization, cyclization, hydrogen transfer and alkylation) of these precursors leads to the formation of coke of different kinds based on the catalyst structure and experimental conditions. Since coke formation is initiated at the acid sites, its adsorption at areas surrounding these sites inhibits the accessibility of acid sites to reactant/intermediate molecules. The position of coke could be on the internal surface of the micropores (called soft/internal coke) blocking the accessibility to the active sites or as a coating on the outer surface of the zeolite crystal (called external coke) blocking the entrance to the internal pores.<sup>190,191</sup> The growth of coke species inside the internal pore is limited by the size and shape of the pore. No such spatial limitation is anticipated for the external coke. The role (chemical nature, amount, and composition) of internal and external coke in deactivation was studied by Lee *et al.*<sup>190</sup> They chose MFI zeolites with different crystallite sizes. Regardless of the crystallite size and the reaction time, the



**Fig. 9** (A) GC-MS chromatogram of organic species occluded in the deactivated SAPO-34 catalyst, reprinted (adapted) with permission from X. Zhao, J. Li, P. Tian, L. Wang, X. Li, S. Lin, X. Guo and Z. Liu, *ACS Catal.*, 2019, **9**, 3017–3025, Copyright (2019) American Chemical Society. (B) Internal and external coke formation mechanism, 673 K,  $P$  (methanol) = 0.025 MPa, WHSV = 6.46 to 86.1  $h^{-1}$ , this article was published in *Journal of Catalysis*, S. Lee and M. Choi, Unveiling coke formation mechanism in MFI zeolites during methanol-to-hydrocarbons conversion, *J. Catal.*, 2019, **375**, 183–192, Copyright Elsevier (2019).



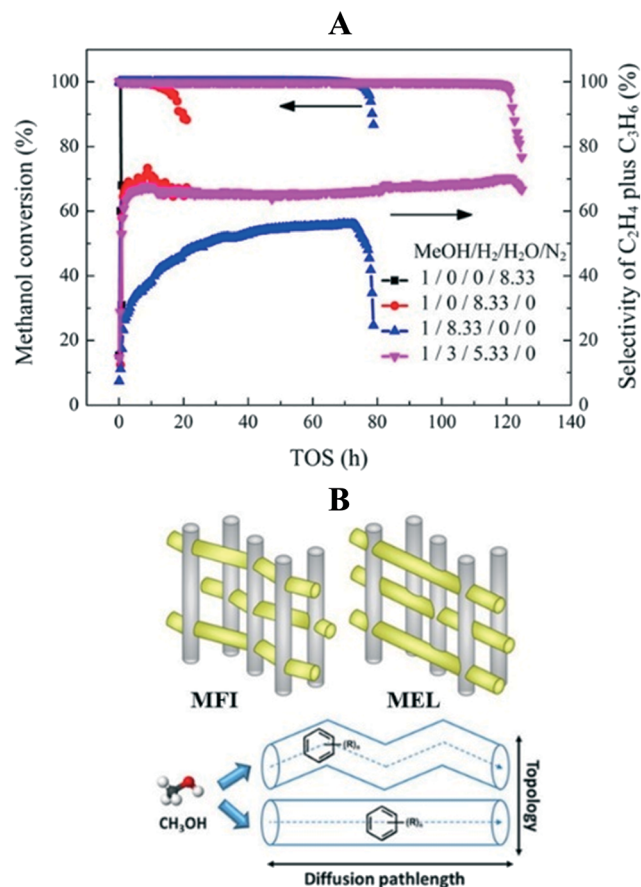


chemical nature of both internal coke and external coke was found to be the same in all zeolites, only their amount was different. The internal coke had an H/C elemental ratio of 1.26 (density is  $1.0 \text{ g cm}^{-3}$ ) and the external coke had a ratio of 0.28 (density is  $1.5 \text{ g cm}^{-3}$ ).<sup>190</sup> Based on these values, the internal coke was proposed to be composed of polymeric structures of methylated acenes (benzene, naphthalene, and anthracene), and the external coke was composed of highly polyaromatic fused rings. Moreover, the internal coke contributed greater to catalyst deactivation than the external coke. Fig. 9B shows a proposed mechanism of internal and external coke formation during the MTH process.<sup>190</sup>

Deactivation by coke demands frequent regeneration of the catalyst by burning off the coke. Therefore, it is highly recommended to increase the lifetime of catalysts either by modifying the reaction environments or *via* the catalyst design.

**2.2.2.1 Effect of co-feeding  $\text{H}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{CO}_2$  on catalyst lifetime.** Arora *et al.*<sup>192</sup> investigated the effect of  $\text{H}_2$  co-feeding (0.4–3 MPa) on catalyst lifetime (SAPO-34) during the MTH reaction (673 K and 0.013 MPa of methanol). Almost 2.8 to 70 times greater catalyst lifetime was observed in the presence of  $\text{H}_2$ . Similar catalyst stability was also observed when ZSM-5 and SSZ-13 catalysts were used (3 and 4.5 times increase in stability for ZSM-5 and SSZ-13, respectively). It was rationalized that  $\text{H}_2$  participated in the hydrogen transfer reactions to intercept the pathways promoting the formation of polycyclic compounds inside the zeolite cage. For instance, the intermediate 1,3-butadiene can undergo hydrogenation in the presence of  $\text{H}_2$ , thus limiting its chances to form aromatic and polycyclic compounds susceptible to coke formation.<sup>185</sup> Zeolites have been reported to perform the hydrogenation/dehydrogenation reactions to a limited extent.<sup>193,194</sup> At a certain methanol partial pressure, the dehydrogenation of methanol to formaldehyde can occur. Formaldehyde can undergo Prins condensation with olefins and aromatics in the HCP to generate inactive polycyclic aromatic species. Co-feeding of  $\text{H}_2$  is presumed to reduce the formaldehyde induced polycyclic aromatics formation. Analysis of the occluded reaction species in the completely deactivated SAPO-34 showed that  $\text{H}_2$  co-feeding did not change the composition of chemical species (pyrene species), but only delayed the deactivation rate.<sup>192</sup> This delayed deactivation behavior caused by  $\text{H}_2$  co-feeding was also observed by others when other zeolite catalysts such as SSZ-39, FER, and BEA were used for the reaction.<sup>185</sup> The only detrimental effect of  $\text{H}_2$  co-feeding is the formation of saturated products when used at very high pressures.<sup>192</sup>

The effect of co-feeding of both  $\text{H}_2$  and  $\text{H}_2\text{O}$  was reported by Zhao *et al.*<sup>195</sup> The authors reported a synergetic effect of  $\text{H}_2\text{O}$  and  $\text{H}_2$  in improving the lifetime of the SAPO-34 catalyst (Fig. 10A). Protonation of  $\text{H}^+$  sites by  $\text{H}_2\text{O}$  generates  $\text{H}_3\text{O}^+$  ions.<sup>196</sup> These  $\text{H}_3\text{O}^+$  ions have been reported to reduce the activation energy for hydrogenation reactions.<sup>197</sup> As a result, the carbenium ions generated from the aromatics, confined in SAPO-34, can easily undergo hydrogenation, inhibiting the coke formation, at the same time, hydrogenating the heavy



**Fig. 10** (A) Effects of different reaction environments ( $\text{N}_2$ ,  $\text{H}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{H}_2$ - $\text{H}_2\text{O}$  mixture, 723 K, 4 MPa, methanol WHSV =  $4.0 \text{ h}^{-1}$ , GHSV =  $13\,069 \text{ h}^{-1}$ ) on the lifetime of a SAPO-34 catalyst, reprinted (adapted) with permission from X. Zhao, J. Li, P. Tian, L. Wang, X. Li, S. Lin, X. Guo and Z. Liu, *ACS Catal.*, 2019, 9, 3017–3025, Copyright (2019) American Chemical Society. (B) Effect of diffusion path length on catalyst lifetime, reprinted (adapted) with permission from Y. Shen, T. T. Le, D. Fu, J. E. Schmidt, M. Filez, B. M. Weckhuysen, and J. D. Rimer, *ACS Catal.*, 2018, 8, 12, 11042–11053, Copyright (2018) American Chemical Society.

aromatic deposits to active aromatic intermediates (HCP mechanism), thereby increasing the catalyst lifetime. The main advantage of co-feeding  $\text{H}_2\text{O}$  along with  $\text{H}_2$  is that the propylene selectivity could be improved.<sup>195</sup> And the main disadvantage of  $\text{H}_2\text{O}$  co-feeding is that, at a high amount of  $\text{H}_2\text{O}$ , the zeolite can undergo dealumination leading to irreversible deactivation.<sup>198,199</sup>

Zachariou *et al.*<sup>200</sup> also found the positive effect of  $\text{H}_2\text{O}$  in improving the catalyst lifetime. The authors used methanol and dimethyl ether as reactants. Rapid deactivation was observed when dimethyl ether was used as a reactant. The deactivation was delayed when methanol was used instead of dimethyl ether. This was ascribed to the presence of  $\text{H}_2\text{O}$  that aided the regeneration of acid sites required for the methylation of aromatic compounds (HCP mechanism). The composition of coke also changed in the presence of  $\text{H}_2\text{O}$ . In its presence, the ratio of aromatic to aliphatic species in the coke was found to be lower.<sup>200</sup>





The effect of CO<sub>2</sub> co-feeding (0.1 MPa) during the MTH reaction has also been reported. Magzoub *et al.*<sup>201</sup> employed a 3D-printed monolith ZSM-5 catalyst doped with various elements like Ga, Cr, Cu, Zn, Mo, and Y. The CO<sub>2</sub> co-feeding slightly improved the lifetime of the catalysts (673 K, WHSV = 0.35 h<sup>-1</sup>), probably *via* the reverse Boudouard reaction. A consequence of CO<sub>2</sub> co-feeding is that it promoted cracking and dehydrocyclization, leading to the production of light alkanes (methane and ethane) and benzene-toluene-xylene compounds.<sup>201</sup>

Overall, the co-feeding of H<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>O was found to be conducive in delaying the deactivation rate thereby improving the catalyst lifetime. Hence during the CTH process, these gases (CO<sub>2</sub> and H<sub>2</sub>) and H<sub>2</sub>O are anticipated to impart a positive effect on the catalyst lifetime.

**2.2.2.2 Effect of catalyst structure and composition on deactivation.** An alternative approach to improve the catalyst lifetime is to modify the catalyst structure, for instance, introduce mesoporosity. Kim *et al.*<sup>184</sup> reported the use of hierarchical ZSM-5 with intracrystalline mesopores for the MTO reaction. In the synthesized catalyst, the Al atoms were predominantly positioned in the straight channels as compared to the conventional ZSM-5 catalyst, where the Al atoms are found in the intersections between sinusoidal and straight channels. The lifetime of the catalyst with hierarchical mesopores was almost 3 times longer than the microporous ZSM-5 catalyst (673 K, WHSV = 4.75). The presence of mesopores served as a carbon reservoir to accommodate the coke and thus minimize the blockage of micropores.<sup>184</sup> The presence of mesopores enhanced the diffusion of coke precursors out of the micropores, allowing the zeolite to accommodate more coke with large structures, and thereby increasing its lifetime.

Another factor contributing to the deactivation of zeolite catalysts during industrial applications is the presence of binders (non-zeolitic materials used to improve the mechanical properties of the zeolite catalysts). Binders can block the pore accessibility, thereby accelerating the propensity of intermediate molecules to form coke precursors.<sup>202</sup> To circumvent this issue, Bingre *et al.*<sup>203</sup> introduced pore-forming agents (surfactants) to a boehmite binder before extruding it with ZSM-5. Calcination of the extrudate catalyst burned off the pore-forming agents leaving meso/macro pores within the extrudate. These meso/macropores solely existed in the binder leaving the zeolite structure intact. Meso/macro pores in the binder favored improved mass transfer of molecules and were able to trap and hold larger quantities of coke as compared to the conventional extrudate catalyst (723 K, WHSV = 2.0). The coke's ideal position in the meso/macro pores was beneficial to retain the exposure of active sites of the zeolite for a longer reaction time, thus indirectly improving the catalyst lifetime to almost double.<sup>203</sup>

In the case of the ZSM-5 catalyst, the coke deposition is usually observed at the outer rim of the zeolite crystal because aromatic products diffusing out the micropores are condensed at the external surfaces of the crystals. Over time, the pore entrance becomes blocked by the coke, causing the

accumulation of hydrocarbons at the channel intersections completely limiting access to internal active sites. Acid sites on the external surface of the zeolites deactivate more quickly than those located inside the crystals due to a lack of shape selectivity. Therefore, to improve the catalyst lifetime, Goodarzi *et al.*<sup>191</sup> attempted a surface passivation technique involving the introduction of an inert porous shell of silicalite-1 with a thickness of 15 nm on the surface of a mesoporous ZSM-5 catalyst, thus replicating a core-shell structure. In comparison to the mesoporous ZSM-5 without the protective shell, the one with the protective shell had 10 times longer catalyst lifetime extending up to 70 hours of reaction as compared to 7 hours, and 12 times higher conversion capacity based on the acid sites (from 27 to 63%).

To unravel the effect of catalyst composition on deactivation, Chowdhury *et al.*<sup>204</sup> compared the performance of Ca-modified and unmodified ZSM-5 in the MTH reaction (773 K, WHSV = 8 h<sup>-1</sup>). The Ca-modification significantly improved the lifetime of the catalyst. This was attributed to the fact that the Lewis acid site may promote (imparted by Ca-incorporation) suppression of the aromatic cycle. The Ca-incorporation isolated the Brønsted acid sites, thereby inhibiting the carbene/ylide species.

In order to investigate the effect of framework topology and diffusion path length on deactivation, Shen *et al.*<sup>205</sup> used a series of ZSM-5 and ZSM-11 catalysts with different crystallite sizes for the reaction (623 K, WHSV = 9 h<sup>-1</sup>). As compared to ZSM-5 with a sinusoidal micropore structure, the ZSM-11 with straight micropore structure had almost a two-fold improved catalyst stability (from 4.5 to 8.5 hours) due to higher diffusivity (Fig. 10B). When the crystallite size of ZSM-11 was reduced from 750 nm to 150 nm, an 8-fold increase in catalyst lifetime was observed (from 1.7 to 13.5 hours), owing to the decrease in the diffusion path length. An increase in diffusion limitation favors the aromatic cycle to produce ethylene as the major product.<sup>205</sup> A general conception regarding the effect of zeolite topology on catalyst lifetime is that the shorter the diffusion length or the smaller the crystallite size, the longer the catalyst lifetime.<sup>206–211</sup>

**2.2.3 Regeneration of deactivated catalysts.** In general, the coke deactivated catalyst is regenerated by high-temperature thermal calcination treatment in the presence of air or oxygen to burn off the coke. The regeneration conditions are normally much more severe than the reaction conditions. The main disadvantages of this approach are the high energy consumption and long time required for coke combustion. Also, care must be taken while selecting the regeneration conditions in order to preserve the catalyst structure, its activity, and selectivity by avoiding irreversible deactivation. Irreversible deactivation of the catalysts is mainly due to changes in textural properties and loss of acidity (dealumination).<sup>212</sup> Other ways to regenerate the deactivated catalyst have also been reported in the literature.

Zhang *et al.*<sup>213</sup> applied room temperature methanol leaching as a regeneration technique for the deactivated ZSM-5 catalyst. After 2 hours of methanol leaching, the regenerated catalyst



showed textural properties similar to the fresh ZSM-5 catalyst. However, the authors found that regeneration by calcination was more efficient in removing the coke than methanol leaching. One of the main disadvantages of methanol leaching in practical application is the requirement of cooling down the reactor for the leaching process.<sup>213</sup>

Li *et al.*<sup>212</sup> introduced a rejuvenating process to the ZSM-5 catalyst bed during the MTH process to reactivate the catalyst. Toluene or H<sub>2</sub>O was fed to the reactor under the same experimental conditions for a certain period. After this, the methanol feeding was continued. The rejuvenation process decreased the pore volume and surface area (textural properties), and the acidity of the catalyst. Rejuvenation by toluene had generated new polyalkylbenzene species in the catalyst. These species could act as HCP intermediates to partially recover the activity of the catalyst. When H<sub>2</sub>O was used, the catalyst was found to be less effective, mainly due to the loss of acidity by dealumination.<sup>212</sup> Altogether, the most efficient way to regenerate a deactivated catalyst is the calcination process and it is successfully practiced in industry *via* the use of fluidized bed reactors.<sup>169</sup>

### 3. Direct hydrogenation of CO<sub>2</sub> to hydrocarbons

Hydrocarbons from CO<sub>2</sub> have been synthesized using two processes; the first is a CO-mediated process and the second is a CH<sub>3</sub>OH-mediated process (Fig. 11). The focus here will be on the CH<sub>3</sub>OH-mediated process, as the CO-mediated process is out of scope of this review. Generally, CO-based hydrocarbon synthesis, called the Fischer-Tropsch process (FT), produces hydrocarbons with a statistical distribution, named Anderson-Schulz-Flory (ASF). The maximum selectivity for a desired hydrocarbon is limited by the ASF model. Apart from this route, the CH<sub>3</sub>OH-mediated hydrocarbon synthesis process has the advantage that the hydrocarbon yield does not follow the ASF model. In recent years, many studies report on the direct conversion of CO<sub>2</sub> to hydrocarbons in a one stage reactor *via* a CH<sub>3</sub>OH-mediated process (Table 3). Direct CO<sub>2</sub> hydrogenation is an efficient way to produce hydrocarbons using bifunctional catalysts. Bifunctional catalysts are a combination of CH<sub>3</sub>OH synthesis and CH<sub>3</sub>OH to hydrocarbon (MTH) catalysts. Up to now,

various Cu, Pd, and oxide-based catalysts (In<sub>2</sub>O<sub>3</sub> and ZnO) have been used for CH<sub>3</sub>OH synthesis from CO<sub>2</sub>, and different types of zeolites have been used for the synthesis of hydrocarbons from CH<sub>3</sub>OH.<sup>17,214,215</sup> The direct route would be more economically and energy-efficient compared to the indirect two-stage route. In the case of the two-stage process, two reactors need to operate separately and in addition to the extra capital costs for another reactor stage there is a need to carry out separation processes between stages to separate the undesired intermediates from the process which requires additional energy. There are also efficiency advantages that a single stage process can offer since the equilibrium limitation of methanol synthesis is alleviated by the fact that methanol is directly converted to hydrocarbon products. CO is a major byproduct from CO<sub>2</sub> hydrogenation, but in a one stage CO<sub>2</sub> hydrogenation process, the selectivity for CO can be reduced since the methanol removal will be positive for the equilibrium limitation for the methanol synthesis from CO<sub>2</sub>, as will be explained below in greater detail. Inui *et al.* investigated the synthesis of gasoline with lower olefins from CO<sub>2</sub> + H<sub>2</sub> *via* the CH<sub>3</sub>OH route in a two stage reactor.<sup>216,217</sup> In the first reactor, CO<sub>2</sub>-rich syngas was converted to CH<sub>3</sub>OH on Cu-Zn-Cr-Al-oxides; further the total reaction mixture was directly fed to a second reactor connected in series, packed with a protonated Fe-silicate crystalline catalyst. Gasoline with 50% selectivity was formed in the second reactor from the CH<sub>3</sub>OH synthesized in the first reactor. As a side product, lower olefins were produced with gasoline, which could be an intermediate compound during gasoline synthesis.

There are various reports on the synthesis of lower olefins (butylenes, propylene, and ethylene) which are used industrially as chemical intermediates and also produced from the dehydration of lower alkanes<sup>218</sup> and cracking of hydrocarbon feedstocks.<sup>219</sup> At the lab scale, lower olefins have been synthesized using two stage processes and as a carbon source, syngas is used for CH<sub>3</sub>OH synthesis and further converted to lower olefins. Meanwhile in the case of CO<sub>2</sub> to CH<sub>3</sub>OH, the formation of water is unavoidable which can lead to deactivation of both catalysts (for CO<sub>2</sub> to CH<sub>3</sub>OH catalysts as well as CH<sub>3</sub>OH to olefin catalysts like zeolite). In addition, water can cause zeolite dealumination if present in too large quantities; however, as mentioned in section 2.2.2.1 of this review, it also prolongs the lifetime of the MTO catalysts by preventing coke deposition. Thus, it is a challenging task to synthesize hydrocarbons from CO<sub>2</sub> in one stage.

Recently, In<sub>2</sub>O<sub>3</sub>-based catalysts have shown their excellent activity for CH<sub>3</sub>OH synthesis in the temperature range of 473–573 K (ref. 44, 142 and 143) (Table 2). While in this temperature range, zeolites are not active for C–C coupling. Generally, it is found that high temperature is more kinetically favorable for C–C coupling from methanol. For the synthesis of lower olefins from methanol, the temperature range of 673–723 K was found optimal over SAPO-34 which is a more favorable temperature range for the RWGS reaction too, but not for methanol yield (Tables 1 and 2).<sup>171,220</sup> Thus, the big challenge is how to combine the two processes, which

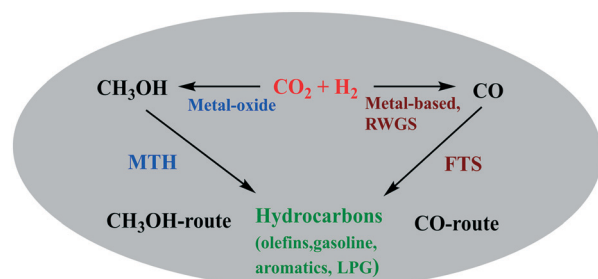


Fig. 11 Pictorial representation of CH<sub>3</sub>OH-mediated or CO-mediated routes for direct hydrocarbon synthesis.



**Table 3** Catalytic performance of bifunctional catalysts for CO<sub>2</sub> hydrogenation to hydrocarbons

Catalysts	H <sub>2</sub> :CO <sub>2</sub>	T (K)	P (MPa)	CO <sub>2</sub> conv. (%)	GHSV (h <sup>-1</sup> )	Major products <sup>a</sup>	Selectivity for major products among hydrocarbons <sup>b</sup> (%)	CO selectivity <sup>c</sup> (%)	S <sub>MeOH/DME</sub> <sup>d</sup> (%)	Ref.
Zr-In <sub>2</sub> O <sub>3</sub> /SAPO-34	3	673	3	35.5	9000	C <sub>2</sub> <sup>=</sup> -C <sub>4</sub> <sup>=</sup>	76.4	85.0	0/n.r.	222
Zn-ZrO <sub>2</sub> /SAPO-34	3	653	2	12.6	3600	C <sub>2</sub> <sup>=</sup> -C <sub>4</sub> <sup>=</sup>	80.0	47.0	n.r./n.r.	227
In <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub> /SAPO-34	3	673	1.5	19.0	3000	C <sub>2</sub> <sup>=</sup> + C <sub>3</sub> <sup>=</sup>	80–90	>80	n.r./n.r.	225
In <sub>2</sub> O <sub>3</sub> /H-ZSM-5	3	613	3	13.1	9000	C <sub>5</sub> <sup>+</sup>	78.6	<45	0/n.r.	221
ZnGa <sub>2</sub> O <sub>4</sub> /SAPO-34	3	643	3	13.0	5400	C <sub>2</sub> <sup>=</sup> -C <sub>4</sub> <sup>=</sup>	86.0	46.0	0/0	229
In <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub> /SAPO-34	3	653	3	26.2	9000	C <sub>2</sub> <sup>=</sup> -C <sub>4</sub> <sup>=</sup>	74.5	63.9	0.2/n.r.	223
In <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub> /SAPO-5	3	573	3	6.7	4000	C <sub>2</sub> -C <sub>4</sub>	83.0	43.0	<0.5/n.r.	226
ZnAlO <sub>x</sub> /H-ZSM-5	3	593	3	9.1	2000	Aromatics	73.9	57.4	<0.5/<0.2	232
In <sub>2</sub> O <sub>3</sub> -ZnZrO <sub>x</sub> /SAP-34	3	653	3	17.0	9000	C <sub>2</sub> <sup>=</sup> -C <sub>4</sub> <sup>=</sup>	85.0	54.0	0/n.r.	224
Cu-CeO <sub>2</sub> -SAPO-34	3	669	2	13.2	5800	C <sub>2</sub> <sup>=</sup> -C <sub>4</sub> <sup>=</sup>	61.8	56.8	n.r./n.r.	231
ZnZrO/HZSM-5	3	593	4	14.1	1200	Aromatics	73.0	44.0	n.r./n.r.	233
Cr <sub>2</sub> O <sub>3</sub> /HZSM-5	3	623	3	33.6	1200	Aromatics	70.5	41.2	0/0	234
CuZnZr@Zn-SAPO-34	3	673	2	19.6	3000	C <sub>2</sub> <sup>=</sup> -C <sub>4</sub> <sup>=</sup>	60.5	58.6	n.r./n.r.	228

<sup>a</sup> Major hydrocarbon product among hydrocarbons. <sup>b</sup> Major hydrocarbon product selectivity among hydrocarbons. <sup>c</sup> CO selectivity based on CO<sub>2</sub> feed. <sup>d</sup> Selectivity for methanol and DME based on CO<sub>2</sub> feed, n.r. = not reported.

have different optimum operating conditions while mitigating the undesired side reactions. Many efforts have been made to synthesize such combined catalysts to achieve stable and excellent catalytic performance. Note that in all cases in the following paragraphs the reported selectivities for certain hydrocarbon products (or major hydrocarbon products) are based only among all hydrocarbon products whereas the reported CO/CH<sub>3</sub>OH/DME selectivities are based on total carbon from the CO<sub>2</sub> feed.

Gao *et al.* prepared a bifunctional catalyst by mixing In<sub>2</sub>O<sub>3</sub> and zeolite (ZSM-5) that showed 78.6% selectivity towards C<sub>5</sub><sup>+</sup> (based on hydrocarbons) with only 1% selectivity for CH<sub>4</sub> at a CO<sub>2</sub> conversion of 13.1%.<sup>221</sup> In addition, less than 45% CO selectivity was observed. Moreover, when using beta zeolite, liquefied petroleum gas products (C<sub>3</sub> and C<sub>4</sub> paraffins) were formed and an enhanced CO<sub>2</sub> conversion was observed at higher pressure and H<sub>2</sub>/CO<sub>2</sub> ratio while the CO selectivity was decreased. Later, the same group reported 76.4% selectivity for lower olefins (C<sub>2</sub><sup>=</sup>-C<sub>4</sub><sup>=</sup>) with ~35% CO<sub>2</sub> conversion over a composite catalyst of In-Zr oxide and SAPO-34 zeolite.<sup>222</sup> However, the CO selectivity over this composite was above 80% under different reaction conditions. The CO<sub>2</sub> activation occurred on the In-Zr oxide, whereas the zeolite was responsible for C-C coupling. The authors studied the effect of reaction pressure and the feed ratio of H<sub>2</sub>/CO<sub>2</sub> and found that CO<sub>2</sub> conversion increased with the H<sub>2</sub>/CO<sub>2</sub> ratio while the selectivity for C<sub>2</sub><sup>=</sup>-C<sub>4</sub><sup>=</sup> decreased with increasing pressure and H<sub>2</sub>/CO<sub>2</sub> ratio. It was also observed that when the space velocity was increased from 4500 to 15 750 mL g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>, the selectivity for lower olefins increased from 68% to 84% and the selectivities for C<sub>5</sub><sup>+</sup> and CH<sub>4</sub> were decreased.

To understand the role of ZrO<sub>2</sub>, a series of bifunctional catalysts composed of In-Zr composite oxides having different atomic ratios of In and Zr, and SAPO-34 zeolite were prepared by Dang *et al.* and screened for direct CO<sub>2</sub> hydrogenation into lower olefins.<sup>223</sup> The catalysts gave 15–27% conversion of CO<sub>2</sub> with 96% selectivity for C<sub>2</sub>-C<sub>4</sub> among the hydrocarbon products (65–80% for C<sub>2</sub><sup>=</sup>-C<sub>4</sub><sup>=</sup> and 13–30% for C<sub>2</sub><sup>0</sup>-C<sub>4</sub><sup>0</sup>), and

the selectivity for CH<sub>4</sub> was merely 2.5%. The selectivity for CO *via* the RWGS reaction was less than 70%. The authors demonstrated by combined experimental and computational studies that In<sub>1-x</sub>Zr<sub>x</sub>O<sub>y</sub> mixed oxide was formed after the incorporation of Zr into In<sub>2</sub>O<sub>3</sub>. This mixed oxide was found to contain more oxygen vacancies with higher binding energies for the reaction intermediates compared to pure In<sub>2</sub>O<sub>3</sub>. Further, the CO<sub>2</sub> adsorption behavior was studied on the mixed oxide using DFT calculations and it was found that the CO<sub>2</sub> and reaction intermediates were adsorbed more strongly on the oxygen vacancy sites which were situated near the Zr dopant than that on pure In<sub>2</sub>O<sub>3</sub>. Thus, the presence of a certain amount of Zr in In<sub>2</sub>O<sub>3</sub> (In:Zr = 4:1) increased the selectivity for CH<sub>3</sub>OH from CO<sub>2</sub> and decreased the RWGS activity. Consequently, the formation of hydrocarbons also increased with the incorporation of Zr. However, it was also observed that an excess amount of Zr in In<sub>2</sub>O<sub>3</sub> significantly decreased the olefin selectivity due to the smaller pore size of the oxides and longer average distance between the metal-oxide and zeolite.

Recently, a composite of In<sub>2</sub>O<sub>3</sub>-ZnZrO<sub>x</sub> oxides and SAPO-34 was prepared in which In<sub>2</sub>O<sub>3</sub> (8 nm) was supported on ZnZrO<sub>x</sub> and mechanically mixed with a series of SAPO-34 zeolites having different crystal sizes and pore structures.<sup>224</sup> The composite catalyst was used for direct CO<sub>2</sub> hydrogenation to lower olefins and a 85% selectivity for C<sub>2</sub><sup>=</sup>-C<sub>4</sub><sup>=</sup> was found among all the hydrocarbons with a CO<sub>2</sub> conversion of 17% and CO selectivity of 54%. It was found that the selectivity for C<sub>2</sub><sup>=</sup>-C<sub>4</sub><sup>=</sup> increased with decreasing pore size. The reason for this was that the diffusion length can be shortened from the surface to the acid sites inside the pores of the zeolite and this helps to provide an efficient mass transfer of intermediate species for C-C coupling to produce lower olefins, whereas the pore structure and the crystal size of the zeolite did not influence the equilibrium of the RWGS reaction. A similar type of composite was synthesized by Gao *et al.*, fabricated from In<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> and SAPO-34 for direct conversion of CO<sub>2</sub> to light olefins (ethylene and propene).<sup>225</sup> The authors reported the selectivity for light olefins in the



range of 80–90% with ~20% CO<sub>2</sub> conversion. The influence of composition on the selectivity for hydrocarbons and conversion of CO<sub>2</sub> was studied and it was found that equal mass of In<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> to SAPO-34 gives a relatively high yield of light olefins, whereas higher content of In<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> in the composite increased the CO<sub>2</sub> conversion and selectivity for CO (>80%) which is a side product during CH<sub>3</sub>OH synthesis over In<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub>. Recently, Wang *et al.* reported results for the same type of catalyst in which SAPO-34 was replaced with SAPO-5.<sup>226</sup> This bifunctional catalyst integrated In<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> and SAPO-5 and exhibited an excellent selectivity towards C<sub>2</sub>–C<sub>4</sub> (83%) lower hydrocarbons with a lower yield of CH<sub>4</sub> at 6.7% conversion of CO<sub>2</sub>. A comparison study for hydrocarbon selectivity over SAPO-34 and SAPO-5 was carried out and it was found that the total selectivity for C<sub>2</sub>–C<sub>4</sub> (83% in hydrocarbons) over SAPO-5 was higher than that over SAPO-34. The selectivity for CO was found to be between 40 and 60% over this composite and it decreased by increasing the space velocity and granule mixing of In<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> and SAPO-5 while it increased with temperature.

Li *et al.* fabricated a tandem catalyst that was a composite of ZnO–ZrO<sub>2</sub> and a Zn-modified SAPO-34 and over this catalyst, they found 12.6% CO<sub>2</sub> conversion with 80% selectivity for lower olefins (C<sub>2</sub>–C<sub>4</sub>) which was the highest among all the hydrocarbon products (3% CH<sub>4</sub>, 14% C<sub>2</sub>–C<sub>4</sub>, and 3% C<sub>5</sub>+).<sup>227</sup> It was concluded that the ZnZrO produced CH<sub>3</sub>OH from CO<sub>2</sub> hydrogenation and the lower olefins occurred on the SAPO catalyst from CH<sub>3</sub>OH with 47% CO selectivity. This catalyst was found to be promising for industrial applications, since it has good sulfur and thermal resistance under the mentioned reaction conditions (Table 3). The highly efficient conversion of CO<sub>2</sub> to lower olefins on tandem catalysts can be attributed to the thermodynamic and kinetic coupling.

To obtain high selectivity towards light olefins from CO<sub>2</sub> hydrogenation, a core-shell structural (CuZnZr)CZZ@SAPO-34 composite catalyst was prepared and compared with CZZ/SAPO-34 which was prepared by physical mixing.<sup>228</sup> CZZ/SAPO-34 (mass ratio of 4:1) gave 9.7% CO<sub>2</sub> conversion with 34.7% olefins selectivity and 58.5% CO selectivity. It was found that the physically mixed CZZ/SAPO-34 with a mass ratio of 4:1 reduced the acidity of the catalyst which is a factor that could increase the selectivity for lower olefins, but surprisingly the catalyst gave lower selectivity to olefins and higher selectivity for CH<sub>4</sub> compared to CZZ/SAPO-34 with a mass ratio of 2:1. This could be due to the strong hydrogenation ability of CZZ at the reported temperature. Meanwhile in the case of the core-shell composite (CZZ@SAPO-34), the higher mass ratio (CZZ@SAPO-34 (4:1)) gave higher selectivity for olefins with lower selectivity for CH<sub>4</sub> compared to the lower mass ratio of CZZ@SAPO-34 (2:1). This is possibly due to the reduced interface between CZZ and SAPO-34, because of the great difference in the particle size of CZZ in CZZ@SAPO-34 and CZZ/SAPO-34 catalysts. In addition, it was stated that the hydrogenation activity was weakened in the case of CZZ@SAPO-34, which was found beneficial for lower olefins as

the selectivity for lower olefins was increased *via* restraining the secondary hydrogenation reaction. It was also found that the acid density of SAPO-34 affected significantly the selectivity for the product. The authors reduced the acid density and total acidity of SAPO-34 by Zn-modification which then greatly increased the CO<sub>2</sub> conversion and selectivity for lower olefins on the CZZ@Zn–SAPO-34 (4:1) catalyst (see Table 3). No change was observed in CO selectivity due to the interface or the acidity of CZZ@Zn–SAPO-34 (4:1), CZZ@SAPO-34 (2:1), and CZZ/SAPO-34 (4:1).

Another new oxide-based catalyst was reported recently by Liu *et al.*<sup>229</sup> This bifunctional catalyst was composed of a spinel structure of ZnGa<sub>2</sub>O<sub>4</sub> and SAPO-34 which gave 86% C<sub>2</sub>–C<sub>4</sub> olefins and 46% CO selectivity with a CO<sub>2</sub> conversion of 13%. It was reported that the molar ratio of Zn/Ga in ZnGa<sub>2</sub>O<sub>4</sub> plays an important role in adsorption, activation and conversion of CO<sub>2</sub> as it influenced the density of oxygen vacancies in the catalyst.<sup>230</sup>

Sedighi *et al.* reported a new composite for direct hydrogenation of CO<sub>2</sub> to lower olefins (C<sub>2</sub>–C<sub>4</sub>) *via* CH<sub>3</sub>OH as an intermediate.<sup>231</sup> A crystalline hybrid catalyst (CuCe/SAPO-34) was prepared by a physical coating process in which the outside surface of the SAPO-34 powder was covered with Cu/CeO<sub>2</sub>. The CO and olefin selectivity were found to be 57.8 and 61.8% (based on hydrocarbons), respectively, with 13.2% CO<sub>2</sub> conversion at 669 K. The CO<sub>2</sub> conversion and CO selectivity were promoted by high temperature.

Several aromatic hydrocarbons have been successfully synthesized by CO<sub>2</sub> hydrogenation. A composite catalyst of ZnAlO<sub>x</sub> and H-ZSM-5 was synthesized and tested for CO<sub>2</sub> hydrogenation.<sup>232</sup> The catalyst yielded 57.4% selectivity for CO, 73.9% selectivity for aromatics (among the HCs) with 9.1% CO<sub>2</sub> conversion, and 0.4% CH<sub>4</sub> selectivity. It was found that Zn<sup>2+</sup> activated the CO<sub>2</sub> hydrogenation in ZnAlO<sub>x</sub> whereas Si-H-ZSM-5, containing the composite zeolite, was selective for *p*-xylene (58.1%), ethylene and propylene. During the reaction, DME, CH<sub>3</sub>OH, and olefins were found as reaction intermediates. The RWGS reaction was suppressed by increasing the ratio of H<sub>2</sub>/CO<sub>2</sub> and introducing CO without affecting the aromatization.

A tandem catalyst ZnZrO/ZSM-5 was prepared and screened for the hydrogenation of CO<sub>2</sub> to aromatics.<sup>233</sup> The catalyst exhibited 14% conversion of CO<sub>2</sub> with an aromatics selectivity of up to 73% (based on HCs) and 44% CO selectivity. Thermodynamic coupling was observed on the tandem catalyst where CH<sub>x</sub>O intermediates were formed on the surface of ZnZrO from CO<sub>2</sub> hydrogenation and then the intermediates transferred to the pores of H-ZSM-5 and produced aromatics. It was found that the presence of H<sub>2</sub>O in H-ZSM-5, produced from CO<sub>2</sub> hydrogenation over ZnZrO, helped stabilize the ZnZrO/ZSM-5 catalyst by suppressing the production of polycyclic aromatics.

Wang *et al.* presented a novel tandem catalytic process for CO<sub>2</sub> hydrogenation to aromatics in a single-step (Fig. 12).<sup>234</sup> A CH<sub>3</sub>OH-mediated pathway was found to occur over Cr<sub>2</sub>O<sub>3</sub>/H-ZSM-5 catalysts, which were prepared by physical mixing of





$\text{Cr}_2\text{O}_3$  and H-ZSM-5. The catalyst yielded 70.5% selectivity for aromatics among all the hydrocarbons and 41% CO selectivity with 33.6% conversion of  $\text{CO}_2$ . Meanwhile, the selectivity for  $\text{CH}_4$  and CO was successfully suppressed to 1.5% and 11.4%, respectively, by co-feeding 5.4 vol% CO in the feed gases whereas the aromatics selectivity and the  $\text{CO}_2$  conversion increased up to 75.9 and 34.5%, respectively. In addition, to enhance the selectivity towards benzene, xylene, and toluene, a structural change was carried out to form a core-shell type catalyst. The core-shell structured zeolite catalyst enhanced the selectivity for benzene, toluene and xylene from 13.2% to 43.6% (in aromatics) while the  $\text{CO}_2$  conversion was decreased from 34.5 to 27.6%. In addition, by tuning the mass ratio of both components of the tandem catalyst and the acid strength of zeolites, the catalytic performance could be influenced. The developed catalyst exhibited excellent stability for a 100 h reaction run. Most studies discussed the effect of space velocity on selectivity. An enhancement in selectivity to hydrocarbons was observed by increasing the space velocity, whereas the selectivity for CO was suppressed after the combination of zeolite with a metal oxide catalyst. The method used to combine catalysts also affects the catalyst activity and selectivity for products which is termed as proximity and will be discussed in section 3.3. In other words, reducing the contact time between the catalyst bed, feed gas and  $\text{CH}_3\text{OH}$  is favorable for timely diffusion into the zeolite pores for conversion to hydrocarbons.

In most of the studies listed in Table 3, lower olefins are the major products among the hydrocarbons. The synthesis of lower olefins was explained based on the synergic interaction between two catalysts which were responsible for methanol synthesis and the MTO reaction. However, it is challenging to selectively synthesize lower olefins from  $\text{CO}_2$  using the reaction coupling strategy, since the MTO reaction is more favorable at higher temperatures ( $>623\text{ K}$ )<sup>235</sup> whereas the  $\text{CO}_2$  to methanol reaction is thermodynamically unfavorable at higher temperature. It was found that after

mixing the two catalysts (methanol synthesis catalyst and MTH catalyst), the bifunctional catalyst shows a unique property which shifts the  $\text{CH}_3\text{OH}$  synthesis equilibrium and decreases the selectivity for CO and  $\text{CH}_4$ . The immediate conversion of methanol into lower olefins might be a driving force for the higher reactivity to methanol and lower selectivity towards CO. Methanol has been reported as an intermediate in most of the studies (Table 3) while DME was also found with methanol in a few studies. It was observed that methanol and CO were the main products with the metal-oxide catalyst alone, but when the metal oxide was mixed with zeolite, then the selectivity for methanol was found to be near zero or less than detectable under the reaction conditions listed in Table 3, whereas the CO selectivity was also reduced. It means that all produced methanol/DME could be converted into hydrocarbons. In some cases, small amounts of methanol were found unreacted when reaction conditions such as the mass ratio of metal oxide and zeolite catalysts, space velocity, pressure, and temperature were changed. For example, aromatics synthesis was examined on a  $\text{ZnAlO}_x/\text{H-ZSM}$  catalyst, and  $\text{CH}_3\text{OH}$  and DME were observed as intermediates.<sup>232</sup> A higher selectivity for methanol (above 98%, excluding CO) was obtained with ZnO alone, whereas the selectivity for  $\text{CH}_3\text{-OH}$  was reduced (to below 60%) after the addition of  $\text{AlO}_x$  and DME was found with  $\text{CH}_3\text{OH}$  with almost equal selectivity. Further, with the addition of H-ZSM, the selectivity for both  $\text{CH}_3\text{OH}$  and DME dropped. The preparation method and the packing method of  $\text{ZnAlO}_x$  and H-ZSM also changed the selectivity for  $\text{CH}_3\text{OH}$  and DME. For example, the selectivity for  $\text{CH}_3\text{OH} + \text{DME}$  was higher than 0.5% when they were prepared by grinding mixing, whereas the selectivity dropped to below 0.5% when both catalysts were mixed by granule mixing. Only DME was observed when both catalysts were packed in a dual-bed configuration in the reactor with  $\text{ZnAlO}_x$  upstream from H-ZSM.

The selectivities for  $\text{CH}_3\text{OH}$  and DME were also increased with higher space velocity in the case of the  $\text{ZnAlO}_x/\text{H-ZSM}$  catalyst. It was stated that the rate of formation of  $\text{CH}_3\text{OH}$  from  $\text{CO}_2$  hydrogenation is higher than the hydrogenation of CO. Thus, there is less chance to obtain  $\text{CH}_3\text{OH}$  from CO over metal oxides.<sup>229</sup> The reason for the lower CO selectivity with combined metal oxide and zeolite catalysts might be because both methanol and CO formation compete for consumption of the same reactants ( $\text{CO}_2$  and  $\text{H}_2$ ). At the high temperature used for direct  $\text{CO}_2$  hydrogenation to hydrocarbons, methanol synthesis should be strongly equilibrium limited and this reaction is favored by high reactant and low product (methanol and water) concentrations. The progress of the competing CO formation reaction lowers the reactant concentration and increases water, which favors reverse methanol synthesis. However, if methanol is immediately consumed by its conversion into hydrocarbons, then methanol synthesis can proceed with less restrictive equilibrium limitations and the negative effects that CO formation would have on its equilibrium. In

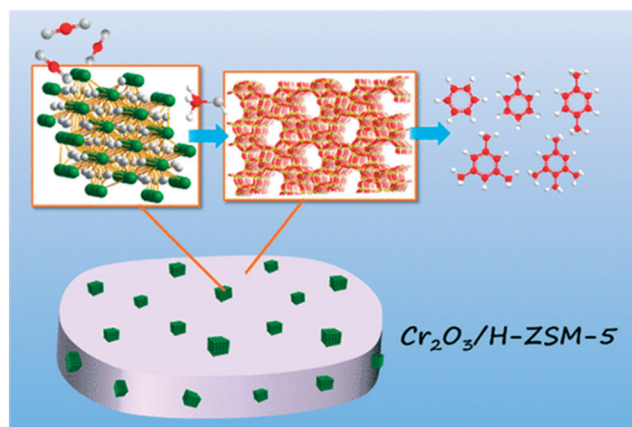


Fig. 12 A pictorial representation on the direct conversion of  $\text{CO}_2$  to aromatics over  $\text{Cr}_2\text{O}_3/\text{H-ZSM-5}$ . "Reprinted (adapted) with permission from Y. Wang, L. Tan, M. Tan, P. Zhang, Y. Fang, Y. Yoneyama, G. Yang and N. Tsubaki, *ACS Catal.*, 2018, 9, 895–901. Copyright (2019) American Chemical Society".



addition, unhindered methanol formation consumes more reactants which reduces the driving force for the CO formation reaction. However, detailed studies of this are still lacking in the literature.

### 3.1 Catalyst preparation methods

We have seen in the sections above and as evident in Table 3 that direct CO<sub>2</sub> hydrogenation to hydrocarbons always involves bifunctional catalyst systems, so in this section, the methods of preparation of these catalysts are discussed, with the intent to achieve varying degrees of contact between the two catalysts. Also, below in section 3.3, the importance of the proximity of the catalysts will be discussed. Most of the bifunctional catalysts are prepared by the solid mixing of methanol synthesis and hydrocarbon synthesis catalysts. Generally, this process is called granulation, which can be categorized into two parts, dry granulation and wet granulation. In the case of dry granulation, a mechanical compression can be used to mix the solid particles, while granulation with a liquid plays a role in facilitating the agglomeration.<sup>236</sup> As most of the studies in the case of bifunctional catalysts use a dry granulation process to prepare catalysts, only this method will be explained in detail here to keep this section brief.

A bifunctional catalyst was prepared using dry granule mixing, in which In<sub>2</sub>O<sub>3</sub> and HZSM-5 were pressed and crushed to obtain 250 to 400 μm granule sizes and then both granule samples were mixed in an agate mortar. Further, the mixed sample was again pressed, crushed and sieved to obtain the above-mentioned particle size.<sup>221</sup> A similar method was used to prepare In<sub>2</sub>O<sub>3</sub>/SAPO-34 and In-Zr/SAPO-34 by the same group.<sup>222</sup> Another group prepared a mixed hybrid catalyst of In<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> and SAPO-34 by mixing these samples in a certain ratio. Then this mixed powder was compressed, crushed, and sieved to 10–20 mesh particles.<sup>225</sup> The In<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> sample was prepared by a deposition-precipitation method. Bifunctional catalysts were reported to be prepared by shaking In<sub>2</sub>O<sub>3</sub>-ZnZrO<sub>x</sub> and SAPO-34 granules in a vessel.<sup>224</sup> In<sub>2</sub>O<sub>3</sub>/ZnZrO<sub>x</sub> was synthesized using an impregnation method and ZnZrO<sub>x</sub> was prepared by a co-precipitation method. A tandem catalyst, namely ZnZrO/SAPO-34, was synthesized using physical mixing in which smaller size solid solutions of ZnZrO were scattered on the outer surface of the zeolite and both components retained their individual structure.<sup>227</sup> Recently, a crystalline CuCe/SAPO-34 composite was prepared using a physical coating method.<sup>231</sup> In this process, the outside surface of SAPO-34 was covered with Cu/CeO<sub>2</sub>, with the help of an alkaline-silica sol binder. Further, the sample was calcined at 823 K for 4 h. A core-shell structure of the (CuZnZr)CZZ@SAPO-34 composite catalyst was prepared with a physical coating method.<sup>228</sup> In this method, the outer surface of CuO-ZnO-ZrO<sub>2</sub> was covered with zeolite SAPO-34 with the help of an alkaline silica binder. Further, the catalyst was calcined at 773 K for 2 h.

### 3.2 Reaction mechanism and intermediates for direct CO<sub>2</sub> hydrogenation to hydrocarbons

One key challenge for the selective synthesis of hydrocarbons from CO<sub>2</sub> is the selection of a suitable CO<sub>2</sub>-to-CH<sub>3</sub>OH active catalyst that appropriately matches with the MTH reaction catalyst. As described above, bifunctional catalysts are effective for the synthesis of hydrocarbons. They are composed of a metal-oxide like In<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>, ZnO-ZrO<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub>, ZnCrO<sub>x</sub>, ZnGa<sub>2</sub>O<sub>4</sub> and ZnAlO<sub>x</sub> which could activate CO<sub>2</sub> and catalyze CO<sub>2</sub> to CH<sub>3</sub>OH and/or DME in the temperature range of 573–673 K and zeolites such as HZSM, SAPO, and beta have been used to control the hydrocarbon selectivity due to their strong acidity and unique pore structure.<sup>225,237,238</sup> It could be possible that the active sites and the intermediates should be mostly the same in the bifunctional catalysts as for the individual catalysts when they are used separately to perform CH<sub>3</sub>OH and hydrocarbon synthesis. However, the product selectivity and catalyst activity were found to be different when both catalyst components were combined and used as a bifunctional catalyst. Some groups have studied the reaction mechanism by DRIFT and DFT calculations.<sup>141,230</sup>

DFT calculations were carried out to study the catalytic cycle of CO<sub>2</sub> to CH<sub>3</sub>OH over In<sub>2</sub>O<sub>3</sub> oxygen vacancies as discussed earlier in this review.<sup>221</sup> Further the formed CH<sub>3</sub>OH transfers to the zeolite where C-C coupling occurs at the acidic site of the zeolite and produces various hydrocarbons *via* the hydrocarbon-pool mechanism which is discussed earlier in section 2.2.1.2. The surface oxygen vacancies are increased by doping Zr into In<sub>2</sub>O<sub>3</sub>.<sup>222</sup> Similar observations were reported by Dang *et al.* after Zr doping into In<sub>2</sub>O<sub>3</sub>.<sup>223</sup> Later, the same group performed various experiments with an empty reactor, bare In<sub>2</sub>O<sub>3</sub>-ZnZrO and SAPO-34 to explain the reaction mechanism of CO<sub>2</sub> hydrogenation over In<sub>2</sub>O<sub>3</sub>-ZnZrO<sub>x</sub>/SAPO-34 catalysts under the same reaction conditions.<sup>224</sup> Over the In<sub>2</sub>O<sub>3</sub>-ZnZrO catalyst, CH<sub>3</sub>OH and CO were the major products. But after combination with the zeolite, the selectivity for CO decreased, and the selectivity for hydrocarbons increased. It was observed that the CH<sub>x</sub>O species generated over In<sub>2</sub>O<sub>3</sub>-ZnZrO<sub>x</sub> further transferred to the zeolite for C-C coupling on the Brønsted acid sites to produce hydrocarbons.

Li *et al.* proposed a reaction mechanism based on *in situ* DRIFT spectroscopy coupled with a mass spectrometer and found mainly HCOO\* and CH<sub>3</sub>O\* intermediates on the surface of ZnZrO but the IR studies showed a weak interaction of CH<sub>3</sub>O\* on ZnZrO that favored the transfer of these species onto SAPO-34 for the formation of olefins.<sup>227</sup> It was concluded that the CH<sub>3</sub>O\*, HCOO\* species, and gas-phase CH<sub>3</sub>OH were produced first *via* CO<sub>2</sub> hydrogenation on ZnZrO and then the formed CH<sub>3</sub>OH transferred to acidic sites of SAPO-34 for lower olefins production. The authors found that the CO selectivity was significantly suppressed and the CH<sub>3</sub>OH selectivity was much higher in the case of a tandem catalyst compared with that for ZnZrO alone. These results indicated an effective coupling of these reactions



(thermodynamic and kinetic coupling), where reactions over the tandem catalyst were more effective than the sum of reactions over individual catalysts ( $\text{CO}_2$  to  $\text{CH}_3\text{OH}$  and MTH). Later, a similar mechanism was observed by the same group over a  $\text{ZnZrO}/\text{HZSM-5}$  catalyst.<sup>233</sup> In this case,  $\text{HCOO}^*$ ,  $\text{CHO}^*$ , and  $\text{CH}_3\text{O}^*$  species were detected over the tandem catalysts during  $\text{CO}_2$  hydrogenation where  $\text{CH}_3\text{O}^*$  species most probably diffuse to zeolite HZSM-5 to make first light olefins and then aromatics from the lower olefins.

Liu *et al.* conducted *in situ* infrared (IR) spectroscopic measurements to propose a possible reaction mechanism for  $\text{CO}_2$  hydrogenation on a  $\text{ZnGa}_2\text{O}_4$  catalyst.<sup>229</sup> The authors demonstrated that the oxygen vacancy sites on  $\text{ZnGa}_2\text{O}_4$  account for  $\text{CO}_2$  activation to a  $\text{CH}_3\text{OH}$  intermediate and interaction with SAPO-34 can suppress the undesirable CO formation *via* the RWGS reaction, and was also responsible for the synthesis of hydrocarbons from  $\text{CH}_3\text{OH}$ . Carbonate species were observed on the pre-reduced  $\text{ZnGa}_2\text{O}_4$  after the adsorption of  $\text{CO}_2$  and after the introduction of  $\text{H}_2$ ,  $\text{HCOO}^*$  and  $\text{CH}_3\text{O}^*$  were generated on the surface of  $\text{ZnGa}_2\text{O}_4$  (Fig. 13). It was found that the  $-\text{Zn}-\text{O}-$  and  $-\text{Ga}-\text{O}-$  pairs were responsible for generating H species ( $\text{H}^*$ ) by activating  $\text{H}_2$  and then these H species bind with activated  $\text{CO}_2$  to form  $\text{CH}_3\text{O}^*$  species. The  $\text{CH}_3\text{O}^*$  species further formed  $\text{CH}_3\text{OH}$  that can be transferred into the pores of SAPO-34 and could produce lower olefins. The effect of oxygen-vacancies and water on  $\text{CO}_2$  adsorption on the (111), (110), and (100) surfaces of  $\text{ZnGa}_2\text{O}_4$  was studied using DFT slab calculations.<sup>230</sup> In some reports, the mesoporous  $\text{ZnGa}_2\text{O}_4$  was found to be an effective photocatalyst for the photoreduction of  $\text{CO}_2$  to  $\text{CH}_4$ .<sup>239</sup>

Ni *et al.* proposed a mechanism for  $\text{CO}_2$  hydrogenation to aromatics over  $\text{ZnAlO}_x/\text{H-ZSM-5}$  based on the catalytic results and DRIFTS studies.<sup>232</sup> According to this mechanism, surface formate species were formed on  $\text{ZnAlO}_x$  and further hydrogenated to form  $\text{CH}_3\text{O}^*$  species. Then, the methoxy species dissociated to intermediates including  $\text{CH}_3\text{OH}$  and DME which when transferred to H-ZSM-5 were further transformed to olefin intermediates. Finally, the formed olefins were converted to aromatics inside the micropores of H-ZSM-5.

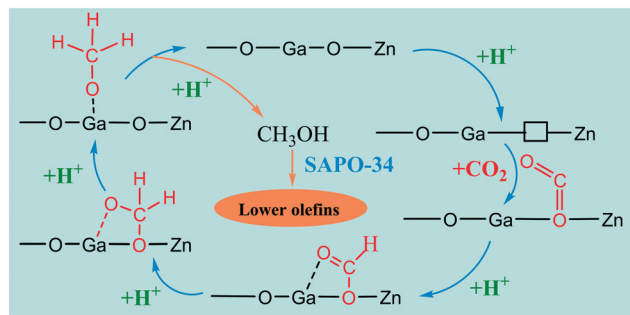


Fig. 13 Possible mechanism of  $\text{CO}_2$  conversion into hydrocarbons *via*  $\text{CH}_3\text{OH}$  intermediates over  $\text{Zn-Ga-O}$  catalysts. Reproduced from ref. 218 with permission from the Royal Society of Chemistry.

In addition,  $\text{CO}_2$  hydrogenation over  $\text{ZnAlO}_x$  generates more surface formate species compared to  $\text{CO}$  hydrogenation.

The mechanism of aromatics synthesis directly from  $\text{CO}_2$  over  $\text{Cr}_2\text{O}_3/\text{HZSM-5}$  was studied by *in situ* DRIFTS to gain more insights into the reaction pathway.<sup>234</sup> On  $\text{Cr}_2\text{O}_3$ , symmetric and asymmetric vibrations were observed related to  $\text{HCOO}^*$  species which have been recognized as an intermediate for  $\text{CH}_3\text{OH}$  synthesis. Meanwhile in the case of  $\text{Cr}_2\text{O}_3/\text{HZSM-5}$ , the vibrations linked to  $\text{HCOO}^*$  almost disappeared, but the  $\text{CH}_3\text{O}^*$  vibrations on the other hand appeared, indicating the formation of C-C coupling after the addition of HZSM-5. In addition, the vibrations related to the benzene ring and the substituted benzene ring were also observed in the spectra. Thus, the DRIFTS findings confirmed that a  $\text{CH}_3\text{OH}$ -mediated pathway applies over the  $\text{Cr}_2\text{O}_3/\text{HZSM-5}$  catalyst for  $\text{CO}_2$  hydrogenation to aromatics. It was found that the selectivity for aromatics over H-ZSM-5 was lower than that for  $\text{Cr}_2\text{O}_3/\text{HZSM-5}$  composites which was used for direct synthesis of aromatics from  $\text{CO}_2$ .

### 3.3 Proximity effect

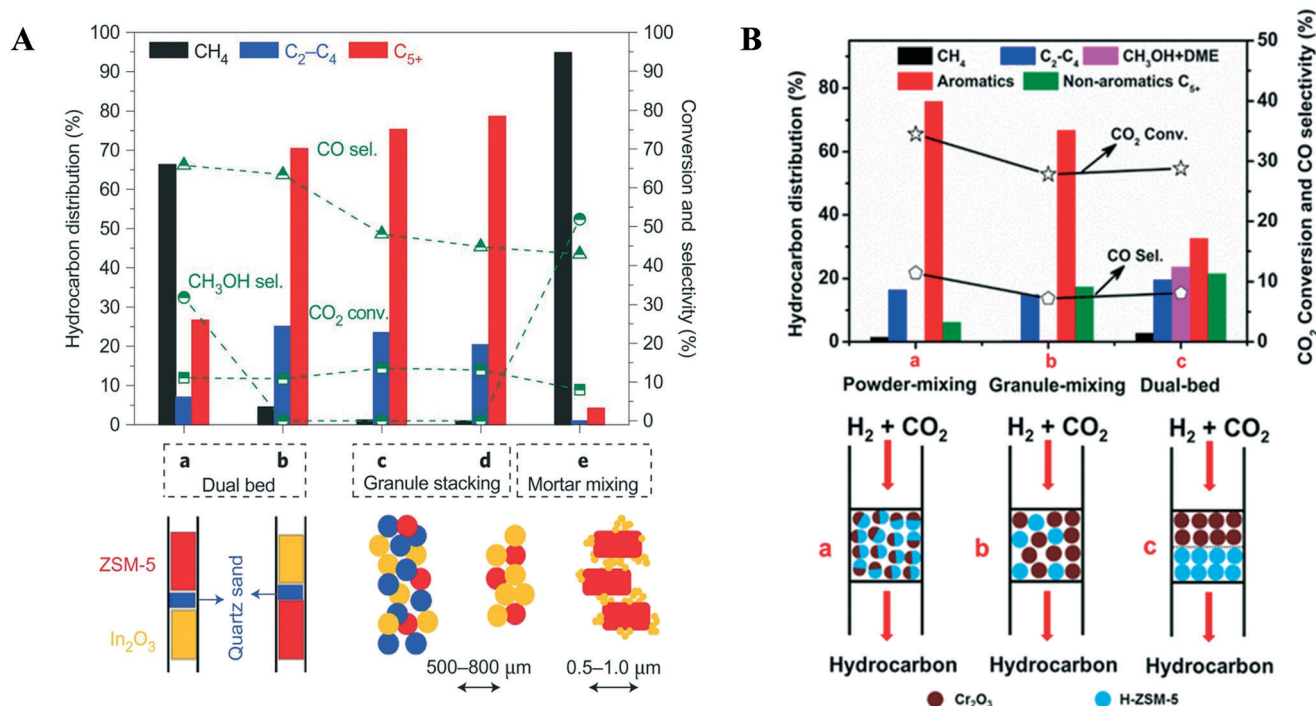
The proximity and integration of the two-components play a crucial role in the catalytic performance of bifunctional catalysts for  $\text{CO}_2$  hydrogenation. The effect of proximity and integration on product distribution has been studied in previous reports.<sup>221,222,226,227,229,237,240</sup> Fig. 14 and 15 show that there are three main methods to study the effect of proximity which include the following: (1) dual-bed mode in which the metal oxide and zeolite are positioned in series inside the reactor without mixing and separated by quartz sand; (2) granule mixing that could be obtained by the mixing of micrometer size granules of both components of a bifunctional catalyst. In some reports, quartz sand is also mixed as a third component to moderate the proximity, and (3) powder mixing (mortar mixing) in which both components are ground to nanometer size and mixed properly to increase their proximity. We have discussed more about granule and mortar mixing in section 3.1.

Gao *et al.* reported maximum conversion and selectivity for  $\text{CO}_2$  and  $\text{C}_2-\text{C}_4$  respectively over  $\text{In}_2\text{O}_3/\text{ZSM-5}$  in the case of granule mixing whereas minimum in the case of mortar mixing, indicating that the proximity decreases the active sites for methanol synthesis as well as hydrocarbon synthesis (Fig. 14A).<sup>221</sup> In another experiment, the catalyst was packed in a dual-bed configuration in which two configurations were compared, one in which HZSM-5 was packed above the oxide and second below  $\text{In}_2\text{O}_3$ . In the first case, the authors found good selectivity for  $\text{CH}_4$  (66.3%) and  $\text{CH}_3\text{OH}$  (31.8%) whereas the  $\text{C}_{5+}$  hydrocarbons selectivity was only 26.7%. However, in the latter case, the selectivity for  $\text{CH}_4$  decreased to 4.5% while the selectivity for  $\text{C}_{5+}$  increased to 70.4%. The CO selectivity was found to have a maximum of 65% in the case of dual-bed packing.

Furthermore, in the case of granule stacking, the  $\text{C}_{5+}$  selectivity enhanced and the selectivity for CO (<45%) and  $\text{CH}_4$





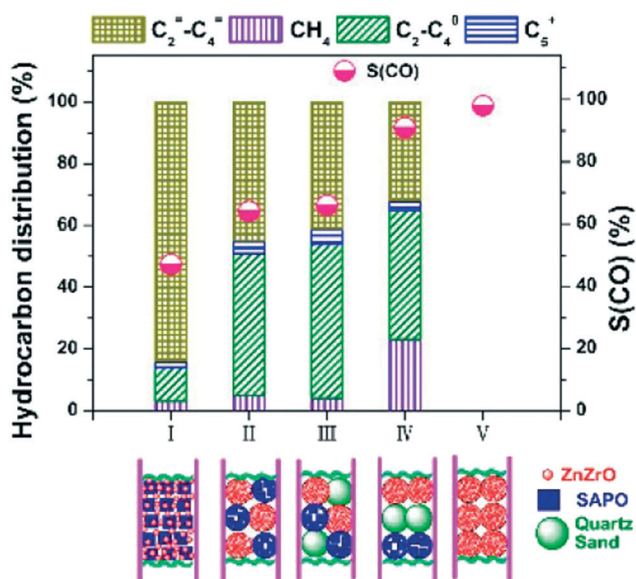


**Fig. 14** Influence of the integration manner of the active components in various studies (A) over the In<sub>2</sub>O<sub>3</sub>/HZSM-5 composite. Reprinted with permission from ref. 221. (B) over Cr<sub>2</sub>O<sub>3</sub>/H-ZSM-5. "Reprinted (adapted) with permission from Y. Wang, L. Tan, M. Tan, P. Zhang, Y. Fang, Y. Yoneyama, G. Yang and N. Tsubaki, *ACS Catal.*, 2018, 9, 895–901. Copyright (2019) American Chemical Society". (B) Over ZnZrO/SAPO. "Reprinted (adapted) with permission from Z. Li, J. Wang, Y. Qu, H. Liu, C. Tang, S. Miao, Z. Feng, H. An and C. Li, *ACS Catal.*, 2017, 7, 8544–8548. Copyright (2017) American Chemical Society".

decreased significantly, whereas the CO<sub>2</sub> conversion only changed slightly. The catalyst performance was the same with and without addition of quartz sand in the case of granule

stacking. Further, the distance between In<sub>2</sub>O<sub>3</sub> and ZSM-5 was decreased by grinding them in an agate mortar into powder form to explore the effect of their intimate contact. In the case of mortar mixing, the much smaller In<sub>2</sub>O<sub>3</sub> particles having a particle size of 10 nm were in a much closer contact with the 500–800 nm HZSM-5 particles. The authors found very low selectivity (4.2%) for C<sub>5</sub><sup>+</sup> hydrocarbons and high selectivity for CH<sub>4</sub> (94.3%) among the hydrocarbons excluding alcohols and CH<sub>3</sub>OH (51.9%) with 8% CO<sub>2</sub> conversion. The results suggested that close contact decreased the synergistic effect between In<sub>2</sub>O<sub>3</sub> and ZSM-5 and caused a significant deactivation of HZSM-5. Similar observations were found over In-Zr/SAPO-34 and Na-Fe<sub>3</sub>O<sub>4</sub>/HZSM-5 catalysts,<sup>237,241</sup> whereas other studies suggest that it may occur due to the poisoning of the acid sites of the zeolite by In species.

ZnZrO/SAPO-34, Cr<sub>2</sub>O<sub>3</sub>/H-ZSM-5 and ZnZrO/H-ZSM-5 gave higher selectivity towards hydrocarbons when both components are packed *via* powder mixing.<sup>227,233,240</sup> The effect of ball milling and granule stacking styles of In<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> and SAPO-34 catalysts was studied.<sup>225</sup> It was found that the activity of the catalysts was reduced in the case of ball milling as it damaged the structure of the SAPO-34 zeolite, which was observed from characterization techniques. In addition, when the mixture of In<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> and SAPO-34 powder was packed in a granule stacking manner, the selectivity for light olefins was increased, due to a timely diffusion of CH<sub>3</sub>OH into the zeolite to convert to hydrocarbons.



**Fig. 15** Over ZnZrO/SAPO. "Reprinted (adapted) with permission from Z. Li, J. Wang, Y. Qu, H. Liu, C. Tang, S. Miao, Z. Feng, H. An and C. Li, *ACS Catal.*, 2017, 7, 8544–8548. Copyright (2017) American Chemical Society".



The best catalytic performance for aromatics production was found when  $\text{Cr}_2\text{O}_3$  and ZSM-5 were in close proximity (Fig. 14B).<sup>234</sup> Further, the closeness of  $\text{Cr}_2\text{O}_3$  and ZSM-5 was increased by ball milling and no change was observed in the selectivity for aromatics. When a prolonged distance was maintained between the two components it was difficult for the intermediate species formed on the metal oxide surface to reach ZSM-5 active sites to begin the subsequent MTA step. In the dual-bed configuration, the  $\text{CH}_3\text{OH}$  selectivity was high when the  $\text{Cr}_2\text{O}_3$  catalyst was placed above the zeolite and quartz wool was loaded between them. Thus, the results suggested that the arrangement of  $\text{Cr}_2\text{O}_3$  and ZSM-5 inside the reactor plays an important role in direct  $\text{CO}_2$  conversion to aromatics or hydrocarbons.

The catalytic performance of a ZnZrO/SAPO-34 catalyst was determined by changing the two individual catalysts' positions and distance inside a tubular fixed bed reactor (Fig. 15).<sup>227</sup> The selectivity for lower olefins was decreased abruptly from 80% to 40%, whereas the selectivity for CO increased from 43% to 62% when the 250–450 nm granules of ZnZrO and zeolite were in mixed form in the reactor, compared to other integrated methods. No change was found in the results when quartz sand particles with the same size were mixed with ZnZrO and zeolite. This suggests that the spatial separation between ZnZrO and SAPO was the main factor influencing the selectivity. Further, when a quartz sand layer was situated between ZnZrO and SAPO-34 particles, the  $\text{C}_2=\text{C}_4$  selectivity dropped sharply, and CO became the major product. The authors found that the excellent performance of the tandem catalyst was due to the effective synergy interaction between ZnZrO and SAPO-34.

## 4. Kinetic modeling

Detailed knowledge of the performance and mechanisms of  $\text{CO}_2$  hydrogenation reactions can be obtained from kinetic modeling. The kinetic models can have widely different levels of detail and are mainly based on different approximations related to the rate determining steps and the nature of surface intermediates of the reaction.

### 4.1 Kinetics of $\text{CO}_2$ hydrogenation to methanol

In continuation of the discussion about the reaction intermediates and mechanisms related to copper-based and different oxide-based catalysts in sections 2.1.1 and 2.1.2, in this section, an overview of the kinetic models for the synthesis of methanol from  $\text{CO}_2$  hydrogenation will be discussed in detail. Methanol is produced on an industrial scale from synthesis gas mixtures consisting of  $\text{CO}/\text{CO}_2/\text{H}_2$  over commercial  $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$  catalysts under typical reaction conditions of 503–553 K and 5–12 MPa.<sup>133</sup> Kinetic modeling for methanol synthesis has been conducted for many years. Initially, most of the kinetic studies focused on macrokinetic modeling based on the Langmuir–Hinshelwood mechanism over Cu–Zn–Al catalysts. Later, the increasing efficiency of DFT and other electronic structure modeling

techniques has led to the development of sophisticated microkinetic models with the introduction of kinetic equations including concentration and temperature effects using the DFT results as an initiation point for the estimation of model parameters.

Different types of kinetic models for methanol synthesis have been reported in the literature.<sup>242–245</sup> Some older models have mostly focused on methanol synthesis from CO over copper-based catalysts, whereas newer studies focus mainly on direct hydrogenation of  $\text{CO}_2$  to form methanol. Villa *et al.* used the Langmuir–Hinshelwood technique considering the non-dissociative adsorption of CO and  $\text{H}_2$  to model the kinetics of methanol synthesis at low pressure from carbon monoxide and hydrogen over a  $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$  catalyst.<sup>246</sup> A kinetic model that quantitatively described the influence of concentration of carbon dioxide on methanol synthesis was introduced by Klier *et al.*<sup>247</sup> They proposed that the highest rate can be obtained by a balance between the promoting effect of  $\text{CO}_2$  that can maintain the catalyst in an active state *via* its oxidizing ability and the decelerating effect from the strong adsorption of CO, when present at higher concentrations.<sup>247</sup> Later, a comprehensive kinetic study on methanol synthesis at low pressure utilizing CO,  $\text{CO}_2$  and hydrogen over a  $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$  catalyst was introduced by Graaf *et al.*<sup>248</sup> which later has been refitted and reused by several other authors to understand their models with rates calculated under industrial conditions with commercially available catalysts.<sup>100,247,249–251</sup> Graaf *et al.*<sup>248</sup> explained their experimental results for methanol synthesis kinetics using a two-site Langmuir–Hinshelwood mechanism depending on dissociative hydrogen adsorption and three independent overall reactions: methanol synthesis from CO and  $\text{CO}_2$  and the reverse water gas shift reaction. The results from the model suggested that methanol could be formed from both CO and  $\text{CO}_2$ , and that hydrogen was adsorbed dissociatively. One site was devoted to the competitive adsorption of CO and  $\text{CO}_2$ , while the other site was committed to the competitive adsorption of  $\text{H}_2$  and water. The adsorption of methanol was supposed to be insignificant. The reactions were studied in a spinning basket reactor at a pressure of 15–50 bar and temperature of 483–518 K.<sup>248,252,253</sup>

A recent study by Diaz *et al.* shows the kinetics of  $\text{CO}_2$  hydrogenation to methanol at atmospheric pressure utilizing a Pd–Cu–Zn/SiC catalyst. They developed three types of Langmuir–Hinshelwood (LH) kinetic models where the adsorption term was changed accordingly (competitive *vs.* two-site *vs.* three-site adsorption mechanisms). The hydrogenation of formate has been proposed as the rate determining step. The first model considered competitive adsorption of the reactants on the catalyst surface, the second model considered Pd and ZnO as two different adsorption sites and finally a three-site kinetic model was suggested where PdZn or PdCu along with ZnO had been considered as the adsorption sites. Finally, the proposed models were compared, and proper model differentiation was performed. It was established that the three-site LH kinetic model bestowed the minimum



unweighted residual sum of squares and satisfied all the confirmed restrictions and fitted well with the experimental results. Therefore, this was concluded to be the most suitable kinetic model.<sup>254</sup> The reaction rate equations for methanol synthesis from CO<sub>2</sub> and the RWGS reaction (eqn (8) and (9)) proposed by Díaz *et al.*<sup>254</sup> are as follows:

CO<sub>2</sub> hydrogenation:

$$r_{\text{MeOH-CO}_2} = \frac{k'_{\text{MeOH-CO}_2} \cdot K_{\text{CO}_2, \text{S}_1} \cdot K_{\text{H}_2, \text{S}_2} \cdot \left( \frac{P_{\text{CO}_2} \cdot P_{\text{H}_2}^3}{K_{\text{eqMeOH-CO}_2} \cdot P_{\text{H}_2}^2} \right)}{D_{\text{MeOH-CO}_2}} \quad (8)$$

RWGS reaction:

$$r_{\text{RWGS}} = \frac{k'_{\text{RWGS}} \cdot K_{\text{CO}_2, \text{S}_3} \cdot \sqrt{K_{\text{H}_2, \text{S}_2}} \cdot \left( \frac{P_{\text{CO}_2} \cdot P_{\text{H}_2}}{K_{\text{eqRWGS}} \cdot P_{\text{H}_2}^{0.5}} \right)}{D_{\text{RWGS}}} \quad (9)$$

where the denominators of the rate equations refer to the adsorption terms as shown in Table 4.

As mentioned above, recent studies have focused more on microkinetic modeling for methanol synthesis from CO<sub>2</sub> hydrogenation considering various presumptions regarding the mechanism and the rate determining steps. A detailed mean-field microkinetic model for methanol synthesis and water-gas-shift reactions that included reaction intermediates *e.g.* HCOOH\* and CH<sub>3</sub>O\* and allowed for the development of formic acid (HCOOH), formaldehyde (CH<sub>2</sub>O), and methyl formate (HCOOCH<sub>3</sub>) as byproducts has been considered by Grabow and Mavrikakis.<sup>133</sup> All the initial model parameters were deduced from periodic density functional theory (DFT) calculations on the Cu (111) surface and thereafter fitted to the experimental results performed under standard conditions using a Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst. It was observed that the WGS reaction mainly proceeds following the carboxyl pathway (that was explained above in sections 2.1.1. and 2.1.2) whereas both CO and CO<sub>2</sub> hydrogenation pathways are mostly operative for methanol synthesis.<sup>133</sup>

Indium oxide has been considered as a highly efficient catalyst for methanol synthesis by direct CO<sub>2</sub> hydrogenation as discussed in section 2.2. Pérez-Ramírez *et al.*<sup>159</sup> explained in detail the mechanistic and kinetic aspects of CO<sub>2</sub> hydrogenation on In<sub>2</sub>O<sub>3</sub>. Microkinetic modeling based on DFT simulations performed on In<sub>2</sub>O<sub>3</sub>(111) supplied values for temperature and concentration-dependent rate expressions, which were shown to be in good agreement with the

experimental results. Microkinetic simulations were used to predict apparent activation energies and reaction orders and these agreed well with the experimental measurements. This is the only report, to date, on the kinetic modeling for CO<sub>2</sub> hydrogenation based on an indium oxide catalyst.<sup>159</sup> Another mean-field microkinetic model was used to forecast the reaction kinetics of different catalyst compositions on CO<sub>2</sub> hydrogenation, based on 33 reversible preliminary steps.<sup>255</sup>

The model incorporates all the reaction pathways as calculated utilizing DFT without any assumptions on the rate determining step. First-principles multiscale modeling was achieved for a commercial-like catalyst (Zn<sub>3</sub>O<sub>3</sub>/Cu) and three other Cu/metal oxide-based catalysts (Cr<sub>3</sub>O<sub>3</sub>/Cu, Fe<sub>3</sub>O<sub>3</sub>/Cu, and Mg<sub>3</sub>O<sub>3</sub>/Cu). From the micro-kinetic modeling, methanol selectivity and conversion were acquired for each of the catalysts under various experimental conditions.<sup>255</sup> Apart from the well-reported static microkinetic models, a dynamic microkinetic model for methanol synthesis was proposed by Norskov *et al.* over a Cu/ZnO catalyst. The model contains the dynamic changes in particle morphology and the active surface area and also describes the kinetic behaviour under transient conditions.<sup>249</sup>

Having discussed both macro- as well as micro-kinetic modeling techniques for CO<sub>2</sub> hydrogenation to methanol, it is necessary to discuss the strengths and weaknesses of these modeling techniques. Macro-kinetic modeling deals with simple models built on power law kinetics or empirical Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetics predict reaction rates directly from the composition of the feed gas, temperature and pressure. Macrokinetic modeling is very practical and highly used in designing chemical reactors, quality control in catalyst synthesis, evaluating catalyst preferences and studies of catalyst deactivation. The models used in macro-kinetic calculations are therefore very robust for the fitting of kinetic data. However, the robustness that makes them so practical when used as empirical expressions makes them less useful for the determination of the mechanism of the reactions. These models do not explain the elementary reaction steps at the molecular level and different model formulations can often adequately describe the same experimental data. Therefore, a more comprehensive inspection of the reaction kinetics can be performed using microkinetic modeling, where an elementary reaction scheme and the molecular states of reactants and intermediates are utilized in simulating the

**Table 4** Adsorption terms for the different types of models as reported by Díaz *et al.*<sup>254</sup>

Models	Conditions	Adsorption term
Competitive adsorption	$D_{\text{MeOH-CO}_2} = D_{\text{RWGS}} = D_x$ $S_1 = S_2 = S_3 = S$	$D_x = (1 + K_{\text{CO}_2, \text{S}} \cdot P_{\text{CO}_2} + \sqrt{K_{\text{H}_2, \text{S}}} \cdot P_{\text{H}_2})^2$
Two-site mechanism	$D_{\text{MeOH-CO}_2} = D_{\text{RWGS}} = D_x$ $S_1 = S_3 = S$	$D_x = (1 + K_{\text{CO}_2, \text{S}} \cdot P_{\text{CO}_2}) \cdot (1 + \sqrt{K_{\text{H}_2, \text{S}}} \cdot P_{\text{H}_2})$
Three-site mechanism	—	$D_{\text{MeOH-CO}_2} = (1 + K_{\text{CO}_2, \text{S}_1} \cdot P_{\text{CO}_2}) \cdot (1 + \sqrt{K_{\text{H}_2, \text{S}_2}}} \cdot P_{\text{H}_2})$ $D_{\text{RWGS}} = (1 + K_{\text{CO}_2, \text{S}_3}} \cdot P_{\text{CO}_2}) \cdot (1 + \sqrt{K_{\text{H}_2, \text{S}_2}}} \cdot P_{\text{H}_2})$

s = active sites.



reaction at the molecular level.<sup>256</sup> Also, kinetic parameters in microkinetic models (like preexponential factors and activation energies) can be predicted from quantum mechanical modeling methods like DFT calculations. These aid in the identification of possible rate determining steps. The verification of microkinetic models depends on more elaborate surface measurement techniques and hence they can potentially make accurate predictions over a wide range of reaction conditions. Microkinetic modeling is computationally more demanding and hence not as robust as macrokinetic modeling. Hence both the modeling techniques have their importance in their own ways and are therefore considered significant in studying the kinetic modeling for catalytic hydrogenation reactions.

#### 4.2 Kinetics of CO<sub>2</sub> hydrogenation from methanol to hydrocarbons

Section 2.2.1 introduced the basic conceptual mechanisms behind the MTH reactions; in this section, we discuss how they are formulated in terms of rate expressions with varying detail. Kinetic modeling of MTH reactions has been studied over many years mostly over ZSM-5 and SAPO. The incorporation of C<sub>6</sub><sup>+</sup> compounds in the models with the ZSM-5 zeolite marks the difference between the models based on ZSM-5 and SAPO.

Detailed kinetic models were formulated by Froment *et al.*<sup>257,258</sup> for the methanol to olefins (MTO) conversion over HZSM-5 catalysts with a Si/Al molar ratio of 200. The primary products (ethylene and propylene) formed from methanol and DME were modeled accurately using the Hougen–Watson model. The emergence of higher olefins was demonstrated with the help of the carbenium ion mechanism. The Evans–Polanyi relation was used to determine the activation energies of each step that considers the different energy levels of the carbenium ions and the olefin isomers.<sup>257</sup> In a continuation of this work, the authors tested eight kinetic models based on the fundamental steps for the conversion of methanol *via* dimethyl ether into olefins and determined 33 parameters. Nonlinear regression was used to minimize the function used for parameter estimation.<sup>258</sup> Zhou *et al.*<sup>259</sup> worked with ethylene, propylene, and *n*-butylene over the SAPO-34 catalyst at 723 K using a fixed-bed reactor with a weight hourly space velocity (WHSV) varying from 1 to 424 h<sup>-1</sup>. The proposed kinetic model showed that the olefin concentrations were in equilibrium using a carbenium intermediate lump. The model was able to predict their results adequately.<sup>259</sup>

Gayubo *et al.* presented extensive modeling on MTO reaction kinetics with SAPO catalysts.<sup>260–263</sup> They proposed a kinetic model for the conversion of methanol to olefins over a SAPO-34 catalyst and further extended their studies on a SAPO-18 catalyst for a wide range of experimental conditions. Fig. 16 shows the kinetic reaction scheme for the methanol to olefins process that is used by Gayubo *et al.*<sup>262</sup> The kinetic model consists of three basic steps that develop gradually over time: an initiation period (formation of the active intermediate

compounds), olefin formation, and finally deactivation stage (coke formation). Through this kinetic model, the authors predicted the experimental progress of the formation of olefins with time. Initially the production rate increases, later it passes through a maximum, where the concentration of the active intermediates reaches the maximum, followed by a reduction when deactivation causes a degeneration of the intermediates to form coke.<sup>260–263</sup> The same group also proposed a kinetic model including the effect of water on the MTG reaction kinetics on the HZSM-5 catalyst. They further extended the study by considering the effect of water in the kinetic model for catalyst deactivation.<sup>264,265</sup>

On the basis of the hydrocarbon pool mechanism (as explained in section 2.2.1.2), Kaarsholm *et al.*<sup>266</sup> proposed a model in which high molecular weight hydrocarbons were formed along with olefins inside the pores of the catalysts. The MTO reaction was studied for a phosphorus modified ZSM-5 catalyst in a fluidized bed reactor. The model involved 15 main reaction steps where, at equilibrium, all olefins are formed inside the pores of the catalyst. Fig. 17A shows the schematic for the reactions accounted for in this model by Kaarsholm *et al.*<sup>266</sup> This model fits well with the experimental data for the olefins but requires modifications in the case of paraffin and C<sub>6</sub><sup>+</sup> species (Fig. 17B). The olefinic species formed as products all through the temperature interval explored were well verified by the model.<sup>266</sup> Recently a new lumped kinetic model was established by Ryu *et al.*<sup>267</sup> with 9 reactions consisting of 7 lumps of products and intermediates that include methane, ethylene, propylene, butenes, propane, C<sub>4</sub> (that includes butane and 1,3-butadiene) and C<sub>5+</sub> (including hydrocarbons with five or more carbon atoms and ethane) to investigate the catalytic activity of SAPO-34 for MTO reactions under various process conditions. This simple kinetic model is based on the hydrocarbon pool mechanism that has been developed from a detailed kinetic model by Bos *et al.*<sup>268</sup> The model is developed based on the assumption that all the reaction rate expressions are first order.<sup>267</sup>

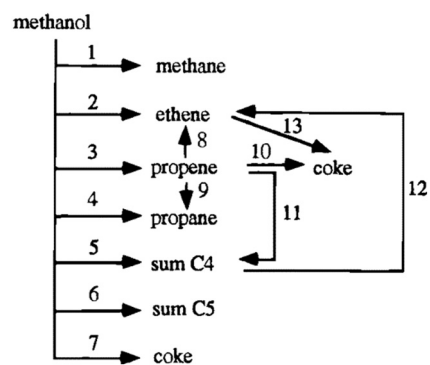


Fig. 16 Kinetic scheme proposed by Bos *et al.*<sup>268</sup> for transformation of methanol on SAPO-34. Reprinted (adapted) with permission from A. G. Gayubo, A. T. Aguayo, A. E. Sánchez del Campo, A. M. Tarrio and J. Bilbao, *Ind. Eng. Chem. Res.*, 2000, 39, 292–300, Copyright (2000) American Chemical Society.



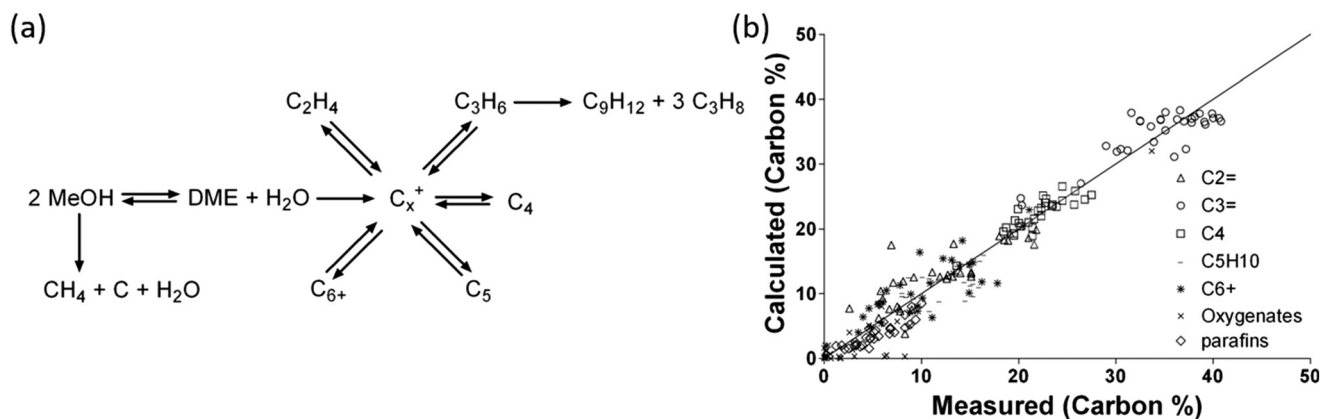


Fig. 17 (a) Schematic drawing of the kinetic model and (b) parity plot showing the comparison of the calculated product distribution to the measured data by Kaarsholm *et al.* Reprinted (adapted) with permission from M. Kaarsholm, B. Rafii, F. Joensen, R. Cenni, J. Chaouki and G. S. Patience, *Ind. Eng. Chem. Res.*, 2010, **49**, 29–38, Copyright (2010) American Chemical Society.

### 4.3 Kinetics of direct CO<sub>2</sub> hydrogenation using bifunctional catalysts

To increase the CO<sub>2</sub> conversion rate to methanol by coupling with MTO reactions, direct CO<sub>2</sub> hydrogenation using bifunctional catalysts has become recently prominent as described in section 3. But there are, to our knowledge, no kinetic modeling studies, as such, for direct CO<sub>2</sub> hydrogenation to hydrocarbons with methanol as an intermediate. It would seem possible to combine the standard models for CO<sub>2</sub> hydrogenation to methanol and MTO (as discussed in sections 4.1 and 4.2 in detail) together to describe the performance of the direct CO<sub>2</sub> hydrogenation procedure. However, it is noted from the experimental studies, as discussed in section 3.1, that with direct CO<sub>2</sub> hydrogenation, the performance of the combined catalyst was greater than the sum of the individual catalysts. Perhaps, this is due simply to coupling the reactions and its favourable effect on methanol synthesis thermodynamics perhaps, or there are other combined synergy effects of the catalysts. It was, for example, presumed that for Cr<sub>2</sub>O<sub>3</sub>/HZSM-5, this combination of catalysts allowed the surface diffusion of methanol intermediates from the oxide to the zeolite. A kinetic modeling study could be used to explore these possibilities and to identify possibly improved operating conditions for direct CO<sub>2</sub> hydrogenation.

## 5. Conclusion and future perspectives

Urgent action is needed in terms of decreasing CO<sub>2</sub> emissions in order to mitigate the challenges given by global warming. Currently, one promising action is to capture CO<sub>2</sub> and recycle it to useful chemicals and fuels. In this review, we have summarized the recent progress in producing chemicals and fuels, like methanol and hydrocarbons, by using CO<sub>2</sub> as a feedstock. The most studied reactions are the catalytic hydrogenation of CO<sub>2</sub> to methanol and hydrocarbons. In the case of indirect production of hydrocarbons, the CO<sub>2</sub> to methanol conversion is explored

on Cu, Pd, Pt, Zn, In, Ga, Ag, Au, ZnO, In<sub>2</sub>O<sub>3</sub>, Ga<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub>. Methanol synthesis from CO<sub>2</sub> is facing some challenges such as the excessive formation of CO which affects the selectivity for the desired product. There are many aspects where future research could be focused, for example, increasing the yield of fuels and chemicals by catalyst development; the uncertainty about the intermediates on the surface of the catalysts; the exact role of support materials; mechanisms of catalyst deactivation; interface composition; structure of active sites if catalysts have more than one active site for example in the case of bimetallic catalysts and when the support material also contains an active site; and different types of modelling such as kinetic modelling.

In recent years, advanced developments have been made by various research groups by developing bifunctional catalysts to convert CO<sub>2</sub> to hydrocarbons and fuels. In the case of bifunctional catalysts, two different catalysts are combined to form hydrocarbons in a one stage process. The mechanism, preparation methods and proximity effects were discussed using various *in situ* experiments and DFT studies. It has been seen that the intimate contact between the catalysts could increase the selectivity for hydrocarbons but the mechanism for this is unclear as intimate intra-particle contact was found to be negative in a few studies. In a few studies, it was concluded that close contact helped to promote the timely diffusion of methanol into zeolites and this increased the selectivity for hydrocarbons while in other studies the zeolites were poisoned by the metal/metal-oxide catalyst used for methanol synthesis. Thus, it is difficult to say exactly what proximity between the catalyst materials is optimal for the highest selectivity and conversion. The thermodynamics and reaction kinetics are different for the reactions (CO<sub>2</sub> to methanol and MTH) as the active site needs different temperatures for the activation of CO<sub>2</sub> and C–C coupling. A mean temperature, that is somewhere between the temperature most often used and favorable for the individual methanol synthesis and MTH processes, was used in recent reports for the activation of the catalysts. However,





the temperature was found a limiting factor for bifunctional catalysts as higher temperature is favorable for the RWGS reaction and CO<sub>2</sub> activation whereas low temperature decreases the CO<sub>2</sub> conversion. Yet, studies have shown that the two reactions could be coupled efficiently to produce hydrocarbons from CO<sub>2</sub> in a single step. Moreover, it was noticed that the lifetime of zeolite catalysts in the MTH reaction could be slightly improved in the presence of H<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>O co-feeds, which are the reactants and byproducts of the CO<sub>2</sub> to methanol reaction step. A suitable choice/modification of the zeolite catalyst could be used to steer the production of hydrocarbons of different carbon numbers.

Most of the studies reported that a decrease in the selectivity for CO and CH<sub>4</sub> could be achieved for bifunctional catalysts due to a synergetic interaction between both catalysts. But the mechanism and factors behind this are still unclear and deserve further research. However, bifunctional catalysts suffer from a low one-pass conversion efficiency and high selectivity towards CO in the case of direct synthesis. Also, the reported methanol selectivity in most studies for bifunctional systems is zero or very minimal and thus it can be concluded that for many systems it is possible to operate under conditions such that the rate of conversion of CO<sub>2</sub> and CO to methanol is limiting, whereas the conversion of methanol to hydrocarbons is relatively fast. Thus, it is possible for the equilibrium limitations for the methanol synthesis reaction to be avoided, which can be a factor allowing for somewhat lower selectivity for CO as compared to the process without further conversion of methanol to hydrocarbons. There is a gap in understanding of the mechanism after methanol synthesis and before C–C coupling in the case of bifunctional catalysts that needs to be addressed. For example, more than one intermediate is observed on the surface of catalysts but only one of them is likely responsible for forming the product, so it is unclear what the rest of the intermediates form and what/how they affect the selectivity and activity of the catalyst. In most cases, the selectivity for longer hydrocarbons is very low due to kinetic limitations of the C–C coupling. Efforts could focus to producing longer hydrocarbons from these bifunctional catalysts by modifications in catalyst structure and composition, changing the synthesis method of catalysts, and modifications in the packing method to obtain an efficient contact between both catalysts. We have assessed the reaction kinetics of both CO<sub>2</sub> to methanol and MTO reactions with a view of developing new kinetic models that couple these reactions and their catalysts for direct CO<sub>2</sub> hydrogenation to higher hydrocarbons with methanol as an intermediate, which warrants investigation.

Thus, we suggest that further research could emphasize the development of highly active catalysts for methanol synthesis as well as selective hydrocarbon synthesis and higher CO<sub>2</sub> conversion under industrially relevant conditions with better understanding of the fundamental activity–structure–composition relationship in bifunctional catalysts.

## Conflicts of interest

There are no conflicts to declare.

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