Advances in the Design of Heterogeneous Catalysts and Thermocatalytic Processes for CO₂ Utilization

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ABSTRACT: Utilization of CO₂ as feedstock to produce fine chemicals and renewable fuels is a highly promising field, which presents unique challenges in its implementation at scale. Heterogeneous catalysis with its simple operation and industrial compatibility can be an effective means of achieving this challenging task. This review summarizes the current developments in heterogeneous thermal catalysis for the production of carbon monoxide, alcohols and hydrocarbons from CO₂. A detailed discussion is provided regarding structure-activity correlations between catalyst surface and intermediate species which can aid in rational design of future generation catalysts. Effects of active metal components, catalyst supports, and promoters are discussed in each section, which will guide researchers to synthesize new catalysts with improved selectivity and stability. Additionally, a brief overview regarding process design considerations has been provided. Future research directions are proposed with special emphasis on the application scope of new catalytic materials and possible approaches of increasing catalyst performance.

KEYWORDS: *CO₂ utilization, Heterogeneous catalysis, Methanol, Hydrocarbons, Multifunctional catalysts, Cascade reactions, Reactor engineering*

1. INTRODUCTION

The combined effect of increasing global population, economic development, and higher standards of living has raised the global energy demand rapidly. In this scenario, it is imperative that the dependence on fossil fuels is diminished not only because of their limited reserves but especially because of the fact that their use has led to an alarming increase in CO₂ levels worldwide. The global CO₂ emissions in 2018 were approximately 33.9 Gt.¹

1.1. Need for Catalyst Design - Impact on Climate Change

It is now a well-established fact that the high atmospheric CO₂ levels are irrevocably linked to climate change. In order to mitigate further carbon emissions, a transition to renewable, non-carbon based energy sources is essential. However, given the current state of the art, we are still at least a few decades away from such a transition and thus we would still be largely dependent on fossil fuels for that period. This dependence would lead to some unavoidable emissions that would need to be captured in order to ensure that we do not go beyond the point of no return (i.e. increase of the average global temperature above 2 °C as compared to pre-industrial levels also known as the “2 degree scenario” or 2DS). However, an extensive debate is going on worldwide about what to do with the captured CO₂ since the quantity captured would not be trivial (in the order of hundreds of Gt).

Currently, two schools of thought exist regarding the post-capture application of CO₂. These consist of Carbon Capture and Storage (CCS) and Carbon Capture and Utilization (CCU). On a surface level, CCU presents itself as an elegant solution – mitigating CO₂ emissions while making useful products out of it. However, Mac Dowell et al. point out that, even if CO₂ were to be used as the sole feedstock for the production of the world’s most demanded chemicals, the impact on overall emissions in terms of volume would still be minimal.² In contrast, CCS has the potential to cause an appreciable impact on global emissions. This report does not however take into account the possibility of production of fuels from CO₂ (resulting in CO₂ neutral fuels). A term gaining rapid popularity in the discussion surrounding CO₂ utilization is about the possibility to bring about a ‘Circular Carbon Economy’. This term encompasses the concept of ‘avoiding’ new CO₂ emissions from fossil sources by recycling the existing CO₂ into chemicals and fuels. In this way, we can eschew a significant overhaul of the energy infrastructure while at the same time circumventing additional CO₂ emissions. In order for this concept to be put to actual practice, either of two possible approaches (or most likely, a combination of them) would need to be employed concerning CO₂ capture.

The first approach is ‘Direct Air Capture’ (DAC) where, as the name suggests, CO₂ is directly captured from the atmosphere and either stored or put into use. This approach is attractive as it offers the possibility of putting a capture station wherever required and would not need the implementation of point sources of capture (i.e., capture systems at points of emission including vehicles, factories and power plants). A significant drawback to this approach is the very low concentration of CO₂ (~400 ppm) in the atmosphere which provides a severe impediment with respect to the thermodynamics of the capture process.³ Therefore, considerable advances in systems and engineering would be required before this process can be deployed at scale.

The second approach is to implement CO₂ capture systems at point sources of emission. This is more feasible to carry out as e.g. CO₂ containing effluent streams from industry or power plants usually

consist of 3–35% of CO₂ making it possible to capture it with relative efficiency.⁴ A disadvantage to this approach is that while point sources of capture are possible at large scale installations like industrial plants or power generation facilities, it is much more difficult to implement at smaller sources of emission like vehicles. The road transportation sector accounts for approximately 16% of total CO₂ emissions and thus it is important to implement a system to curb the emissions from this sector.⁵ Another possible drawback of this system could be the lack of available transport and storage infrastructure (e.g., underground reservoirs) close to a source of emission such as a power plant. In order to overcome this second drawback, a proper distributed network of CO₂ pipelines would need to be established in order to ensure appropriate transport of the captured CO₂ to adequate storage facilities.

Having defined the concept of a circular carbon economy and the requirements regarding CO₂ capture for its implementation, we next try to quantify the potential CO₂ that can be avoided if it is fully utilized for the production of chemicals and fuels (Table 1). Multiple works have been published which highlight the possibility of the production of liquid fuel from CO₂.^{6,7} Similarly, the production of methane (which is the majority component of natural gas) has also been demonstrated via CO₂.⁸ The fuel consumption (and the corresponding market size) is many times bigger than that of the chemical market in terms of volume. For instance, the global consumption in 2017 of oil and natural gas was approximately 4.6 and 3.1 Gt of oil equivalent respectively.¹ Approximately, 20 gallons of gasoline are produced per barrel of crude oil and thus, if the only liquid fuel to be produced from CO₂ was to be gasoline, it would already account for a massive reduction of CO₂ emissions.⁹ As stated earlier, chemical production from CO₂ will have a relatively minor role to play in terms of volume for CO₂ emission reduction but it cannot be discounted due to the potential economic benefits and especially since the demand for these chemicals keeps on increasing every year. The vast majority of carbon-based chemicals most used globally is derived from fossil fuel sources and are thus termed petrochemicals. The most demanded petrochemicals include ethylene, propylene, benzene, methanol, toluene and xylenes.¹⁰ Table 1 provides an overview of potential CO₂ avoided if all the demand for these chemicals was fulfilled via production from CO₂.

Table 1. Potential CO₂ avoided in the circular carbon economy scenario

Entry	Product	tonCO ₂ /unit pdt. ^a	2017 Global Demand	Potential CO ₂ avoided (mmt)
Fuels				
1	Gasoline	0.009 ^b	6.75x10 ¹¹ gallons ¹	~6000
2	Natural Gas	0.0549 ^b	1.27x10 ¹¹ mcf ^{d,1}	~7000
Chemicals				
1	Ethylene	3.1 × 10 ^{6c}	152 mmt ^{e,11}	477
2	Propylene	3.1 × 10 ^{6c}	102 mmt ¹¹	320
3	Methanol	1.4 × 10 ^{6c}	135 mmt ¹¹	185
4	Benzene	3.4 × 10 ^{6c}	46 mmt ¹¹	155
6	Paraxylene	3.3 × 10 ^{6c}	41 mmt ¹¹	136
Total				14273
^a Implies tons of CO ₂ contained per unit of product where the unit is provided in the ‘2017 Global Demand’ column. ^b Value taken from ref ¹² , ^c based on carbon number equivalency i.e. 1 mol of ethylene contains 2 moles of C and thus 2 moles of CO ₂ can be used to make 1 mol of ethylene. ^d mcf = thousand cubic feet, ^e mmt = million metric tons.				

From the values in Table 1, we see that it is possible to reuse around 14.2 Gt of CO₂ from the, for instance, 33.9 Gt of CO₂ emitted in 2018. This number is of course a very crude estimate as demands for these products can (and will) vary significantly at different points in time so this number can be significantly higher or lower depending on the degree of implementation of CO₂ utilization worldwide. Another factor to consider is the relative climate benefits of different uses of CO₂. For instance, CO₂ can also be used in the production of building materials (not considered in this review) and this use is considered to have a high climate benefit as the CO₂ thus used can be considered sequestered for the long term if not permanently.¹³ Figure 1 provides a relative estimate of climate benefits and potential level of CO₂ utilization for various products.¹³

Figure 1. Relative climate benefits and potential for CO₂ utilization of different products. Adapted from ref. 13.

Nevertheless, if 14.2 Gt of CO₂ can be potentially endlessly recycled to make certain chemicals and fuels, we still need to consider the disposal of the remaining 19.7 Gt of CO₂ (assuming 33.9 Gt of annual emission in 2018 as mentioned above). This, inevitably, would need to be carried out via CCS. However, one factor that is often not taken into account when making these estimates is the natural role of land and/or sea acting as CO₂ sinks. It has been estimated that approximately 25% of anthropogenic CO₂ emissions is reabsorbed by the oceans and another 25% is reabsorbed by terrestrial land sinks.^{14, 15} This would then imply that only half of the global CO₂ emissions would need to be addressed (i.e. ~17 Gt). If 14.2 Gt can be reused, then it implies that only 2.8 Gt of CO₂ would need to be disposed of via man made CCS. However, there are a number of drawbacks of considering this approach. The first drawback that is immediately apparent is that while both aquatic and terrestrial sinks can absorb approximately half of the current CO₂ emissions, this capacity would slowly deteriorate and thus, we cannot rely on it indefinitely. A second, more serious, drawback is that CO₂ absorption by the oceans is leading to their acidification causing significant ecological damage. Thus, in effect, we would also have to account for the 25% of emissions that are absorbed by the oceans with manmade CCS installations.

In summary, considering 33.9 Gt of CO₂ emissions, about 14.2 Gt of CO₂ could be reused, about 8.5 Gt can be accounted for by natural terrestrial carbon sinks and the remaining 11.2 Gt of CO₂ would have to be sequestered via CCS. As before, these numbers are very crude estimates and can vary significantly depending on a number of geographic, political and socioeconomic factors. Finally, it has to

be mentioned that successful application of CCU is contingent upon the availability of cheap, renewable H_2 . The production of fuels and/or chemicals from CO_2 is possible by carrying out CO_2 hydrogenation. While H_2 itself can act as a clean source of energy, it is of course quite difficult to empower a H_2 supply chain and distribution system due to its high flammability and the fact that it is quite tricky and expensive to compress it to a sufficient degree in order to enable transport in pressurized containers. Currently, cheap H_2 comes from fossil sources (e.g., steam reforming of methane) which is carbon intensive since CO/CO_2 are side products (unless it is coupled with CCS). A non-carbon intensive approach for H_2 production is water electrolysis. However, this is a much more expensive endeavor as the H_2 produced via this approach is 3–4 times more expensive than H_2 produced from fossil sources.¹⁶ In the latter case, the source of energy used to carry out the electrolysis is also important. If the electricity used is generated from fossil sources, then the net process is once again carbon intensive. Thus, H_2 would need to be produced in an economic manner via water electrolysis using clean and/or renewable energy (e.g., wind, solar, nuclear etc.) before it can be utilized towards CCU.

Based on the earlier discussion, it is evident that there is no single panacea for controlling CO_2 emissions and an innovative integration of approaches needs to be adopted to ensure that we can meet the 2DS goals. One such innovative approach has been proposed by Dittmeyer et al.¹⁷ They recommend the retrofitting of air-conditioning units as devices capable of producing fuels that can enable energy democratization and reduce dependence on crude oil. It can thus be argued that if the production of renewable energy can be scaled enough to empower (i) DAC and (ii) water electrolysis, we can be well on our way to solve the climate crisis. This is because the huge problem of the intermittent nature of renewable energy (i.e. wind and/or solar) can be solved by storing this energy in the form of carbon fuels made from the captured CO_2 and the H_2 generated via electrolysis. Since the carbon emitted from these fuels could be recycled, we would arrive at a state of net zero emissions. An added incentive that would make this approach attractive is of course the fact that most of the existing energy infrastructure can remain in use thus avoiding the capital costs associated with developing new infrastructure.

In this frame, it is evident that CCU can make a significant contribution towards the mitigation of new carbon emissions and play an important role when used in conjunction with other approaches. One of the most important factors for effective implementation of CCU is proper catalyst design. Assuming that cheap, plentiful H_2 is available, the correct catalyst would have to be employed in order to ensure an economically viable process. In fact, one of the aspects of CCU catalyst design would be to ensure efficient utilization of H_2 in order to improve the process sustainability. Therefore, a careful, rational approach is required for designing such a catalyst as multiple challenges abound for CO_2 conversion.

1.2. Need for Catalyst Design – Challenges in CO_2 Conversion

Despite the high abundance of CO_2 in nature, the main challenge in its catalytic conversion is associated with the inertness of this molecule. The crucial task is therefore to find active, selective and stable catalysts as well as to gain a proper understanding of the reactivity of CO_2 in different catalytic environments. Along this line, homogeneous catalysts such as different transition metal complexes, *N*-heterocyclic carbenes (NHCs), and frustrated Lewis pairs have shown high activity for CO_2 activation under milder reactions.^{18–23} However, the current industrial infrastructure is not suitable for the production of a large volume of chemicals and fuels over homogeneous catalysts due to complications regarding separation of catalyst from products and poor process economy. More importantly, the total production

over homogeneous catalysts cannot fulfil the current worldwide demand of renewable products. Therefore, significant focus has been turned to using heterogeneous catalysts, which are expected to offer better process economy and meet the targeted production limit.²⁴⁻²⁸ A representative example is the “George Olah Renewable Methanol Plant” in Iceland, the first commercial CO₂ to methanol recycling plant established in 2012, which started with an initial annual production capacity of 4500 m³ of methanol (10 ton per day) recycling ~5600 tons of CO₂ per annum.²⁹ The plant is currently run by the Carbon Recycling International (CRI) company and the required H₂ is produced by water electrolysis using cheap, geothermally produced electricity. The required energy for CO₂ conversion is also obtained from the readily available local geothermal energy sources. Therefore, this project has been demonstrated as being quite successful in terms of economical utilization of CO₂ captured from flue gases with minimum adverse effects on the environment.

Current efforts made in heterogeneous catalysis for CO₂ conversion mainly focus on the electrochemical and thermal reduction of CO₂.^{30, 31} Apart from these two approaches, photochemical reduction is another alternative strategy for CO₂ transformation,³²⁻³⁴ but the maximum efficiency achieved till date is much lower than the targeted production. So far, the electrochemical reduction approach has been operated on a small scale, which is more suitable for limited CO₂ conversion and fine chemical production. The main advantage of electrocatalytic CO₂ reduction is that the required H₂ comes from water, which is beneficial compared to thermal reduction considering that pressurized molecular H₂ is required in the latter case. However, the Faradic efficiency of the electrocatalytic CO₂ reduction process is significantly lower as compared to the H₂ evolution rate, and thus it limits its application in large scale production. A number of excellent reviews have recently been published on the efforts made in the field of electrocatalytic CO₂ conversion process and catalyst development.³⁵⁻³⁷

In terms of substrate scope and application, catalytic conversion of CO₂ can provide numerous useful products including building block intermediates (such as CO, methane, formic acid, methanol, dimethyl ether, carbonates, lower olefins etc.) and readily usable chemicals/fuels (such as renewable polymers, hydrocarbons etc.). Extensive studies have been done on focusing the production of each chemical, but there seems to be a general consensus in literature that the production of syngas, alcohols and hydrocarbons is the most promising. Thus, this review will focus on the recent development of catalyst design targeting the production of these three products (Figure 2). Special emphasis will be given on rational approaches to identify structure-activity correlations between active sites and different reaction intermediates in order to guide towards the discovery of promising catalysts for specific reactions.

Figure 2. Schematic diagram showing the scope of this review.

2. ACTIVATION OF CO₂: THERMODYNAMIC CONSIDERATIONS

The highest oxidation state of carbon makes CO₂ comparatively inert thereby making its chemical transformations thermodynamically unfavorable. Therefore, using CO₂ as a feedstock is challenging and one must consider the relative stability of the final products as compared to CO₂. Figure 3 gives an overview of Gibbs free energy of formation (ΔG_f°) for different carbon-containing molecules, which directly reflects the comparative stability of CO₂. Based on energy considerations, C–O bonds are relatively stronger than C–H bonds, and therefore oxygenated molecules possess higher thermodynamic stability compared to hydrocarbon molecules. As a result, substantial energy is required for carbon reduction in the former case. Another difficulty in the transformation of CO₂ is that the final products derived from CO₂ are mostly liquid in nature (e.g., formic acid, methanol, higher hydrocarbons). Since these reactions involve a phase change from gaseous reagent into liquid products, they are entropically unfavorable.

Figure 3. Gibbs free energy of formation (ΔG_f°) for some carbon compounds at different oxidation states of carbon. H₂ and H₂O are also included as they are frequently involved in the reactions.

The chemical transformation of CO₂ is thermodynamically more favorable when it is used as a co-reactant with another molecule that has a higher Gibbs free energy. For example, production of CO from CO₂ requires much higher energy when CO₂ is used as the single reactant, while the presence of H₂ significantly reduces the enthalpies of reaction (Equations 1 and 2, Table 2). Therefore, most of its transformations use a second molecule, usually H₂, to make useful chemicals and fuels. Another way to make the CO₂ transformation more feasible is to use a solvent. For example, the transformation of CO₂ into formic acid in gaseous phase is thermodynamically unfavorable (Eq. A), while addition of water makes the reaction slightly exergonic (Eq. B).

Based on the energy requirement, reactions involved in CO₂ conversion can be classified into two major categories. Firstly, reactions where the second reactants (with higher Gibbs free energy) supply energy as is the case for addition of CO₂ to other reactants. Production of carboxylates and lactones, carbamates, ureas, isocyanates, and carbonates fall in this category. These processes are energetically favorable and often run without any catalyst. Secondly, reactions where carbon is reduced and therefore a substantial amount of external energy is required. Reduction of CO₂ into formates, oxalates, carbon monoxide, formaldehyde, methanol, and methane fall in this category. The external energy is generally provided in terms of heat energy, but the strong C=O double bond in CO₂ often requires a catalyst to overcome the high activation barrier.

The most important aspect of CO₂ conversion is controlling the selectivity of different intermediates in the reaction, which requires a thorough understanding of the thermodynamics and kinetics of each step. Therefore, multiple parameters need to be considered for optimizing the desired process and most importantly, efficient and selective catalysts are a prerequisite to overcome the thermodynamic and kinetic barrier in CO₂ conversion. For instance, the production of CO from CO₂ is endothermic in nature (Eq. 2, Table 2) implying that the forward reaction is favoured by higher temperatures. Increasing the pressure, on the other hand, has no effect on the yield of CO since there is no change in the number of molecules during the reaction (Figure 4). The CO₂:H₂ ratio is an important factor influencing the CO yield and it has been observed that increasing the H₂ content in the feed greatly increases the amount of CO obtained from CO₂.³⁸

Table 2. Standard enthalpies ($\Delta H^{\circ}_{298\text{K}}$) and Gibbs free energies ($\Delta G^{\circ}_{298\text{K}}$) for different products formed via CO_2 . Values taken from ref 38.

Equation number	Reaction	$\Delta H^{\circ}_{298\text{K}}$ (kJ mol ⁻¹)	$\Delta G^{\circ}_{298\text{K}}$ (kJ mol ⁻¹)
(1)	$\text{CO}_2 \rightarrow \text{CO} + \frac{1}{2}\text{O}_2$	293.0	257.2
(2)	$\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$	41.2	28.6
(3)	$\text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$	-49.5	3.5
(4)	$\text{CO}_2 + 3\text{H}_2 \rightarrow \frac{1}{2}\text{C}_2\text{H}_5\text{OH} + \frac{3}{2}\text{H}_2\text{O}$	-86.7	-32.4
(5)	$\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	-165.0	-113.5
(6)	$\text{CO}_2 + \frac{7}{2}\text{H}_2 \rightarrow \frac{1}{2}\text{C}_2\text{H}_6 + 2\text{H}_2\text{O}$	-132.1	-78.7
(7)	$\text{CO}_2 + \frac{10}{3}\text{H}_2 \rightarrow \frac{1}{3}\text{C}_3\text{H}_8 + 2\text{H}_2\text{O}$	-125.0	-70.9
(8)	$\text{CO}_2 + \frac{13}{4}\text{H}_2 \rightarrow \frac{1}{4}\text{n-C}_4\text{H}_{10} + 2\text{H}_2\text{O}$	-121.6	-66.9
(9)	$\text{CO}_2 + 3\text{H}_2 \rightarrow \frac{1}{2}\text{C}_2\text{H}_4 + 2\text{H}_2\text{O}$	-64.0	-28.7
(10)	$\text{CO}_2 + 3\text{H}_2 \rightarrow \frac{1}{3}\text{C}_3\text{H}_6 + 2\text{H}_2\text{O}$	-83.6	-42.1
(11)	$\text{CO}_2 + 3\text{H}_2 \rightarrow \frac{1}{4}\text{n-C}_4\text{H}_8 + 2\text{H}_2\text{O}$	-90.3	-45.2

Figure 4. Equilibrium CO_2 conversion for CO_2 hydrogenation to CO . Reproduced with permission from ref. 38. Copyright 2016 Elsevier.

On the other hand, evaluating the thermodynamics of methanol production from CO₂ we observe that it is exothermic in nature (Eq. 3, Table 2). This implies that lower temperatures are beneficial for methanol production. Furthermore, higher pressures favour both CO₂ conversion and methanol selectivity during CO₂ hydrogenation (Figure 5) due to the reduction in the number of molecules. Finally it is also seen that a higher H₂ content in the feed (i.e. higher H₂:CO₂ ratio) promotes higher CO₂ conversion and methanol selectivity. In contrast, ethanol production from CO₂ is more exothermic and thermodynamically favoured as compared to methanol (Eq. 4, Table 2). Similar to methanol production, lower temperature and higher pressures facilitate ethanol production from CO₂.³⁸

Figure 5. Equilibrium CO₂ conversion and methanol selectivity for CO₂:H₂ ratio of 1:3 (left) and 1:10 (right) at pressures of (a) 10 bar (b) 30 bar (c) 100 bar (d) 200 bar (e) 300 bar (f) 400 bar (g) 500 bar. Reproduced from ref. 24.

Lastly, for the production of hydrocarbons from CO₂, it is well known that olefins and paraffins follow opposing thermodynamic trends. The production of higher paraffins is less exothermic as compared to lower paraffins and is thermodynamically less favoured (Eqs. 5–8, Table 2). Conversely, the production of higher olefins is more exothermic and thermodynamically more favourable as compared to lower olefins (Eqs. 9–11, Table 2). As before, the exothermicity and volume reduction implies that the production of hydrocarbons from CO₂ is promoted by lower temperatures and higher pressures (Figures 6 and 7). For olefins, it is also seen that higher pressures and higher H₂:CO₂ ratio favour the formation of longer chain olefins as compared to lighter olefins.

Figure 6. Equilibrium CO_2 conversion for CO_2 hydrogenation to light alkenes. (a) 1 bar and $\text{CO}_2:\text{H}_2$ ratio of 1:1, (b) 50 bar and $\text{CO}_2:\text{H}_2$ ratio of 1:1, (c) 1 bar and $\text{CO}_2:\text{H}_2$ ratio of 1:5, and (d) 50 bar and $\text{CO}_2:\text{H}_2$ ratio of 1:5. Reproduced with permission from ref. 38. Copyright 2016 Elsevier.

Figure 7. Equilibrium CO_2 conversion for CO_2 hydrogenation to light alkenes. (a) CH_4 and (b) C_2H_6 . Reproduced with permission from ref. 38. Copyright 2016 Elsevier.

3. CATALYTIC CONVERSION OF CO₂

In CO₂ conversion, identifying the most crucial intermediate is always important to obtain the desired products. Stabilization of those intermediates is the key to achieve better selectivity and therefore the catalysts should be designed based on the interaction of intermediate species with the catalyst surface. For example, CO is found as the key intermediate in MeOH synthesis, which gives different MeOH selectivity based on CO-catalyst interaction. It was observed that stronger binding of CO over catalyst surface generally favors MeOH formation, while weaker binding favors RWGS.³⁹ In this section, different catalytic systems will be discussed with their unique properties that are essential for particular reactions.

3.1. Production of CO

Carbon monoxide (CO) is considered as the most important intermediate in CO₂ conversion as it can be used as the starting material for multiple processes like Fischer-Tropsch synthesis and hydroformylation. Catalytic conversion of CO₂ to CO is generally achieved via RWGS reaction (Eq. 2, Table 2). So far, various catalysts based on both noble metals and transition metals on different oxide supports have been studied with different reaction pathways reported depending on the catalyst surface.^{31, 40-42}

3.1.1. Noble metal-based catalysts

According to the state of the art, the most extensively studied catalysts for CO production from CO₂ were based on Pt or Cu.⁴¹ Porosoff and Chen reported both monometallic and bimetallic Pt catalysts (such as PtNi and PtCo) on different oxide supports, where the activity and selectivity were found to be dependent on the nature of supports.⁴³ For monometallic Pt catalysts, CeO₂ showed higher activity than γ -Al₂O₃ support, while the CO selectivity followed the opposite trend. Among bimetallic combinations, PtCo/CeO₂ showed the best CO/CH₄ selectivity due to low interaction energy between the metallic interface and CO. According to d-band center theory, the CO selectivity increases as the values of d-band center move towards more negative and the reported activity trend also followed the theoretical assumption. This study suggests that it is also possible to predict the activity of different bimetallic systems based on d-band energy.

While early studies on RWGS mainly used Al₂O₃ and SiO₂ supported catalysts, the use of CeO₂ as a support started to attract an increasing amount of attention after revealing its excellent reducible property.^{31, 40, 44-46} Apart from reducibility, CeO₂ also shows high intrinsic activity toward CO₂ adsorption. Although, CeO₂ itself shows poor performance in the catalytic reaction, its reducibility and the ability to form oxygen vacancies can be improved by introducing other metals.⁴⁷ Mechanistic studies have shown that direct dissociation of CO₂ to CO is facilitated by the exchange of O from CO₂ with pre-reduced CeO₂.^{48, 49} In addition to the advantage of oxygen vacancies, another advantage of using CeO₂ as support is its ability to create strong metal-support interaction (SMSI) with other metals. In a report by Li et al., it was shown that the chemical state of Ir metal was a key factor responsible for CO selectivity and this chemical state could be tuned by altering the loading of the metal.⁴⁴ In the Ir/CeO₂ system, lower Ir loading (5 wt%) resulted in high population of partially oxidized Ir species which adsorb CO very weakly as compared to metallic Ir at higher Ir loading (15 or 20 wt%). As a result, the partially oxidized Ir/CeO₂ surface could effectively catalyze the dissociative chemisorption and further reaction of CO₂, and fast desorption of resulting CO in order to give ~100% CO selectivity (Figure 8a). Both EXAFS and XPS data

showed the evidence that the catalyst with lower Ir loading consisted of mainly Ir–O species as a result of SMSI (Figure 8b & 8c). Furthermore, it was also noted that the isolated Ir species (e.g., at 0.7 wt% Ir loading) and the smaller Ir NPs displayed identical CO selectivity, indicating that the existence of isolated metal sites is not a prerequisite factor for the inhibition of methanation reaction. Rather, it is evident that a strong interaction between the support and the active species is the key factor on the catalytic performance at sub-nano scales.

Figure 8. (a) Catalytic selectivity of Ir/CeO₂ catalysts (at different Ir loadings) against the coordination number of Ir–Ir and Ir–O shells. (b) Ir L₃-edge EXAFS of the Ir/CeO₂-used catalysts. (c) XPS analysis of the Ir/CeO₂-used catalysts. Reproduced with permission from ref. 44. Copyright 2019 Wiley-VCH.

Other redox active supports such as TiO₂ and ZrO₂ were also promising for CO₂ adsorption by generating O vacancies. Chang Hong and coworkers reported Pt/TiO₂ catalyst in RWGS and showed that the catalyst had higher CO₂ conversion rate than the Pt/Al₂O₃ catalyst.⁵⁰ H₂ TPR and FT-IR studies confirmed the formation of high electron donating Pt–O_v–Ti³⁺ (O_v is O vacancy) sites due to the reducible nature of TiO₂ support. These active sites were responsible for the formation of surface carbonate species, which was the key intermediate in the mechanism. On the other hand, since the Pt/Al₂O₃ catalyst was irreducible in nature, the RWGS reaction could not proceed through carbonate species. Another study by Kattel et al. showed that the CO selectivity on bimetallic PtCo catalysts can be tuned by simply changing the support.⁵¹ TiO₂ supported PtCo catalysts preferentially formed CO, whereas high selectivity towards CH₄ was observed on CeO₂ or ZrO₂ supports. The main reason for difference in CO selectivity was associated with different reaction pathways over different catalysts. On PtCo/TiO₂, *HCOO/*HOCO were formed as reaction intermediates, which further dissociated into *CO and *OH. In contrast, both *HCOO/*HOCO and *CH₃O were observed on PtCo/CeO₂ and PtCo/ZrO₂, and *CH₃O further formed CH₄ through *CH₃OH intermediate. Similar results were obtained with commercial Au-based catalysts supported on Al₂O₃ and TiO₂, where Au/TiO₂ was better in terms of CO production rate.⁵² Transient and steady-state operando DRIFTS studies revealed that Au/Al₂O₃ proceeds through the formate

intermediates, while the Au/TiO₂ catalyst follows a redox mechanism due to the presence of both the surface hydroxyls and oxygen vacancies. Another interesting feature of TiO₂ is its different crystal phases (anatase and rutile), which can be changed at different calcination temperature in order to tune the CO/CH₄ selectivity. One recent study revealed that CO is predominantly formed over anatase TiO₂ supported Co catalyst, while CH₄ was the main product on the Co/rutile-TiO₂ catalyst.⁵³

Additionally, to improve the intrinsic activity of irreducible supports (such as Al₂O₃, SiO₂ etc.), another metal oxide phase with reducible property can be introduced. For example, the apparent activation energy of RWGS reaction on Pt/SiO₂ system could be decreased significantly by the addition of Fe₂O₃ and MoO_x in order to increase the intrinsic activity by several times.^{54, 55} This type of promotional effect can be highly enhanced by introducing alkali metals, such as lithium or potassium.⁵⁶⁻⁵⁹ Liang et al. showed that the addition of potassium as promotor to Pt/mullite (mullite is a mixed oxide with a nominal composition of 3Al₂O₃·2SiO₂) catalyst can enhance the TOF of RWGS reaction by 7 times.⁵⁸ The RWGS mechanism in Figure 9 shows that the dissociative adsorption of H₂ molecules first occurs on the Pt NPs, while at the same time CO₂ molecules mainly adsorb at the interface of K–Pt species or K-mullite support. K plays multiple roles, such as (i) stabilization of Pt in a higher oxidation state through the strong interaction between KO_x and Pt, (ii) creation of a new interface between KO_x and Pt that can serve as the active site for formate decomposition to produce CO, and (iii) weakening the strength of CO adsorption on Pt in order to hinder the subsequent hydrogenation of CO into CH₄ through C–O bond dissociation. Another study based on Pt/zeolite catalyst showed that the chemical state of Pt could be altered by the addition of K promoter, where the formation of Pt-O(OH)-K interfacial sites was evidenced by X-ray absorption near edge structure (XANES) and XPS studies.⁵⁹ Due to the charge transfer from Pt surface to K, Pt-O(OH)-K active interface could facilitate the formation of bridge-bonded formate intermediates and CO desorption.

Figure 9. Effect of potassium as promoter in the RWGS reaction over K–Pt/mullite catalyst. Reproduced with permission from ref. 58. Copyright 2017 Elsevier.

3.1.2. Non-noble metal-based catalysts

Along with the above discussed Pt-based catalysts, other precious metals such as Rh,⁶⁰ Ru,^{61, 62} Ir,⁴⁴ Au,⁶³ Pd⁶⁴ were also reported to give high activity due to their good hydrogenation properties. However, the high cost restricts their real application in large scale production of CO and therefore the research in the field is increasingly shifting to non-noble metal systems. Among the non-noble metals,

Cu, Fe, Co, Ni, and Mn were found to be active and therefore used as alternative catalysts for industrial RWGS process.⁶⁵⁻⁷⁴ A recent report explored different transition metal-based catalysts (M/ZIF-8-C; M = Ni, Fe, Co and Cu) supported on zeolitic imidazolate framework-derived carbon support enriched with pyridinic N sites.⁶⁶ The main advantage of using these materials was the dual functionalities, where metal/metal carbide phase performs H₂ dissociation and pyridinic N adsorbs CO₂. DFT calculations showed that the reaction mechanism followed direct cleavage of *CO₂ into *CO and *O rather than decomposition of *COOH. Ni and Fe were more selective toward CO due to the lower energy required for *CO desorption as compared to Co and Cu. Zhao et al. reported lanthanum–iron–nickel perovskite catalysts, where the selectivity of CO₂ hydrogenation was significantly tuned by controlling the valence state of Ni.⁶⁷ CH₄ was predominantly formed over LaNiO₃, whereas LaFe_{0.5}Ni_{0.5}O₃ preferentially formed CO. Combined studies by in situ XRD, XANES, and AP-XPS revealed that LaNiO₃ formed metallic Ni under reaction conditions, while the higher valent Ni species were formed in LaFe_{0.5}Ni_{0.5}O₃. According to DFT calculations, CO binds weakly on NiO(111) surface resulting in easy desorption of *CO which leads to higher CO selectivity. In addition to the effect of oxidation state, structural changes of metals can also affect product selectivity. For example, low loading of Ni (0.5 wt%) in Ni/CeO₂ catalyst showed high selectivity to CO over CH₄ as compared to the catalyst with higher Ni loading (1.5 wt%), although both catalysts contained Ni in the metallic state.⁶⁸ The results suggest that metal-support interactions and distributions of metal sizes also account for the different selectivities.

A recent study revealed that Cu catalyst supported on CeO₂ outperformed other Cu catalysts supported on nonredox oxides like SiO₂ irrespective of loading, particle size, and dispersion of Cu.⁴⁵ The Cu/CeO₂ catalyst showed 100% CO selectivity and approximately 4 times higher activity than the corresponding Cu/SiO₂ catalyst at low temperature (300 °C) and ambient pressure. The improved activity was attributed to the facile hydrogen spillover over the interfaces formed between well-dispersed Cu NPs and Ce³⁺ species. In situ XRD and XAS studies also revealed that the presence of Cu NPs on the CeO₂ lowered the reduction temperature of CeO₂ to create oxygen vacancies at <300 °C. A detailed analysis on the effect of CeO₂ morphology was done over Cu catalysts supported on two types of ceria structures, nanorods (CeO₂-NR) and nanospheres (CeO₂-NS).⁷⁵ Cu/CeO₂-NR catalyst showed stronger affinity to CO₂ at high temperature and thus preferentially formed active bidentate oxo-species, such as carbonate and formate. The main reason was probably the presence of CeO₂(110) termination in CeO₂-NR structure, which binds bidentate formate stronger than on CeO₂(111) (mostly present in CeO₂-NS structure).

Being the cheapest metal among all transition elements, iron can be a potential replacement of existing RWGS catalysts due to its high oxygen mobility and thermal stability.⁷⁶ Although there are only a few examples of iron-based RWGS catalysts reported to date, the potential of some recently reported catalysts was remarkable in terms of both activity and stability.^{66, 76-79} An early report by Weatherbee et al. showed that CO can be produced over Fe/SiO₂ catalyst in CO₂ hydrogenation, but the formation rate was much lower when compared to other transition metals of the same group.⁸⁰ Fishman et al. obtained 28% CO₂ conversion over hematite nanosheets at 510 °C, and 50% CO₂ conversion over hematite nanowires at a very high temperature of 750 °C.⁷⁷ To achieve a decent conversion at low temperature, different promoters were recently used by some groups. Loiland et al. observed that the addition of potassium to the Fe/Al₂O₃ catalyst (Fe/K mass ratio = 1.24) led to a threefold increase in CO₂ hydrogenation rate.⁷⁸ DRIFTS studies confirmed an associative mechanism on Fe–K/Al₂O₃, which was not observed in the case of Fe/Al₂O₃. Transition metal promoters such as Cu, Ni and Mo were also reported to enhance the activity

of iron-based catalysts, where Cu was proven to be the best candidate to provide high CO selectivity and long term stability.⁷⁶

3.1.3. Single atom catalysts (SACs)

As we have seen that the reactivity and selectivity in CO₂ hydrogenation depend on the metal particle sizes of the catalysts, single atom catalysts (SACs) could be an excellent choice in order to achieve high productivity and study the mechanism at the atomic level. Based on fundamental understanding, single atom-based catalysts are promising in RWGS reaction as they are only able to perform the 2e⁻ redox cycle. On the other hand, to produce over-hydrogenated products (e.g., CH₄), one requires clusters or particles that can perform full hydrogenation of CO₂ (the 8e⁻ redox cycle).⁸¹ In recent years, some SACs have been studied for the conversion of CO₂ into CO and it was observed that the selectivities over SACs were very different from metal nanoparticle-based catalysts.⁸²⁻⁸⁹ For example, Kwak et al. studied a series of Ru/Al₂O₃ catalysts with different Ru loading in the reduction of CO₂ with H₂.⁸³ CO was selectively formed over the catalysts with low Ru loadings ($\leq 0.5\%$) where the active metal phase was mostly atomically dispersed. With increasing Ru loading, population of clusters and nanoparticles increased and therefore the selectivity toward CH₄ formation increased. From the slopes of Arrhenius plots, apparent activation energies for the two competitive processes (i.e., CO and CH₄ formation) were calculated as 82 and 62 kJ/mol irrespective of Ru loading. The higher activation energy for CO formation suggests that CO is not an intermediate in the formation of CH₄, and the formation of CO and CH₄ follow different reaction pathways or proceed on different active sites. This was also supported by the results of activity measurements over a 0.1% Ru/Al₂O₃ catalyst, which showed ~ 125 °C onset temperature difference between the CO₂ (~ 325 °C) and CO (~ 450 °C) reduction. One drawback of this system was that the catalysts with low metal loading were unstable under reaction conditions and formed large metal clusters, thereby reducing the CO selectivity. Christopher and coworkers reported single atom and nanoparticle-based Rh catalysts on TiO₂ support for CO₂ reduction and observed a strong correlation between the RWGS TOF and the fraction of isolated Rh sites.⁸⁴ It was also observed that Rh NPs were disintegrating under the reaction conditions to form isolated Rh species, which changed the reactivity with time on stream. Another example with Ru/CeO₂ showed that Ru NPs on CeO₂ support can be transformed into single atomic RuO_x species after oxidative pretreatment in O₂ at low temperatures (210 °C) to become a suitable RWGS catalyst, preferentially forming CO with selectivity above 90%.⁸⁸ In contrast, after reductive pretreatment of the catalyst in H₂, the Ru NPs remain metallic, thereby increasing the selectivity for CH₄.

To understand the difference in the catalytic behavior of single-atoms and nanoparticles in CO₂ reduction, a clear understanding on an atomic-level is required. A recent study based on Pt/CeO₂ bifunctional catalyst system showed that the isolated Pt atom binds CO weakly, and therefore restricts further hydrogenation and prevents CO poisoning.⁸⁶ Although in situ spectroscopic studies demonstrated that CO₂ activation primarily occurs on the oxide support, product selectivity (CO or CH₄) depends on the single-atom or nanoclustered nature of active metal (here Pt for example). Based on different characterization techniques (in situ DRIFT, XPS, and EPR) and activity results, a reaction mechanism was proposed showing different pathways of CO₂ reduction over Pt single-atoms and nanoclusters (Figure 10). Activation and adsorption of CO₂ (steps 1–3) occur in the same way for both systems as the surface oxygen defects of CeO₂ are found to play the key role. On the other hand, Pt helps to dissociate molecular H₂ to form adatoms (H_{ad}). Compared to a Pt (111) surface, isolated Pt sites possess lower activation

energy for H_2 dissociation and much weaker binding of H atoms, thereby facilitating better H diffusion.⁹⁰ In case of a nanocluster catalyst, interaction of bicarbonate intermediate with H_{ad} on the Pt nanoclusters is believed to happen in two ways: (i) generating formate ($HCOO$) species by reacting with H_{ad} and/or (ii) carbon directly bonding with the Pt cluster to form a $C\equiv O$ triple bond. These two steps may occur either simultaneously or at different temperatures. H_{ad} then subsequently attacks strongly bound $C-O$, $C=O$, and $C\equiv O$ species (in formate and/or CO) to generate CH_4 as the final product. A different mechanism is followed over isolated Pt sites. The $-OH$ group of bicarbonate is replaced by H_{ad} to generate an aldehyde group that further undergoes cleavage of $C-H$ bond to form $C\equiv O$ attached on a Pt single atom. Weak interaction of CO with Pt single-atom causes easy desorption of CO into the gas phase as a product.

Figure 10. Proposed mechanism of CO_2 reduction over Pt/CeO₂ catalysts containing Pt single-atoms and Pt nanoclusters. Reproduced with permission from ref. 86. Copyright 2018 American Chemical Society.

Although there are only a few examples of SACs reported in CO_2 hydrogenation till date, there is a clear indication that SACs have promising future application due to their completely different reactivity. However, one of the main issues of using SACs for RWGS reaction is their poor thermal stability. Since RWGS usually requires high temperature, most of the SACs might agglomerate under such reaction conditions.⁸³ To overcome this issue, Zhang and coworkers recently designed a thermally stable Ir₁/TiO₂ catalyst based on the lattice-match principle. Due to the same crystal structure (with similar lattice parameters) of the active IrO₂ and pure rutile phase TiO₂ (r-TiO₂), Ir species were lattice-matched and epitaxially bonded to the surface of r-TiO₂ to achieve extreme stability at high reaction temperature.⁹¹ A solid solution approach was reported to synthesize single atom Ni catalyst on MgO, which was stable over 100 h on stream without forming any cluster or particle.⁸¹

3.1.4. Reaction mechanism

As mention above, two different pathways were reported for the conversion of CO₂ to CO (Figure 11). According to path A, activation of CO is followed by the direct cleavage of C–O bond in reactive *CO₂ to give *CO and *O, and then *CO is desorbed from the catalyst surface to form gaseous CO as product. This is also termed as redox mechanism, which is mainly observed on Cu-based catalysts due to easy conversion between two oxidation states of Cu (Cu⁰ and Cu⁺¹).⁹² Detailed investigation was done by density functional theory (DFT) calculations, where it was shown that C atom of *CO₂ is attached to the metal center and one of the O atoms is attached to the cationic metal center of the oxide supports.^{93, 94} On the other side, molecular H₂ is dissociated on the metal center and the active H atom is transferred through the spillover mechanism. Path B is the formate mechanism, where CO₂ is hydrogenated to formate and then cleavage of the C=O bond occurs. Essentially, the catalysts should consist of two functional groups that can perform both hydrogenation and C=O bond cleavage.⁴⁰ Several metal/metal-oxide catalysts have been reported for this process.^{41, 42}

Figure 11. Possible pathways for CO₂ hydrogenation to form CO. *(X) indicates reactive species adsorbed on catalyst surface.

The activity of a RWGS catalyst is determined by various factors, including hydrogenation capability of active metals, reducibility and oxygen vacancy of metal oxide supports, metal-support interaction, degree of metal dispersion, etc. However, the CO selectivity is mainly dependent on the binding capability of the metal/support interface for CO. Weak binding of CO on metal/support interface is selective toward CO formation simply due to facile desorption of active *CO. On the other hand, stronger binding of CO on metal/support interface assists further hydrogenation of CO to give CH₄. To elaborate this point, some in situ studies on mechanistic investigations are discussed here. According to the in situ FTIR studies over Pd/Al₂O₃ system by Arunajatesan et al., some carbonates and trace amount of formates were mainly observed when a bare Al₂O₃ support was exposed to a supercritical mixture of CO₂ and H₂ (P = 138 bar; T = 342 K; CO₂/H₂ = 19).⁹⁵ On the other hand, carbonates, formates, and CO were observed on Pd/Al₂O₃, which confirmed that a formate mechanism is followed over Pd. One of the most important findings of this work was the appearance of a peak at 1900–1920 cm⁻¹ after 20 min of reaction, which corresponds to bridged CO on Pd. After 5 h, the peak became significant and thus caused the catalyst deactivation by CO, however there was no evidence of forming methane in this case. This study clearly suggests that a short-residence time continuous reactor would be preferred over batch

reactors to maximize the catalyst lifetime. Furthermore, the CO peak was not observed on other Al_2O_3 -supported metal catalysts, such as $\text{Ru}/\text{Al}_2\text{O}_3$ or $\text{Ni}/\text{Al}_2\text{O}_3$, suggesting that the choice of metal is important in RWGS reaction. In addition to the metal type (i.e., strength of metal–CO bond), the degree of metal dispersion is a crucial factor in determining the conversion and product selectivity. For instance, 5% Pd loading over $\gamma\text{-Al}_2\text{O}_3$ (~11% metal dispersion) gave higher CO_2 conversion as compared to the catalyst with 0.5% Pd loading (~100% metal dispersion).⁹⁶ However, the CH_4 selectivity on 5% $\text{Pd}/\text{Al}_2\text{O}_3$ also increased by a factor of 2–3 than that on 0.5% $\text{Pd}/\text{Al}_2\text{O}_3$. Based on the observation of different rate expressions and apparent energies of activation for CO and CH_4 formation, authors pointed out that RWGS and CO_2 methanation pathways are probably catalyzed at different surface sites of the catalysts. Combined in situ DRIFTS and mass spectroscopic results demonstrated that for both catalysts CO_2 first reacted with surface –OH groups on the oxide support to form bicarbonates, which further reacted with dissociatively adsorbed H on Pd particles to produce adsorbed formate species, confirming the formate mechanism again (Figure 12a). The remarkable difference between the two catalysts was the rate of change in the concentration of surface bicarbonate species under reaction conditions ($\text{CO}_2 + \text{H}_2$ at 513 K) as observed by in situ IR studies (Figures 12b & 12c). Since the formation rate of bicarbonate depends on the partial pressure of CO_2 , which should be identical for both catalysts, the higher consumption of bicarbonate on 5% $\text{Pd}/\text{Al}_2\text{O}_3$ than that on 0.5% $\text{Pd}/\text{Al}_2\text{O}_3$ must be caused by the higher concentration of active H species on the former catalyst, which contains larger Pd particles. The as-formed formates near metal/oxide interface reacted rapidly with adsorbed H to produce CO, which then adsorbed on the metallic Pd particles. Since 5% $\text{Pd}/\text{Al}_2\text{O}_3$ contains larger Pd particles and therefore a larger fraction of active terrace sites are available for forming multiple Pd–CO bonds, it eventually produced CH_4 after subsequent hydrogenation.

Figure 12. (a) Mechanism of CO_2 hydrogenation on $\text{Pd}/\text{Al}_2\text{O}_3$ with different Pd loading. Normalized integrated IR intensity of different adsorbed species as functions of time when the feed gas was switched from H_2 to $\text{CO}_2 + \text{H}_2$ on (b) 5% $\text{Pd}/\text{Al}_2\text{O}_3$ and (c) 0.5% $\text{Pd}/\text{Al}_2\text{O}_3$ at 513 K. Reproduced with permission from ref. 96. Copyright 2018 American Chemical Society.

Although the reports discussed above proposed the plausible pathways for both RWGS and CO₂ methanation, the factors governing CO/CH₄ selectivity under steady-state CO₂ reduction conditions were not completely clear. To shed light on this, an interesting and powerful technique called “steady-state isotopic transient kinetic analysis” (SSITKA) was applied by Wang et al.⁹⁷ This technique allowed measurements at steady state in order to determine the abundances and mean surface lifetimes of intermediates leading to products. In addition, *operando* transmission FTIR was coupled with SSITKA to identify the chemical nature of the surface species. In the controlled experiment with Pd/Al₂O₃ system, the decaying signals of ¹²CH₄ and ¹²CO and the rising signals of ¹³CH₄ and ¹³CO crossed at $y = 0.5$ when the feed gas was switched from ¹²CO₂/H₂/Ar to ¹³CO₂/H₂ at 533 K (Figures 13a & 13b). The results indicated that the rates for CH₄ and CO formation were constant regardless of isotopic substitution and the steady state of the catalyst surface was not perturbed during the switch. Another important observation was that the concentrations of products (¹²CH₄ and ¹²CO) decreased more slowly than that of ¹²CO₂, indicating the large mean residence times for C-containing surface intermediates leading to the products, and the intermediates which equilibrate with CO₂ were not involved in the rate-determining steps for CO₂ methanation and RWGS. Based on detailed *operando* FTIR studies and SSITKA theory, the authors provided a scheme showing the key factors governing the product selectivities in CO₂ reduction (Figure 13c), according to which the reduction of formate produces *CO that first occupies strong adsorption sites on the Pd particles (to form *CO_s pool). Once the strong adsorption sites of Pd particles are saturated, the excess *CO can only occupy the weak adsorption sites of Pd particles (to form *CO_w). The *CO_s gets further hydrogenated to CH₄ while the *CO_w is desorbed. The rate of CO formation (r_{CO}) is calculated as the rate of HCOO* conversion (r_{HCOO^*}) subtracted by the rate of CH₄ formation (r_{CH_4}), i.e., $r_{\text{CO}} = r_{\text{HCOO}^*} - r_{\text{CH}_4}$. Since *CO_s and HCOO* do not share and compete for active sites, as they are located on Pd metal and Al₂O₃ support, respectively,⁹⁶ rate of CO formation can be tuned by changing [*CO_s] and [HCOO*]. For example, higher CH₄ selectivity can be achieved either by increasing [*CO_s] or by decreasing [HCOO*]. From the perspective of catalyst design, higher metal loading should result in increased number of metal sites for forming *CO_s and decreased number of support sites to accommodate HCOO*. This hypothesis was tested on Pd/Al₂O₃ catalysts with different Pd loadings but similar Pd particle size distributions, and it was observed that CH₄ selectivity increased with increasing Pd loading (Figure 13d). Similar trends were observed on Ru/Al₂O₃ and Ni/SiO₂ systems in previous studies.^{83, 98, 99} Hence, all these systematic studies indicate that lower metal loading and high surface area of support are essential when targeting high CO selectivity.

Figure 13. (a & b) Normalized mass spectrometry signals of gases in the effluent during the switch of feed gas from $^{12}\text{CO}_2/\text{H}_2/\text{Ar}$ to $^{13}\text{CO}_2/\text{H}_2$ over $\text{Pd}/\text{Al}_2\text{O}_3$ catalysts at 533 K. (c) Scheme showing the pathways from formate to products in CO_2 methanation and RWGS. (d) CH_4 and CO selectivities and CO_2 conversion as a function of Pd loading at 573 K. Reproduced with permission from ref. 97. Copyright 2017 Springer Nature.

3.1.5. Summary and challenges

In summary, in situ spectroscopic and kinetic studies have proven that RWGS and CO_2 methanation are not two parallel reactions even if they share the initial steps and intermediates starting from bicarbonate to formate until after the decomposition of the latter. The rate of CO formation depends on decomposition of adsorbed formate, whereas the rate of CH_4 formation is proportional to the hydrogenation rate of adsorbed carbonyl. The balance of the hydrogenation kinetics between adsorbed formates and carbonyls governs the selectivities between CO and CH_4 . All the examples discussed in this section provide guidance on design and synthesis of selective RWGS catalysts, which should have the following features: (i) weaker CO adsorption than H adsorption on active metal, (ii) presence of oxygen vacancies and reducible character of the support, (iii) strong metal-support interaction, and (iv) addition of promoters. Table 3 summarizes the catalytic performance of selected promising catalysts in CO_2 hydrogenation to CO .

Table 3. Catalytic performance of different catalysts in CO₂ hydrogenation to CO

Catalyst	Reaction conditions				Catalytic performance		Ref.
	<i>T</i> (°C)	<i>P</i> (bar)	H ₂ /CO ₂	GHSV (mL g _{cat} ⁻¹ h ⁻¹)	<i>X</i> _{CO₂} (%)	<i>S</i> _{CO} (%)	
0.1Ru/Al ₂ O ₃	480	1	3	72000	~44	~51	83
9Cu/CeO ₂	300	1	3	550	~18	~100	45
2Ru ₄₅ Fe ₅₅ /SDC(CeO ₂)	500	1	1	120000	~23	~100	46
2Ru ₄₅ Fe ₅₅ /SDC(CeO ₂)	500	1	4	120000	~46	~99.5	46
5Cu/CeO ₂ -nanorod	450	1	5	150000	~50	~100	75
0.3Pt/zeolite	500	1	1	30000	13.1	~97	59
24K-0.3Pt/zeolite	500	1	1	30000	27.4	100	59
1.6%Ru@mSiO ₂ -N ₂	400	1	4	15000	23.0	83.5	61
1.7%Ru@mSiO ₂ -Air	400	1	4	15000	19.9	4.8	61
5Pd/BCNT alginate	600	1	4	15000	48.0	99.0	64
7.6Fe/ZIF-8-C	420	1	4	15000	43.8	97.3	66
7.4Ni/ZIF-8-C	420	1	4	15000	43.8	97.5	66
LaFe _{0.5} Ni _{0.5} O ₃	400	1	2	24000	16.3	96.6	67
1.3Cu/β-Mo ₂ C	400	1	2	300000	24.3	97.6	70
1.3Cu/β-Mo ₂ C	600	1	2	300000	47.7	99.2	70
Octapods-Fe _{1.5} Ni ₁ Zn MOF	400	1	4	-	29.9	81.0	73
Fe _{16.2} /CeAl	500	1	4	30000	~39	~98	76
Fe _{15.4} Ni ₁₀ /CeAl	500	1	4	30000	~55	~53	76
Fe _{15.3} Cu _{9.4} /CeAl	500	1	4	30000	~46	~99.5	76
0.5%Pd/Al ₂ O ₃	400	1	3	72000	~20	~65	82
0.05Pt/CeO ₂	300	1	12.5	48000	~67	100	86
2Pt/CeO ₂	300	1	12.5	48000	~35	100	86
0.05Pt/CeO ₂	400	1	12.5	48000	100	100	86
2Pt/CeO ₂	400	1	12.5	48000	~74	~29	86
8Pt/Au@Pd@1Co NP	400	20	3	12000	18.2	96.1	100
Pt/Au@Pd@UIO-66	400	20	4	24000	35.4	78.0	101
α-MoC _{1-x}	600	1	4	36000	~60	100	102

GHSV: gas hourly space velocity, *X*_{CO₂}: CO₂ conversion, *S*_{CO}: CO selectivity.

3.2. Production of Alcohols

3.2.1. CO₂ to Methanol

From the stages of early development until now, a wide variety of catalysts have been studied for methanol production with a few of them achieving commercial application. Among the catalysts evaluated in literature, copper-based catalysts have been the most widely studied system. In fact, more than 75% catalysts studied in the last 10–15 years contain copper as an active metal phase.^{31, 103} In the 1960's, Imperial Chemical Industries developed highly active ternary phase Cu–ZnO–Al₂O₃ catalyst for the selective production of methanol from naphtha and natural gas under mild conditions.¹⁰⁴ Based on this study, major focus has been given to Cu-based catalysts, mainly Cu–Zn combinations.¹⁰⁵⁻¹⁰⁹

3.2.1.1. Cu-based catalysts

Typical preparations of Cu-ZnO-Al₂O₃ catalysts follow the co-precipitation method, which has produced catalysts with higher activity as compared to other reported methods. The main reason for this superior performance is the high dispersion and stability of Cu species due to the unique microstructure of the catalyst achieved after reduction. ZnO acts as a matrix/spacer to achieve high dispersion of Cu and the inert Al₂O₃ phase enhances the thermal and chemical stability. On comparing Cu catalysts synthesized with similar preparation protocols, it was observed that catalysts with different extents of accessible Cu surface area exhibited different activities, indicating that methanol synthesis over Cu is a structure-sensitive reaction. Several experiments were done to understand the role of Cu and Zn as well as the interaction between catalyst surface and reaction intermediates.^{94, 110-113} It was proposed that the defects and lattice strain in the Cu NPs affect the intrinsic activity of the Cu surface. Behrens et al. studied the role of defects in Cu-ZnO-Al₂O₃ catalyst system and observed that presence of steps at the Cu surface was essential to achieve high activity.¹¹¹ A highly active Cu surface could be stabilized by bulk defects like stacking faults or twin boundaries terminating at the surface. The presence of Zn^{δ+} at the defective (stepped) Cu surface induces a dynamic SMSI effect, which increases the binding capability of the oxygen-bound intermediates in order to increase the activity. Sehested and coworkers observed that the activity of methanol production is highly dependent on the surface Zn coverage of industrial-type Cu-ZnO-Al₂O₃ catalyst.¹¹² Catalysts with smaller ZnO particles are more active because of an enhanced spillover of Zn to the Cu surfaces. Although the role of Zn was investigated in some reports, identifying the active species was a matter of debate. Between the two possibilities, one possibility could be the interface of Cu and ZnO that activates CO₂. The second possibility was the formation of highly active ZnCu bimetallic alloy by partial reduction during the reaction. Studies by Kattel et al. showed that during the reaction, active ZnCu phase undergoes surface oxidation by *O species (produced from *CO₂ dissociation) to form ZnO.⁹⁴ This lead to high dispersion of Zn sites on Cu surface which increased the overall methanol production.

Since the CO₂-to-methanol transformation reaction is sensitive towards the size and structure of the active phase of the catalyst,¹¹⁴⁻¹¹⁸ it is very important to maintain the particle size of active metals and stabilize them against sintering under reaction conditions. Considering the example of novel ternary phase Cu-ZnO-Al₂O₃ catalyst, water is formed as one of the main byproducts due to its significant activity in RWGS reaction.¹¹⁹ As a result, deactivation of the active phase occurs by water-induced sintering.¹²⁰ Taking advantage of the high activity of copper, several studies were done with other materials such as ZrO₂, TiO₂, CeO₂, SiO₂ and zeolites as support in order to achieve high dispersion of Cu, and as expected, the CO₂ hydrogenation activity was improved in most cases.^{113, 121-133} For example, Cu has been reported to strongly interact with ZrO₂, leading to more dispersed NPs and enhanced catalyst stability.¹³⁴ It was also observed that the Cu-ZrO₂ interface was more active than pure Cu surface due to formation of oxygen vacancies by ZrO₂.^{93, 113, 135} Along this line, Tada and coworkers studied the formation mechanism of specific active Cu sites on ZrO₂ samples of different phases (such as amorphous, tetragonal and monoclinic). When copper nitrate solution was impregnated in amorphous ZrO₂ (a-ZrO₂), most of the Cu species entered into a-ZrO₂, leading to the formation of a Cu-Zr mixed oxide (Cu_aZr_{1-a}O_b), which upon H₂ reduction produced the active Cu NPs. Relatively higher dispersion of Cu species was observed on a-ZrO₂ than those on m-ZrO₂ and t-ZrO₂, and the Cu⁺ species next to the oxygen vacancy sites were supposed to work as acid sites active for methanol production. A recent study has also shown that ZrO₂ can form a solid solution with another oxide (e.g., ZnO) to make a binary oxide catalyst, which showed a

methanol selectivity of up to 86 to 91% with CO₂ single-pass conversion of more than 10%.¹³⁶ More interestingly, the catalyst was resistant to sintering at higher temperatures for at least 500 h on stream, showing the advantage of using ZrO₂ in making a high performance solid solution catalyst. Taking the advantage of ZnO–ZrO₂ interaction, Wang et al. recently prepared ternary phase three-dimensional ordered macroporous Cu/ZnO/ZrO₂ catalyst that was able to achieve 80% methanol selectivity at a CO₂ conversion of ~19%.¹³⁷ The ZrO₂–ZnO interface was supposed to act as active sites for CO₂ adsorption to carbonate species and its subsequent conversion to formate, which was further hydrogenated to methanol over the active Cu sites.

Although most of the studies based on a Cu–Zr system explained the reason behind improved activity as the better adsorption properties of the Cu–Zr interface, the actual role of the ZrO₂ support was not clear at a molecular level. In many studies, it was proposed that the oxygen vacancies created on ZrO₂ and the electronic charge transfer between Cu and the support could be the most probable reasons for the enhanced performance.^{93, 134, 138} However, the nature of the Zr site participating in CO₂ hydrogenation, i.e. Zr(III) vs Zr(IV), was a matter of debate because the earlier characterization techniques were mainly applied to probe the reactivity of ZrO₂ in the bulk phase. Copéret and coworkers recently developed an interesting approach to understand the local properties of Zr atoms next to active Cu centers on the surface.¹³⁹ Using a surface organometallic chemistry approach, they functionalized a silica support with isolated Zr(IV) surface sites and doped Cu NPs (~3 nm) on it (Figure 14a). The designed catalyst exhibited increased activity and CH₃OH selectivity compared to the Cu catalyst supported on SiO₂ without Zr promotion, while the catalytic activity was comparable to the corresponding Cu/ZrO₂ containing bulk ZrO₂ phase (Figure 14b). As observed by solid-state NMR studies, similar surface intermediates (formate and methoxy) were formed on both Cu/Zr_{0.9}@SiO₂ and Cu/ZrO₂, but not on Cu/SiO₂ (Figure 14c), implying that the Cu–Zr interaction was a crucial factor and the reaction proceeded via a similar mechanism on both Cu/Zr_{0.9}@SiO₂ and Cu/ZrO₂. Based on the catalytic results, it could be concluded that the structural and bulk properties of ZrO₂, such as oxygen vacancies or alloy formation, were not the important factors behind different activities. Rather, the presence of isolated Lewis acidic Zr(IV) sites on the silica surface was sufficient to increase the activity and selectivity. Furthermore, ex situ and in situ X-ray absorption spectroscopy showed no change in oxidation state of the isolated Zr(IV) sites in Cu/Zr_{0.9}@SiO₂ system under pretreatment or reaction conditions (Figure 14d), which confirmed that Zr⁴⁺ was the actual species responsible in CO₂ activation. Following this work, the authors recently reported better intrinsic activity by introducing Ga(III) single sites in the system.¹⁴⁰ The improved performance was attributed to Cu(0)/Ga(III) interfaces that only stabilized methoxy and not formate intermediates.

Figure 14. (a) Schematic diagram of Cu/ZrO₂ and Cu/Zr_{0.9}@SiO₂ systems showing bulk and surface properties of ZrO₂. (b) Comparison of catalytic activities of three different catalysts. (c) Ex situ solid-state NMR studies of Cu/Zr_{0.9}@SiO₂ after exposure to ¹³CO₂ and ¹H₂ (in a 3:1 ratio) at 5 bar and 230 °C. (d) In situ X-ray absorption spectroscopy (showing Zr K-edge XANES spectra) of Cu/Zr_{0.9}@SiO₂ under different conditions. Reproduced with permission from ref. 139. Copyright 2018 American Chemical Society.

Other than ZrO₂, Li et al. achieved improved dispersion of Cu with high surface areas over layered double hydroxide (LDH) nanosheets, producing high space-time yield of methanol.¹⁴¹ Ultrathin LDH structures feature distinctive local steric and electrostatic stabilization to embed active Cu(Zn) species in the cationic layers. Due to the high surface area of silica materials, they can stabilize high metal loadings without agglomeration. For example, micro-spherical SiO₂ prepared by the spray-drying method was able to maintain uniform distribution of Cu and Zn up to a metal loading of 48 wt% due to its highly porous nature.¹⁴² However, the CO₂ conversion started to decrease slightly above Cu loading of 28 wt% due to pore blockage and decreased reducibility of catalysts caused by excess metal incorporation into the pores of SiO₂. In some cases, basic support (such as lanthanum oxide) showed good performance due to both superior dispersion and increased CO₂ adsorption capacity.^{143, 144} Formation of Cu^{δ+} species at the Cu/La₂O₂CO₃ interfacial area and presence of basic sites work together to play a synergetic effect that can stabilize *HCOO and *CH₃O intermediates against their decomposition into CO.

An excellent technique to stabilize and restrict particle growth of the active Cu phase was reported by Rungtaweeworanit et al., where a metal-organic framework (MOF)-based Cu catalyst (Cu@UiO-66) was prepared by encapsulating 18 nm single Cu nanocrystal (NC) within Zr-based single crystal UiO-66 MOF.¹⁴⁵ The catalyst outperformed the benchmark Cu/ZnO/Al₂O₃ catalyst to give a steady 8-fold enhanced yield and 100% methanol selectivity. Multiple oxidation states of Cu and the higher interfacial contact area between Cu NCs and Zr oxide secondary building units of the MOF were believed

to be the main reasons behind high TOF for methanol formation. A similar approach was reported by An et al., where they used metal-organic frameworks (MOFs) to anchor ultrasmall Cu/ZnO_x NPs (Figure 15a).¹⁴⁶ Zr and bipyridine were used to construct a thermally stable UiO-bpy MOF, in which bipyridine moieties worked as anchoring units. A sequential post-synthetic metalation of Cu and Zn precursors followed by an in situ hydrogenation at 250 °C was used in order to obtain the final catalyst. NPs of diameter less than 1 nm were entrapped in tetrahedral and octahedral cages confined by the ligands providing excellent stability against sintering. The resulting Cu/ZnO_x@MOF catalysts showed high stability over 100 h and a space-time yield of up to 2.59 g_{MeOH} kg_{Cu}⁻¹ h⁻¹ with 100% methanol selectivity. The excellent activity was attributed to the high degree of mixing between Cu and ZnO_x phases, leading to the formation of low-valence Zn and Zr in the presence of H₂ at 250 °C. Very recently, Kobayashi and coworkers reported a catalyst consisting of Cu NPs covered with a zirconium/hafnium-based MOF and demonstrated the correlation between activity and metal-support interaction.¹⁴⁷ To compare the support effect, CO₂ hydrogenation was studied over different catalysts such as Cu/γ-Al₂O₃, Cu/ZIF-8, Cu/MIL-100 and Cu/UiO-66 composites that contained different metals in the MOF skeleton. Among the tested catalysts, Cu/Zr-UiO-66 was found to be the most effective, producing methanol at a rate 70 times larger than that of Cu/γ-Al₂O₃ and the activity was increased by three times when Zr⁴⁺ was replaced by Hf⁴⁺ in UiO-66. Interestingly, the substituent in the MOF structure played a crucial role in the catalytic activity. For example, methanol production rate on Cu/Zr-UiO-66-COOH was significantly higher compared to Cu/Zr-UiO-66 or Cu/Zr-UiO-66-NH₂, which was mainly due to the higher degree of charge transfer from Cu to UiO-66, as evidenced from XPS analysis (Figure 15b). Very recently, Liu et al. developed a series of Cu@ZrO_x catalysts with a three-dimensional porous framework structure via partial pyrolysis of size-confined Cu@UiO-66 precursor.¹⁴⁸ The final catalysts could achieve a highest methanol space-time yield of 0.796 g_{cat}⁻¹ h⁻¹ at 260 °C.

Figure 15. (a) Synthesis of CuZn@UiO-bpy catalyst via postsynthetic metalation followed by in situ reduction. (b) Relationship between methanol production rate and binding energy shift for Cu/γ-Al₂O₃ and Cu/MOF catalysts. Reproduced with permission from ref. 146 and 147. Copyright 2017 American Chemical Society and 2019 Royal Society of Chemistry.

3.2.1.2. Non-Cu-based catalysts

Recently, some intermetallic catalytic systems other than the classical Cu-Zn combination were found to be comparably active or better in terms of both CO₂ hydrogenation kinetics and methanol selectivity.¹⁴⁹⁻¹⁶⁰ Studt et al. reported silica supported Ni-Ga catalyst as better than the existing

Cu/ZnO/Al₂O₃ catalyst in terms of reduced RWGS activity.¹⁴⁹ The catalyst was able to reduce CO₂ to methanol at ambient pressure and it was observed that a specific stoichiometric ratio (Ni₅Ga₃) was required in the catalyst formulation to achieve high selectivity. Similarly, after the discovery of excellent methanol selectivity and remarkable stability of indium oxide (In₂O₃),¹⁶¹ different bimetallic indium catalysts were also studied.^{147, 150, 151, 153, 162-169} A second metal is usually required because the H₂-splitting ability of In is limited. Among recent examples, Pd-In bimetallic system showed that intermetallic Pd-In nanoparticles were able to produce methanol at around 70% higher rates as compared to Cu/ZnO/Al₂O₃ catalyst at 210 °C.¹⁵¹ The catalyst was far more active than individual Pd(0) or In₂O₃ catalyst in liquid phase CO₂ hydrogenation, but a stoichiometric ratio (Pd:In = 1:1) was important to form Pd-In intermetallic phase, which means a significant amount of Pd was required. Furthermore, the Pd-In catalyst was highly active for the parasitic RWGS reaction when applied in the gas phase as nanoparticles supported on silica. To overcome this problem, Pérez-Ramírez and his group recently adopted co-precipitation (CP) method to incorporate isolated Pd atoms in the In₂O₃ lattice.¹⁶⁴ Indium atoms in the active In₃O₅ ensemble were replaced by Pd atoms that attracted additional Pd atoms and deposited onto the surface forming low-nuclearity Pd clusters. The catalyst produced a record space-time yield of 0.96 g_{MeOH} h⁻¹ g_{cat}⁻¹ even after 500 h on stream. A microkinetic model was derived to explain the Pd promotion in this system (Figure 16). The apparent activation energy for methanol production was lowered by 56 or 4 kJ mol⁻¹ when 1 or 2 exposed Pd atoms were present, respectively, and the RWGS reaction was hindered by a barrier higher by at least +80 kJ mol⁻¹ compared with In₂O₃. When 3 or more exposed Pd atoms were present (in case of catalyst prepared via dry impregnation (DI) method), the barrier of the RWGS reaction was decreased by -7 kJ mol⁻¹ and the active sites started behaving like metallic Pd that hindered the methanol production.

Figure 16. Promotion effect of Pd in In₂O₃ catalysts. (a) Arrhenius plots and calculated apparent activation energies (E_a) for CO₂ hydrogenation over In₂O₃, Pd-In₂O₃-CP, Pd-In₂O₃-DI, and Pd-TiO₂ catalysts. (b) Schematic representation of the distinct role of Pd in equilibrated CP and DI systems with In₂O₃ and Pd-TiO₂ as references. The thickness of the arrows qualitatively indicates the products formation rates. Reproduced with permission from ref. 164. Copyright 2019 Springer Nature.

Another promising In based system was recently reported by Bavykina et al.¹⁶⁵ In particular, the authors developed a highly stable bimetallic In@Co system that achieved CO₂ conversion levels close to thermodynamic equilibrium at 300 °C. While the individual In and Co components act as CO and methane producers, respectively, their combination (In@Co) acts as an active methanol catalyst. DFT calculations showed that the charge transfer between the Co support and the In₂O₃ enhanced the surface of In₂O₃ with O vacancies, which served as the active sites for this reaction. A similar phenomenon was observed in case of In₂O₃–ZrO₂ mixed oxide system, but only monoclinic ZrO₂ showed pronounced effects on In₂O₃ due to the lattice mismatching.¹⁷⁰ The performance of the catalysts was highly dependent on their synthesis method. In₂O₃–ZrO₂ materials synthesized via coprecipitation formed a solid solution to create maximal interaction between the two metal oxides, which resulted in inferior activity. By contrast, deposition synthesis method formed subnanometric islands of In₂O₃ on the carrier to pronounce more tensile forces, which triggered the formation of an excess of oxygen vacancies and enhanced the indium-specific activity. Taking the advantage of In₂O₃–ZrO₂ synergy, Jiang et al. did a combined experimental and DFT study to elucidate the role of water on the activity and selectivity of In₂O₃/ZrO₂ catalyst.¹⁷¹ It was found that the CH₃OH formation rate could be enhanced by ~20% by adding an appropriate amount of H₂O (0.1 mol%) in the feed gas. XPS and TPD analyses revealed the formation of H₂O-induced oxygen vacancies and InOOH species on the In₂O₃(110)/ZrO₂ surface, which appeared to improve CO₂ adsorption and hydrogenation ability. According to DFT calculations, addition of H₂O facilitated surface InOOH formation, suppressed CO formation from COOH* intermediate, and promoted CH₃OH formation through HCOO* intermediate. The activation energy for HCOO* formation was reduced by ~29% due to the presence of H₂O at an adjacent In site (Figure 17), and altered the transition state formation route and stability as compared to the case without H₂O. As a result, the COOH* pathway to produce CO was suppressed and the methanol production was enhanced via the HCOO* intermediate.

Figure 17. Promotional effect of water: the reaction energy and activation barrier for CO₂ hydrogenation to HCOO* intermediate in the absence and presence of H₂O on the In₂O₃(110)/ZrO₂ surface. Reproduced with permission from ref. 171. Copyright 2020 Elsevier.

Similar bimetallic effects were observed in case of PdZn alloy supported on CeO₂.¹⁵² About ~100% methanol selectivity was achieved when Ca was doped on this system as a promoter. The improved activity and selectivity of the catalyst were mainly because of the excellent H₂ dissociation

ability of the PdZn alloy to actively hydrogenate the adsorbed carbonaceous species. Furthermore, according to XPS analysis, Ce^{3+} ions facilitated the generation of oxygen-vacant sites over the surface of the catalyst, which assisted CO_2 dissociation effectively in order to achieve higher methanol formation rates. Very recently, Jiang et al. reported Pd-Cu bimetallic catalysts, where CO_2 was found to be adsorbed as carbonate and bicarbonate species on the surface.¹⁷² The bimetallic catalysts were observed to provide a significant enhancement of CO_2 adsorption as compared to their monometallic counterpart. The synergetic effect was maximum at a particular Pd/(Pd + Cu) atomic ratio of 0.33, where the formation of HCOO^* experienced the lowest energy barrier. The alloy effect of Pd-Cu bimetallic system was studied in detail by DFT calculations and proved with experimental results.¹⁷³ According to the DFT calculations, the stepped PdCu(111) surface (with low-coordinated Pd atoms exposed on top of the surface) showed better adsorption and activation of CO_2 and H_2 , resulting in superior activity for CO_2 hydrogenation as compared to the flat Cu-rich PdCu₃(111) surface. Complementary to the DFT results, experiments over SiO_2 -supported bimetallic catalysts showed that the Pd-Cu(0.50), rich in the PdCu alloy phase, was more selective to methanol than the PdCu₃-rich Pd-Cu(0.25).

Apart from these examples discussed above based on metal-metal interaction, electronic modification can also be achieved through the metal-support interaction. For instance, an electronic polarization at the metal-support interface was observed in case of Au nanoparticles anchored and stabilized on a $\text{CeO}_x/\text{TiO}_2$ substrate.¹⁷⁴ Small coverages of CeO_x (~ 0.1 ML) were found to stabilize the formation of small Au nanoparticles, which significantly promoted their activity in RWGS to produce CO. On the other hand, electronic metal-support interaction led to charge redistribution in the metal near the Au- CeO_x interface that effectively adsorbed and activated CO_2 and stabilized carboxylate species. The combined effect led to the selective formation of methanol through RWGS via $^*\text{HCO}$, $^*\text{H}_2\text{CO}$, and $^*\text{H}_3\text{CO}$ intermediates. Following these examples, Zeng and coworkers showed that the presence of nitrogen can significantly change the hydrogenation activity of Co.¹⁷⁵ Incorporation of N atoms into Co nanosheets resulted in a huge drop in activation energy compared to pure Co nanosheets and therefore exhibited excellent TOF for methanol. According to mechanistic studies by in situ DRIFTS, Co_4N nanosheets were reconstructed into Co_4NH_x by adsorbing H atoms on N atoms (stretching vibration of N-H at 3140 cm^{-1} in Figure 18). These amido-hydrogen atoms in Co_4NH_x species directly interacted with the CO_2 to form HCOO^* intermediates. In addition, the adsorbed H_2O^* species were found to activate amido-hydrogen atoms via H-bonding, which also facilitated the hydrogenation process. This example shows an effective way to boost the catalytic activity of non-noble metal catalysts toward hydrogenation reactions just by incorporating N atoms.

Figure 18. Mechanistic studies by in situ DRIFT analysis showing Co₄N nanosheets after the exposure to (a) CO₂ and (b) CO₂/H₂ mixed gas (CO₂/H₂ = 1:3, 1 bar) at different temperatures with a purge time of 30 min. Reproduced with permission from ref. 175. Copyright 2017 Springer Nature.

Another interesting approach was recently employed by Li et al., where the synergetic interaction between neighboring active centers played a significant role in CO₂ hydrogenation.¹⁷⁶ A detailed activity comparison was made between two distinct catalytic systems, in which one consisted of isolated Pt atoms (0.2%Pt/MoS₂) and the other consisted of neighboring Pt atoms with dense population (7.5%Pt/MoS₂). In case of 7.5%Pt/MoS₂ catalyst, activated S atoms (those which were directly bonded to Pt atoms) were close to each other, which triggered the H₂ dissociation more efficiently. Therefore, the catalyst containing neighboring Pt monomers was found to produce much higher activity than isolated Pt atoms. Combined characterization by TPD, in situ DRIFTS, in situ XPS, and DFT calculations showed that the two systems followed different reaction mechanisms. In case of isolated Pt monomers, CO₂ was transformed into methanol without the formation of formic acid, whereas neighboring Pt monomers followed sequential formation of formic acid and then methanol. On 0.2%Pt/MoS₂ system, COOH* was considered as the stable intermediate upon the addition of the first H atom to CO₂ with an energy barrier of 0.40 eV (Figure 19a). The stable COOH* intermediate was then transformed into C(OH)₂*, which was further hydrogenated to form CH(OH)₂*, CHOH* and CH₂OH* sequentially. In contrast, HCOOH was more favorable than C(OH)₂* on 7.5%Pt/MoS₂ system because of lower energy barrier (1.01 eV vs. 1.34 eV), and the formed HCOOH was directly observed in the catalytic test (Figure 19b). In the subsequent steps, HCOOH was further hydrogenated into CH(OH)₂*, CHOH* and CH₂OH*. Most interestingly, the energy barrier for the transformation of CH₂OH* into CH₃OH over 7.5%Pt/MoS₂ system (0.44 eV) was much lower than that over 0.2%Pt/MoS₂ system (1.19 eV), which probably made the 7.5%Pt/MoS₂ system more active (Figures 19c & 19d).

Figure 19. Optimized reaction paths in CO₂ hydrogenation for (a) 0.2%Pt/MoS₂ and (b) 7.5%Pt/MoS₂ system, respectively. Catalytic performance of different Pt/MoS₂ catalysts: (c) Comparison of products obtained over different Pt/MoS₂ catalysts ranging from atomically dispersed Pt to Pt NPs at different Pt loadings. (d) Comparison of TOFs for methanol production with 0.2%Pt/MoS₂ and 7.5%Pt/MoS₂ catalysts at different temperatures. Reproduced with permission from ref. 176. Copyright 2018 Springer Nature.

3.2.1.3. Reaction mechanism

From the viewpoint of the reaction mechanism, the transformation of CO₂ to methanol is still a matter of debate. According to literature reports, the two accepted pathways are (i) CO intermediate pathway (through the RWGS reaction and subsequent hydrogenation) and (ii) formate (*HCOO) pathway with the reaction pathway being dependent on the catalytic system. In most cases, it is observed that the catalysts active for CO₂ to methanol transformation are also active for CO to methanol transformation. Therefore, it is obvious that the catalysts suitable for CO to methanol transformation would most likely follow the CO intermediate pathways. Although the formation of *HCOO species is easier and there is a higher possibility to follow the formate pathway, in reality, the exact pathway depends on the stability of the intermediates. For example, considering the examples of Cu/TiO₂ and Cu/ZrO₂ systems, significant

amount of $^*\text{HCOO}$ species can be formed on both surfaces (as evidenced by DRIFTS measurements).⁹³ However, methanol production via the formate pathway becomes inefficient over time due to the poisoning effect of $^*\text{HCOO}$ species, and as a result, the RWGS/ CO -hydrogenation pathway becomes the dominating route. In general, it is usually observed that oxide supports with reducible properties (such as TiO_2 , Cu/ZrO_2 , CeO_2 etc.) follow CO intermediate pathway as they are efficient for RWGS process. On the other hand, in case of catalysts with nonreducible supports (such as industrial Cu/ZnO catalysts), formate pathway dominates over RWGS. This is mainly due to the stabilization of HCOOH via Zn-O interaction, which leads to activation of the HCOO^* through hydrogenation.⁹⁴

During the past decades, several studies were carried out in order to obtain the performance descriptors required to lower the activation energy of this process. It was observed that the CO_2 hydrogenation activity can effectively be improved by modifying different surface electronic properties such as negative charge density, d-band center and electronic polarization. Studies have shown that this type of modification can be easily achieved by tuning the arrangement and composition of surface atoms. For example, bimetallic catalysts with different shapes based on Pt and Co were designed by combining sharp-tip and alloy effects.¹⁷⁷ A unique feature was observed in the Pt_3Co octapod structure showing the accumulation of negative charges on Pt in the vertices of the nanocrystals due to the charge transfer between Pt and Co. Highly negative Pt atoms promoted the activation of CO_2 and accordingly enhanced the catalytic activity. Similar studies were done with RhW system, where the accumulation of negative charge was observed on Rh for RhW nanosheets.¹⁷⁸ As a result, the negatively charged Rh atoms strongly adsorbed CO_2 to transform it into $\text{CO}_2^{\delta-}$ and further into HCOO^* . Based on mechanistic studies, the authors claimed that the enhanced adsorption and activation of CO_2 on $\text{Rh}_{75}\text{W}_{25}$ nanosheets was due to the higher d-band center induced by one-dimensional quantum confinement and negatively charged Rh surface because of alloy effects.

The reader is invited to refer to two recently published excellent reviews by Jiang et al. and Zhong et al.^{26, 27} for a detailed overview with updated information regarding the reaction mechanism of the CO_2 -to-methanol process.

3.2.1.4. Summary and challenges

In summary, multiple catalytic systems have been developed for MeOH production from CO_2 with some of the above discussed examples having commercial prospects. A complete overview of these systems can be found in Table 4. For practical applications, the catalyst preparation method should be simple, cheap, scalable, and reproducible. Until now, Cu-based catalysts are used for large-scale methanol production due to their low price, well established reproducible synthesis methods and good methanol formation rate. However, the methanol selectivity is compromised significantly at higher CO_2 conversions and therefore there is still some room for enhancing the overall productivity (or space-time yield). Besides the conversion-selectivity issue, water-tolerance ability of Cu-based catalysts is another concern as they suffer from low stability due to Cu oxidation. Several studies have been reported, not only on developing various new Cu-based catalysts, but also on optimizing reaction parameters and reactor configuration. For instance, use of membrane reactors has attracted great attention to improve methanol yield by removing water after reaction.^{26, 179} Along this line, more research is required to improve the permeation ability of membrane materials, which can scale up the process from laboratory-scale to large-scale production.

Recently, the use of intermetallic systems, such as In- and Ga-based materials, has shown emerging prospects to deal with both activity and stability issues. As observed from Table 4, In-based catalysts can provide decent space-time yields with very high methanol selectivity (> 80%) and a comparable formation rate (as compared to Cu-based catalysts). Although higher selectivity is achieved due to suppressed RWGS reaction, the conversion is still compromised at lower temperature and therefore a high temperature is usually required. This creates thermodynamic limitation since CO₂-to-methanol favors low temperature due to its exothermic nature. According to descriptor-based computational calculations a new class of Ni–Ga low-pressure catalysts was developed, which experimentally showed unique activity for CO₂-to-methanol transformation with suppressed CO production.¹⁴⁹ Above 220 °C, the Ni₅Ga₃ catalyst showed 10 times lower CO-to-methanol ratio and higher methanol yield (per active metal center basis) than the well-established Cu/ZnO/Al₂O₃ catalyst, which is indeed a good start towards a new alternative catalyst. Furthermore, we have seen that water has a promotional effect on methanol synthesis and In-based catalysts are generally water-resistant in nature compared to the Cu-based catalysts. In spite of these advantages, there are still some drawbacks of In-based catalysts that need to be considered for future task. For example, high oxygen vacancy of In₂O₃, which is responsible for CO₂ adsorption and activation, also causes high H₂ consumption and the consumed vacancy cannot be recovered by air-calcination. Besides this, another major issue is the growth of crystallite size of In₂O₃ that reduces the active surface area for the reaction and causes deactivation.¹⁶¹

As we have seen that low temperature is always favored in methanol synthesis due to thermodynamic constraints, a new catalyst or a new catalytic route is required to tackle this issue. Recently, Ting et al. reported well-dispersed subnanometer sized Re catalyst on TiO₂ support that exhibited activity (total TON of 44 based on Re and 82% methanol selectivity) at 150 °C.¹⁸⁰ Another ReO_x/TiO₂ catalyst was reported by Vidinha and co-workers for selective CO₂-to-methanol conversion in a supercritical flow process at 200 °C, where 98% methanol selectivity could be achieved at ~20% CO₂ conversion.¹⁸¹ Tsubaki and co-workers developed a new concept of low-temperature methanol synthesis (LTMS) in liquid medium from syngas containing CO₂ using Cu/ZnO/Al₂O₃ catalysts prepared by oxalate-gel coprecipitation (Figure 20).^{182, 183} LTMS can be achieved from pure syngas over strong base catalysts, but the situation is very different when CO₂ is used, because a trace amount of CO₂ or water can quickly deactivate the basic catalyst. Therefore, an alcohol (including methanol itself) is used as both solvent and homogeneous cocatalyst to change the reaction pathway to low-temperature direction. Using a semi-batch reactor at 170 °C and 50 bar pressure, 25.9% CO₂ conversion was achieved with 72.9% methanol selectivity when 2-octanol was used as solvent. In a recent study, they managed to get a space-time yield of 0.456 g_{MeOH} g_{cat}⁻¹ h⁻¹ using binary Cu/ZnO catalyst at 200 °C in a continuous fixed-bed reactor.¹⁸⁴ This is indeed a new promising approach that can be adopted for future methanol production process. The externally added alcohols can be recycled during the reaction, which is a big advantage of this process. Since the process is not well established yet, reactor design and parameter optimization would be essential tasks to commercialize the process.

3.2.2. CO₂ to Higher Alcohols (HAS)

Production of ethanol and higher alcohols from CO₂ is usually considered as a combination of different steps including the RWGS reaction followed by the subsequent reaction of syngas through C–C coupling. Because of the multistep nature and requirement of keeping one C–O bond intact throughout the process, CO₂-to-ethanol transformation is far more challenging than CO₂-to-methanol transformation. Based on the reaction steps, it is obvious that a suitable catalyst should have the capabilities of performing both FT synthesis and methanol synthesis.

3.2.2.1. Catalyst development

Early efforts made on this transformation process achieved low yield and selectivity to ethanol, and in most cases methanol and higher (C₂₊) hydrocarbons were observed as major byproducts.¹⁵³ Although a few catalysts such as [Rh₁₀Se]/TiO₂, physically mixed Fe- and Cu-based composites, and K/Cu-Zn-Fe achieved significant selectivity for C₂₊OH, the reaction temperature was considerably higher (330–350 °C).^{186–188} Recently, Han and coworkers reported high selectivity for C₂–C₄ alcohols over Pt/Co₃O₄ carrying out the reaction in liquid phase as opposed to gas phase in different solvents including water and other organic solvents.¹⁸⁹ Based on D₂O and ¹³CH₃OH labeling experiments, water was found to act as a H₂ source in order to promote the reaction kinetically with other solvents, producing ethanol via CH₃OH as an intermediate. However, one of the main drawbacks of this work was the use of high boiling organic solvents, such as 1,3-dimethyl-2-imidazolidinone (DMI) to achieve high yield, which restricts its application in large scale production. Liu et al. reported mesoporous Co₃O₄ catalysts for the production of higher alcohols and studied the promotion effect of Pt to decrease the hydrocarbon selectivity.^{190, 191} Compared to the Co₃O₄ NPs, mesoporous Co₃O₄ showed higher efficiency in the growth of carbon chains and reduced the selectivity for CH₄ to give a higher yield of C₂₊OH. Introduction of Pt further helped to decrease the formation of CH₄ and increase the selectivity for CO and alcohols due to its excellent RWGS activity, but the CO₂ conversion was decreased with lower yield of alcohols. Recently, Yang et al. studied Rh-based catalysts supported on TiO₂ nanorods (RhFeLi/TiO₂ NR) and achieved 31.3% ethanol selectivity at a CO₂ conversion of 15.7%.¹⁹² Although the catalyst showed high selectivity for methane due to the high reducing ability of Rh, this is one of the best results achieved in terms of ethanol yield in a continuous flow reactor in the gas phase. Based on the catalytic results and in situ DRIFTS studies, it was proposed that the abundant hydroxyl groups on TiO₂ NRs helped to stabilize the formate species and protonate the as formed methanol, which was easily dissociated into *CH_x and favored the formation of ethanol upon CO insertion. The same mechanism was experimentally supported by Wang et al., where vanadium oxide promoted Rh-based catalysts were studied.¹⁹³

From the above discussion, it can be inferred that the selective production of ethanol is quite challenging because mixed alcohols are often formed during carbon chain growth. Therefore, a fine tuning in catalyst composition and structure is required to make CO₂-to-ethanol transformation practically viable. Along this line, Huang's group designed bimetallic ordered nanoparticle catalysts based on Pd and Cu, and studied the effect of different supports on product distribution.¹⁹⁴ Pd was chosen due to its excellent C–C coupling activity and reducibility, as well as to replace the scarcer noble metals (e.g., Rh). Among the different supports (SiO₂, CeO₂, Al₂O₃ and P25) studied, P25 showed the highest activity (Figure 21b). Further optimization of Pd/Cu ratio resulted in the highest activity on Pd₂Cu NPs/P25 (Figure 21c), exhibiting 92% ethanol selectivity and the highest TOF of 359 h⁻¹. DRIFTS results

indicated that the rate-determining step was $^*\text{CO}$ hydrogenation to $^*\text{HCO}$, which was beneficial to decrease $^*\text{CO}$ coverage on the catalyst surface and weaken $^*\text{CO}$ poisoning. Furthermore, upon increasing the Pd/Cu ratio, the bonding mode of $^*\text{CO}$ on Pd was changed from 2-fold bridge-bond (in case of Pd₁Cu NPs/P25) to 3-fold bridge-bond (in case of Pd₂Cu NPs/P25), and as a result, $^*\text{CO}$ species were more easily converted into ethanol over Pd₂Cu NPs/P25 (Figure 21a). Another recent report by Caparrós explored Pd-based single atom catalyst supported on Fe₃O₄ for the selective hydrogenation of CO₂ into ethanol.¹⁹⁵ At 300 °C, ethanol was selectively formed at 0.1 wt% Pd loading where the catalyst contained mostly atomically dispersed Pd at very low CO₂ conversion levels. Increase in Pd loading resulted in a drop in selectivity due to the formation of Pd cluster/NPs. At higher temperatures, CO was formed as the major product. Other inorganic oxide supports like Al₂O₃, ZrO₂, and CeO₂ were also tested, but they showed negligible or no selectivity for ethanol, implying that a specific interaction between Pd single atoms and Fe₃O₄ was necessary for C–C coupling. Wang et al. did a comparative study by screening different noble metals (such as Pd, Rh, Ir, Au, and Pt) on different supports, where Au-based catalysts supported on anatase TiO₂ showed the highest efficiency with a space time yield of over 900 mmol_{EtOH} g_{Au}⁻¹ h⁻¹ and an ethanol selectivity of >99%.^{196, 197} But the use of organic solvents, such as *N*-methyl-2-pyrrolidone (NMP) and *N,N*-dimethylformamide (DMF), was one of the key strategies to dissolve CO₂ and other reaction intermediates.

Figure 21. (a) Schematic diagram of bimetallic Pd-Cu catalyst showing different binding mode of CO. Effect of (b) different supports and (c) catalyst composition on the product selectivity. Reproduced with permission from ref. 194. Copyright 2017 American Chemical Society.

Based on the literature of CO₂-to-ethanol catalysts, it can be observed that Pd and Rh are highly active for this reaction, but they are also active in overhydrogenation reaction to make hydrocarbons if not engineered properly. Some recent reports showed that Co- and Cu-based catalysts can be very active due to their C–C coupling activity and therefore can replace expensive noble metals.¹⁹⁸⁻²⁰² Contrary to the earlier study by Han's group,¹⁸⁹ which showed the formation of mixed alcohols over mesoporous Co₃O₄, Wang et al. achieved high ethanol selectivity over a mixed Co oxide catalyst.¹⁹⁸ The catalysts derived from a Co-Al layered double hydroxide (LDH) outperformed all abundant-metal catalysts previously

employed for this reaction, producing 92.1% ethanol selectivity at 140 °C with an ethanol time yield at 0.444 mmol g⁻¹ h⁻¹. The exact reason behind this superior activity was not clear, but it was proposed that the presence of surface oxide species with coexisting Co-CoO phases improved the formation of relatively stable *CH_x (key intermediate for ethanol production) for converting formate into acetate via an insertion mechanism as observed by operando FT-IR spectroscopy. Zhang et al., on the other hand, claimed that Co₂C was the active phase, which was generated by CO induction during reaction.²⁰⁰ The active Co₂C phase was stabilized on SiO₂ and Si₃N₄ support due to strong metal–support interaction (SMSI) obtained by Si–O–Co bond. According to in situ DRIFTS results, CO produced from RWGS inserted into *CH_x intermediates to form ethanol.

A very interesting study was done by An et al., where Cu-based methanol-selective catalyst was transformed into ethanol-selective catalyst just by tuning the oxidation state of Cu (Figure 22).²⁰¹ Cooperative Cu^I sites stabilized on a Zr₁₂-MOF exhibited a high ethanol selectivity of >99% with the assistance of a Cs promoter. The excellent activity was attributed to the cooperative nature of the bimetallic Cu^I₂ centers, which facilitated both H₂ activation and C–C coupling of methanol and formyl species. Multiple hydrogen addition to CO₂ was fulfilled by H spillover from adjacent Cu sites. The formyl intermediate was stabilized by the electron-rich Cu center aided by the alkali metal promoter and the extent of formyl-stabilization was controlled by changing the promoter from Li to Cs. Higher electron-donating capacity of Cs⁺ resulted in more electron-rich Cu centers and increased the basicity of an oxygen atom coordinated to Cu, which facilitated the formation of formyl species from CH₂O₂ intermediate (6 in Figure 22c). In addition, the electron-rich Cu centers also promoted the oxidative addition of hydrogen and increased the hydricity of Cu^I–H[–] to enhance the activity.

Figure 22. Schematic showing (a) Cu supported on ZrO_2 for CO_2 hydrogenation to methanol and (b) bimetallic Cu centers supported on Zr_{12} -SBUs in a MOF for producing C_{2+} oxygenates. (c) Proposed mechanism of methanol and ethanol synthesis from CO_2 hydrogenation over Zr_{12} -bpdc-Cu catalysts. Reproduced with permission from ref. 201. Copyright 2019 Springer Nature.

Recently, a plasma-assisted selective CO_2 -to-ethanol conversion was reported over commercial $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalyst.²⁰³ Instead of using molecular H_2 , water was used as the H source. Ethanol was claimed as the only liquid product and the production rate of ethanol was dependent on the input power and water vapor content. The adsorbed species on the surface of the catalyst during reaction were analyzed by FTIR (Figure 23). As $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalyst is well known for CO_2 -to-methanol conversion, the key intermediate was methanol in this case. The excellent ethanol selectivity was supposed to have been achieved by efficient decomposition of methanol by high-energy electrons from the negative corona plasma to produce CH_3OH^- , which could be further dissociated into $^*\text{CH}_3$ and $^*\text{OH}$.

Figure 23. Schematic diagram showing different intermediates during plasma-assisted CO₂-to-ethanol transformation on Cu/ZnO/Al₂O₃ catalyst. Reproduced with permission from ref. 203. Copyright 2018 Elsevier.

3.2.2.2. Summary and challenges

Summing up, the production of HAS from CO₂ is way more challenging than the methanol counterpart as achieving high selectivities is not straightforward due to the multistep nature of the process. Moreover, we can observe that these results (see Table 5) lie far from the ones discussed for the methanol synthesis (see Table 4), and therefore, the major challenge here is to find a catalytic system that could display high activity and selectivity towards ethanol. Additionally, most of the literature on CO₂-to-ethanol focuses on batch synthesis where reasonable ethanol selectivities can be achieved. This fact highlights the challenge of continuous heterogeneous gas phase synthesis of HAS from CO₂, whereas there are several excellent catalysts reporting high C₂₊OH selectivity in batch mode. From the practical application point of view, continuous flow operation is more attractive for large-scale production, and therefore more efforts need to be given in this direction.

Another major concern is the design of future catalysts as the HAS selectivities over most of the explored catalysts are quite low. Until now, noble metals (Rh, Pd, Pt) have shown some promising activities for HAS synthesis. The main reason is the high activity of these metals for C–C coupling reaction, which is the key step for HAS synthesis. However, all these metals are highly expensive and need to be replaced by cheaper alternatives. Although a few transition metal-based catalysts have shown good selectivities for higher alcohols at a descent CO₂ conversion, their synthesis is not straightforward and not scalable for large-scale use. For instance, Cu containing MOF catalysts showed excellent activity (96% CO₂ conversion, 99% ethanol selectivity),²⁰¹ but the activity depends on the precise control of the oxidation state of Cu, which is difficult for a large-scale operation. Therefore, the urgent need is the design of a robust catalyst (similar to the matured Cu–ZnO system for methanol synthesis), which will be cost-effective and will operate under industrial conditions. Compared to the matured CO₂-to-methanol process, CO₂-to-HAS conversion is a new field and therefore it requires more in depth studies on reaction mechanism and reactant-catalyst interaction to identify the active catalysts.

Table 5. Catalytic performance of different catalysts in CO₂ hydrogenation to C₂₊OH alcohols

Catalyst	Reactor configuration	Reaction conditions				Catalytic performance			Ref.
		<i>T</i> (°C)	<i>P</i> (bar)	H ₂ /CO ₂	GHSV (mL g _{cat} ⁻¹ h ⁻¹)	<i>X</i> _{CO₂} (%)	Selectivity (%)		
							C ₂ +OH	EtOH	
KFeCuAl	Continuous	350	80	3	32000	43.3	-	8.2	187
KCuZnAlGaPd + KFeCuAl (1:1)	Continuous	330	80	3	20000	47.0	-	17.4	187
1%Pt/Co ₃ O ₄	Batch ^a	200	80	3	-	-	82.5	-	189
1%Rh/Co ₃ O ₄	Batch ^a	200	80	3	-	-	65.4	-	189
1%Pt/Co ₃ O ₄ -nanorod	Continuous	200	20	3	6000	27.8	3.2	-	191
2.5%RhFeLi/TiO ₂ NRs	Continuous	250	30	3	6000	15.7	-	31.3	192
2Rh-0.3VO _x /MCM-41	Continuous	250	30	3	6000	12.1	-	24.1	193
1.23%Pd ₂ Cu NPs/P25	Batch ^b	200	32	3	-	-	-	92.0	194
0.1%Pd/Fe ₃ O ₄	Continuous	250	30	3	8000	1.4	98.0	-	195
0.1%Pd/Fe ₃ O ₄	Continuous	300	30	3	8000	2.9	46.1	-	195
0.3%Au/a-TiO ₂	Batch ^c	200	60	3	-	-	-	>99.0	197
CoAlO _x (Co/Al = 2.7)	Batch ^b	140	40	3	-	-	-	92.1	198
Co _{0.52} Ni _{0.48} AlO _x	Batch ^b	200	40	3	-	-	-	85.7	199
2%Na-20%Co/SiO ₂	Continuous	250	50	3	4000	18.8	-	6.0	200
Zr ₁₂ -bpdc-CuCs	Batch ^d	100	20	3	-	96.0	-	>99.0	201
Zr ₁₂ -bpdc-CuLi	Batch ^d	100	20	3	-	50.0	-	66.3	201
Cs-Cu _{0.8} Fe ₁ Zn ₁	Continuous	330	50	3	4500	36.6	19.8	-	202

^aH₂O/DMI as solvent (15:85, v/v), ^bH₂O as solvent, ^cDMF as solvent, ^dTHF as solvent. GHSV: gas hourly space velocity, *X*_{CO₂}: CO₂ conversion.

^aH₂O/DMI as solvent (15:85, v/v), ^bH₂O as solvent, ^cDMF as solvent, ^dTHF as solvent. GHSV: gas hourly space velocity, *X*_{CO₂}: CO₂ conversion.

3.3. Production of Multi-carbon Hydrocarbons

There are different possible routes to synthesize hydrocarbons from CO₂, either by direct hydrogenation of CO₂ or by converting CO₂ into CO/methanol and subsequent transformation into hydrocarbons (Figure 24). Current technologies have shown rapid development in designing advanced catalysts for the direct transformation of CO₂ into hydrocarbons.²⁰⁴⁻²¹⁰

Figure 24. Different possible routes for the production of value-added hydrocarbons from CO₂ hydrogenation.

This direct (single pot) transformation of CO₂ can be carried out by (i) standalone catalysts (usually containing Fe and/or Co as a component) via a Fischer-Tropsch like reaction (CO₂-FT) and (ii) tandem

catalysts where a zeolite/zeotype is paired with either an Fe/Co catalyst as described in (i) or a methanol synthesis catalyst.

3.3.1. Standalone catalysts

As mentioned before, since Fe- and Co-based materials are well known catalysts for the pure FT process, most of the catalysts reported in literature have been designed including one or the other element. Specifically, Fe has gained much more attention due to its high RWGS and FT activity and stability under the required reaction conditions. When compared to the CO-FT process, earlier catalysts designed for CO₂-FT showed much higher CO conversion (up to 87%) than CO₂ conversion (up to 45%),²¹¹ indicating that better catalysts are needed to improve the CO₂ conversion.

Initial improvements were achieved by introducing different promoters. For instance, addition of K in Fe-based catalyst stabilizes the iron carbide phase and addition of boron increases the selectivity of light olefins.²¹² It is most likely that K promotes CO₂ adsorption and hinders H₂ adsorption in order to suppress the methane formation. There are many recent studies from different groups using K promoter with Fe catalysts to produce mainly light olefins with improved selectivities.²¹³⁻²¹⁸ Along with K, various other promoters ranging from alkali metals to transition base metals were also investigated.^{219, 220} For example, a systematic study of the effect of different promoters on hydrocarbon selectivity was recently reported by our group.²¹⁹ An interesting approach of deriving well dispersed Fe/C catalyst with high metal loading (up to 41 wt% Fe) was described, where Fe-based metal organic framework (Basolite F300) was chosen as catalyst precursor (Figure 25a) and a promoter was subsequently incorporated. Various incorporated elements (Cu, Mo, Li, Na, K, Mg, Ca, Zn, Ni, Co, Mn, Fe, Pt, and Rh) were studied and a diverse variety of promotional behaviors was observed. For instance, Cu and Pt increased the CO₂ conversion and the selectivities for CH₄ and C₂–C₆ paraffins; Mn, Mg, and Mo enhanced CO selectivity; and Ni, Co, and Rh mostly promoted methanation. However, most interestingly, only K was found to enhance the olefin selectivity (Figure 25b). Further investigation showed that the K-promoted catalyst was very different from other catalysts since it formed both the Fe₅C₂ and the Fe₇C₃ carbides, and the Fe₇C₃ phase had the highest intrinsic activity among iron carbides.²⁰⁶ On the other hand, unpromoted and Pt/Mo-promoted catalyst only formed the Fe₃C phase, which was reported as less active than the Fe₅C₂ and Fe₇C₃ phases in FTS.

Figure 25. (a) Synthesis of Fe/C catalyst via carbonization of Basolite F300 MOF. (b) Effect of different promoters on product distribution during CO₂ hydrogenation; reaction conditions: 320 °C, 30 bar, H₂/CO₂ = 3, and GHSV = 24000 mL g⁻¹ h⁻¹, TOS = 50 h. Reproduced with permission from ref. 219. Copyright 2018 American Chemical Society.

Most of the catalysts reported have focused on the efficient utilization of CO₂ as a strategy to mitigate climate change. Our group recently reported on a strategy that not only provides high yields of light olefins from CO₂ but also provides an avenue to address an additional environmental problem in the form of red mud utilization.²²¹ Large amounts of red mud are produced (0.3–2.5 ton per ton of alumina) as waste during the production of aluminum oxide via the Bayer process. This creates a waste management crisis since red mud presents an ecological hazard.

Sodium (Na) has also been explored as an effective promoter by increasing the basicity of the support, which favors higher olefin selectivity.^{222, 223} In addition, increasing Na content significantly improves the carbonization of the Fe catalysts. A recent study by Liang et al. showed evidence that the content of Fe₅C₂ is related to the amount of Na.²²⁴ Another study by the same group showed that further addition of Mn to the Na/Fe catalyst could facilitate the formation of active Fe₅C₂ phase that helped to achieve 30.2% selectivity of light olefins with high olefin/paraffin ratio (7.5).²²⁵ Combined characterization by Mössbauer spectroscopy, XRD and XPS evidenced the strong interaction between the Mn promoter and Fe species, which decreased the CO adsorption ability and consequently inhibited the chain-growth reaction in order to achieve high selectivity of light olefins.

In addition to alkali metals (such as Na, K), transition base metals like Cu were also reported to promote CO₂ hydrogenation to synthesize hydrocarbons.²²⁶ The promotion behavior of Cu was different from other promoters typically used (e.g., K, Mn, Zn, etc.). Cu promoted Fe catalyst showed decreased selectivity of C₂⁺–C₄⁺, but a significant improvement in C₅⁺ product selectivity. Recently, bimetallic

catalysts with Fe as active metal were studied to promote CO₂ conversion.²²⁷⁻²³¹ Especially, addition of Co was found to increase the carbide formation, which was beneficial for the chain propagation reaction. It was also observed that the product selectivity could be tuned by changing the Fe/Co ratio. For example, Gnanamani et al. showed that the selectivity to C₂–C₄ hydrocarbons over Co–Fe catalyst was increased with increasing Fe fraction, while alcohol selectivity was found to increase with increasing Fe content up to 50%, but then it dropped with further addition of Fe.²²⁷

Finally, although Co is active in CO-FT process, very few reports are available on Co-based catalysts for CO₂-FT.^{232, 233} The main issue with pure Co-based catalysts is their low RWGS activity and that they act as methanation catalysts under CO₂/H₂ regime and restrict FT chain growth. This problem however can be overcome by introducing a second functional group that can drive the formation of chain growth by increasing the CO productivity via RWGS reaction. Xie et al. designed a bifunctional CeO₂–Pt@mSiO₂–Co core–shell catalyst for the targeted synthesis of C₂–C₄ hydrocarbons.²³⁴ High RWGS activity of CeO₂/Pt facilitated the formation of CO, which underwent FT process on the neighboring Co/mSiO₂ interface to yield C₂–C₄ hydrocarbons. However, the CH₄ selectivity was still significantly high (~60%), suggesting that Fe-based catalysts are far better than Co-based catalysts in CO₂-FT process.

3.3.2. Tandem catalysts

While standalone catalysts following the CO₂-FT route have proven effective in providing large hydrocarbon yields from CO₂, selectivity towards a target product remains an issue since the product mixture formed tends to consist of a large variety of hydrocarbons. This limits the potential for industrial application as low selectivity tends to lead to large separation costs thus making the process uneconomical. Tandem catalysis offers a solution to this problem wherein a zeolite placed downstream from the CO₂-FT catalyst can play a product ‘redistribution’ role by catalyzing several reactions including hydrocracking/isomerization, oligomerization, cyclization etc. thus improving selectivity to target products. This characteristic of zeolites also allows for their pairing with methanol synthesis catalysts where the methanol generated by the preceding catalyst gets converted to hydrocarbons in the zeolite via the classical Methanol-to-Hydrocarbons (MTH) reaction. This approach has been successful in offering high selectivities for target products at least in the hydrocarbon fraction of the products. Thus, this section will discuss the advancements in catalyst development for the direct transformation of CO₂ into higher hydrocarbons using tandem catalysis focusing on the two alternate pathways i.e. (a) a Fischer–Tropsch like synthesis (CO₂-FT) pathway with CO as an intermediate and (b) a methanol-mediated pathway where the methanol obtained from CO₂ is subsequently transformed into hydrocarbons over a zeolite.

3.3.2.1. CO₂-based Fischer–Tropsch pathway

The production of hydrocarbons via this pathway has the advantage of high hydrocarbon yields and very low CO selectivity even at high CO₂ conversions. The choice of an appropriate zeolite becomes an important factor for tuning the selectivity of products. Thus, Wei et al. designed a multifunctional catalyst by coupling Na–Fe₃O₄ CO₂-FT catalyst with different zeolites, which showed different product distribution based on the nature of the zeolites.⁷ This approach has also been advocated as a strategy to overcome the ASF distribution limit of the CO₂/CO-FT process due to the product redistribution capability of zeolites. Over Na–Fe₃O₄/HZSM-5 catalyst, gasoline-range (C₅–C₁₁) hydrocarbons with selectivity up to 78% were achieved at a CO₂ conversion of 22% and low methane selectivity (only 4%).

The main reason was the multifunctional nature of the catalyst providing the appropriate proximity of three types of active sites (Fe_3O_4 , Fe_5C_2 and acid sites), synergistically catalyzing the tandem reaction. Fe_3O_4 sites performed RWGS, Fe_5C_2 sites performed α -olefin synthesis, while oligomerization/aromatization/isomerization was facilitated over zeolite acid sites (Figure 26a). It was observed that the degree of olefin oligomerization and product selectivity were dependent on the acidity and pore structure of the zeolite. Among the different zeolites (HY, HBEA, HMOR, HZSM-23, HMC-22 and HZSM-5) used, three types of zeolites with 10 member ring channels (HZSM-5, HMC-22, and HZSM-23) exhibited higher C_5 – C_{11} selectivities (Figure 26b). Furthermore, the zeolite with stronger acidity was found to cause the over-cracking of heavy hydrocarbons to C_1 – C_4 hydrocarbons, whereas the zeolite with weaker acidity was unable to perform the oligomerization/isomerization/aromatization of primary CO_2 -FT products, thus both disfavored the production of C_5 – C_{11} hydrocarbons. Tuning the acidity of the zeolite, HZSM-5(Si/Al = 160) was found to be selective for C_5 – C_{11} hydrocarbon synthesis due to the presence of medium/strong acid sites and 10-ring 3-dimensional pore structure. The same group investigated a similar multifunctional catalyst Na- Fe_3O_4 /HMC-22, which produced 74% isoparaffins at a CO_2 conversion of 26%.²³⁵ In this case, Brønsted acidity of HMC-22 effectively promoted isomerization, while suppressing aromatization. However, the main disadvantage was that the microporous nature of HMC-22 initiated the coke deposition inside the micropores, which caused the decline of isoparaffin yield.

Figure 26. (a) Role of different active sites of a multifunctional catalyst in CO_2 hydrogenation to make gasoline-range hydrocarbons. (b) Product selectivity over different Na- Fe_3O_4 /zeolite catalysts; reaction conditions: $\text{H}_2/\text{CO}_2 = 3$, GHSV = 4000 $\text{mL g}_{\text{cat}}^{-1} \text{h}^{-1}$, 320 $^\circ\text{C}$, 3 MPa. Reproduced with permission from ref. 7. Copyright 2017 Springer Nature.

Considering the fact that ZSM-5 has the ability to generate aromatics and mordenite (MOR) has ethylene shape selectivity within the 8-membered ring, our group recently highlighted the importance of appropriate zeolite selection by studying the effect of the combination of these zeolites with a highly active $\text{Fe}_2\text{O}_3@\text{KO}_2$ catalyst in a single reactor.²³⁶ The bifunctional catalysts gave high CO_2 conversion (~50%) with low CO selectivity (12.8%) with ZSM-5 selectively producing aromatics and MOR enhancing the production of light olefins with high space-time yields. In-depth characterization via solid-state nuclear magnetic resonance (ssNMR) spectroscopy revealed that the reaction mechanism was driven by the incorporation of CO in the network in the form of surface formate species. In addition, DFT simulations demonstrated that carbenium ions are crucial intermediates for the conversion of hydrocarbons in zeolites, with ZSM-5 succeeding in activation of long alkenes to form aromatics via carbenium ions. Subsequent reports from our group have also revealed that coupling the $\text{Fe}_2\text{O}_3@\text{KO}_2$ catalyst with either Ca modified ZSM-5 or ZrS modified SAPO-34 leads to higher light olefin selectivity compared to MOR zeolite.^{237, 238}

A recent study by Liu and coworkers demonstrated a nice strategy to achieve selective formation of aromatics over a composite catalyst consisting of Na/Fe and HZSM-5.²³⁹ Under industrially relevant conditions, total selectivity to aromatics in liquid hydrocarbons reached over 94%. The most striking results were observed regarding the selectivity to para-xylene in total xylenes, which was remarkably increased from 24–26% to 70% when HZSM-5 zeolite was coated with SiO_2 . According to the experimental results and DFT calculations, the combined effect of Na-promoted Fe catalyst and high Brønsted acidity of HZSM-5 were believed to be the key factors for enhancing both CO_2 conversion and aromatics selectivity. High Brønsted acidity of HZSM-5 zeolite played a critical role in converting CO_2 -FT intermediate products into aromatics rather than isoparaffins as the ability of cracking and aromatization increases with increasing Brønsted acidity. Furthermore, coating SiO_2 on the external surface of the zeolite efficiently decreased the coverage of the exterior acidic sites, which suppressed the isomerization of as formed para-xylene and para-ethyltoluene in the inner channels of HZSM-5 in order to keep a constant rate of aromatics formation (Figure 27). This study showed an effective way to shift the product distribution from several aromatics to a single product, which can make the separation process easier.

Figure 27. Isomerization of *p*-xylene and *p*-ethyltoluene over the external surface of uncoated and SiO_2 -coated HZSM-5 zeolite. Reproduced with permission from ref. 239. Copyright 2019 Royal Society of Chemistry.

3.3.2.2. Methanol-mediated pathway

In this pathway, tandem catalysts composed of a methanol synthesis catalyst (see section 3.2) and a zeolite/zeotype are paired together for production of hydrocarbons from CO₂. This pathway is characterized by high selectivity towards target products but suffers from low hydrocarbon yields.

The first report on this transformation was made by Fujimoto and Shikada in 1987.²⁴⁰ Combination of a Cu-Zn catalyst and a dealuminated Y zeolite (high-silica zeolite) produced C₂–C₅ hydrocarbons with selectivities over 90%. A number of recent works have emulated similar combinations for this reaction because of the high activity of the Cu-Zn catalyst and zeolite in methanol production and MTH, respectively. For example, Chen et al. used core-shell structured bifunctional CuZnZr@Zn-SAPO-34 catalysts for direct hydrogenation of CO₂ with a focus on light olefins production.²⁴¹ Distribution of products was significantly affected by the mass ratio of CuZnZr and SAPO-34 as well as the acid density of SAPO-34. Compared to the physically mixed CuZnZr/SAPO-34, the composite catalyst selectivity produced olefins and suppressed CH₄ formation due to reduced contact interface and hydrogenation ability on the metal sites. Interestingly, modification of SAPO-34 by Zn addition reduced the acidity of SAPO-34, which consequently increased the olefin selectivity by inhibiting the secondary hydrogenation reactions. Over CuZnZr@Zn-SAPO-34 (4/1) catalyst, C₂–C₄ olefin selectivity of 72% was achieved in the hydrocarbon fraction at reaction conditions of H₂/CO₂ = 3, GHSV = 6000 mL g⁻¹ h⁻¹, 400 °C and 2 MPa. On the other hand, decrease in mass loading of CuZnZr fraction lowered the yield of methanol, which induced the hydrogenation and hydrogen transfer reactions of primary olefins to produce C₃ and C₄ hydrocarbons.

Based on the high activity of ZnO-ZrO₂ solid solution in methanol production, Li and coworkers reported ZnZrO/SAPO-34 tandem catalyst to achieve lower olefins with 80–90% selectivity among hydrocarbon products.²⁴² To explain the tandem catalysis, they compared the catalytic performance of the ZnZrO/SAPO catalyst with those of the two individual catalyst components integrated in varying degrees of proximity in a tubular fixed bed reactor (Figure 28). The highest olefin selectivity was observed over the tandem catalyst, which was far better than any other physical mixture of individual components. The results obtained here suggest that the product selectivity is highly dependent on the spatial separation between two active phases of the catalyst and close proximity is essential to create a synergistic effect in tandem catalysis. Similar studies focusing on short chain olefin production were reported over different multifunctional catalysts such as In-Zr/SAPO-34,^{243, 244} In₂O₃-ZrO₂/SAPO-5,²⁴⁵ In₂O₃/SAPO-34,²⁴⁶ and ZnGa₂O₄/SAPO-34²⁴⁷ catalysts. From the literature reports described here, one thing is clear that SAPO-34 has been widely used to obtain high selectivity for lower olefins. The main reason could be the presence of weak acidic sites and small 8-member ring (8MR) windows in SAPO-34, which are essential features to produce small molecules. In fact, the shape-selective nature of SAPO-34 has already been proven since its 8-ring pore structure was found to be beneficial for C₂–C₄ formation.²⁴⁸

Figure 28. Comparison of catalytic performances between tandem catalyst (ZnZrO/SAPO) and physical mixtures of ZnZrO and SAPO in the hydrogenation of CO₂; reaction conditions: 380 °C, 2 MPa, GHSV = 3600 mL g_{cat}⁻¹ h⁻¹. Reproduced with permission from ref. 242. Copyright 2017 American Chemical Society.

As we have seen that zeolites with 10-ring pore structure are suitable for higher hydrocarbon production,⁶ ZSM-5 has also been used by multiple groups to achieve selective production of C₅+ hydrocarbons/aromatics.^{6, 216, 249-252} High Brønsted acidity of ZSM-5 also facilitates the aromatization process to convert primary olefins into aromatics. Wang et al. recently studied a bifunctional catalyst composed of Cr₂O₃ and H-ZSM-5 zeolite, which provided aromatics selectivity of ~76% in the hydrocarbon fraction with a single-pass CO₂ conversion of 34.5%.²⁴⁹ Special emphasis was given towards the modification of zeolite in order to realize the target synthesis of BTX (benzene, toluene, and xylene), especially *p*-xylene (PX). The acidic sites at outer surface of H-ZSM-5 were neutralized by encapsulating with silicalite-1 (S-1) to suppress the undesired alkylation and isomerization of PX to *o*- or *m*-xylene (Figures 29a & 29b). Compared to the unmodified catalyst, modified Cr₂O₃/H-ZSM-5@S-1 catalyst improved the fractions of BTX and PX in aromatics products from 13.2% and 7.6% to 43.6% and 25.3%, respectively. In another study, Ni et al. observed that silica modified ZnAlO_x&Si-H-ZSM-5 catalyst could achieve 58.1% *p*-xylene in xylenes (Figure 29c).²⁵⁰ The hydrogenation of CO₂ was initially activated by Zn²⁺ in ZnAlO_x as observed by operando DRIFTS study. The as-formed formate species blocked the ZnAlO_x surface to make the metal sites less accessible for hydrogenation of unsaturated olefin intermediates which in turn improves the aromatics selectivity at the expense of CO (or saturated hydrocarbons) selectivity.

Figure 29. (a) Effect of modification on product selectivity and (b) scheme of highly selective production of BTX over Cr₂O₃/H-ZSM-5@S-1. (c) Effect of modification on catalytic behaviors in CO₂ hydrogenation. Reproduced with permission from ref. 249 and 250. Copyright 2019 American Chemical Society and 2018 Springer Nature.

3.3.3. Reaction mechanism

Unraveling the reaction mechanism for the formation of hydrocarbons from CO₂ remains a challenging task since this has not been studied to a great degree especially in the case of tandem catalysis. While a lot of classical reaction mechanisms involving hydrocarbons on zeolites can be applied, the presence of CO₂, CO, and H₂O in the feed going to the zeolite possibly causes subtle differences which are yet to be discerned.

In case of the CO₂-FT process, a reverse water gas shift (RWGS) mechanism where the CO₂ is converted to CO followed by a carbide mechanism is widely accepted. As discussed in Section 3.3.1, alkali metals have proven to be effective promoters of Fe based catalysts for enhancing hydrocarbon yields. Potassium, in particular, seems to be beneficial for the initial conversion of CO₂ to CO. This was reported in our study where the CO₂ in the feed reacts with the potassium on the Fe catalyst leading to the formation of a K₂CO₃ phase.²¹⁶ This K₂CO₃ undergoes several transformations eventually releasing CO (Figure 30). Then CO is dissociated over the Fe phase and the carbon thus obtained is hydrogenated to form active CH_x (1 ≤ x ≤ 3) species as chain initiators and monomer units for chain growth. The chain growth can be terminated either by hydrogenation to produce paraffins or by β-hydride abstraction to form α-olefins. Since FT mechanism follows the Anderson–Schulz–Flory (ASF) law in product distribution, the main challenge of this process is to find proper catalysts that can prevent the formation of methane and light saturated hydrocarbons.

Figure 30. Reaction scheme of the CO_2 capture and transformation on the $\text{Fe}_2\text{O}_3 @ \text{K}_2\text{CO}_3$ catalyst. The process takes place in two steps: (i) the CO_2 is initially activated on the K_2CO_3 that undergoes several transformations yielding KCOOH and CO , which is subsequently hydrogenated (ii) to olefins via FTS. Reproduced from ref. 216.

In the case, of tandem catalysis where a zeolite is paired with a CO_2 -FT catalyst most of the reactions occurring over the zeolite are classical hydrocracking, H-transfer, oligomerization, cyclization reactions etc. However, as noted above, additional phenomena can occur which has not been widely studied. For instance, we have observed in our studies that the overall CO selectivity in a tandem catalyst is lower than a standalone CO_2 -FT catalyst due to the incorporation of CO in the zeolite via a ketene-like intermediate giving rise to higher production of light olefins (Figure 31).^{236, 237} Therefore, in depth studies need to be performed where possible reaction intermediates including $\text{CO}/\text{H}_2\text{O}$ are co-fed with CO_2/H_2 in order to unravel their effect on product formation.

Figure 31. Reaction pathways of the Fe₂O₃@KO₂/zeolite-catalyzed hydrogenation of CO₂ to light olefins and aromatics. (A) CO₂ hydrogenation pathway on the stand-alone Fe₂O₃@KO₂ catalyst. (B) CO incorporation pathway on MOR and ZMS-5. (C) Aromatization pathway on ZSM-5. Reproduced from ref. 236.

Considering now the methanol-mediated pathway, the main advantage of this route is that the ASF law of product distribution does not apply to it and therefore it is possible to obtain selectivities to olefins in the hydrocarbon fraction higher than 80%. However, the main obstacle is associated with the fact that methanol-to-olefin (MTO) transformation requires high temperatures (>350 °C) and it is hard to achieve significant CH₃OH selectivity at this temperature due to the exothermic nature of the CO₂-to-methanol process.

In the first step, CO₂ is converted to methanol and the details of the mechanism can be found in Section 3.2.1.3. The methanol thus obtained is then converted into hydrocarbons via the classical methanol-to-hydrocarbon (MTH) mechanism over an acidic zeolite (see Figure 32).²⁵³ The reaction mechanism follows a short induction period where direct C–C bond formation takes place aided by surface methoxy species adsorbed on the zeolite acting as intermediates. This is succeeded by an autocatalytic period where a dual cycle/hydrocarbon pool (HCP) type mechanism takes over. The latter has been widely studied in literature with several reports available.²⁵⁴⁻²⁵⁶ The autocatalytic dual cycle mechanism consists of an olefinic and an aromatic cycle which can be further divided into multiple elementary steps – methylation and cracking of olefins, methylation and dealkylation of aromatics, hydrogen transfer and cyclization. The last two steps also act as a bridge between the two cycles.

Figure 32. Schematic of MTH mechanism. (a) Steady state kinetics of MTH reaction over ZSM-5 by a sequence of olefins methylation followed by their cracking or aromatization to give either olefins or aromatics. (b) The hydrocarbon-pool (HCP) mechanism of MTH over SAPO-34 – an active intermediate of aromatic nature – through which light olefins are formed by dealkylation. (c) The dual cycle describing two competing cycles running in the zeolite channels governed by olefins and aromatics, both acting as co-catalysts for MTH and being active HCP species. Adapted from ref. 253. Copyright 2018 Springer Nature.

It has been observed that the olefinic cycle is primarily responsible for the production of propylene while the aromatic cycle gives rise to both ethylene and propylene. Thus, suppression or propagation of one cycle or the other by manipulating the operating conditions and/or catalyst modification can allow for the control of product selectivity. Nevertheless, the exact mechanism for the MTH reaction is still a matter of some debate and as noted for the CO₂-FT route, starting from CO₂ and using tandem catalysis via the MeOH route implies that the role of additional intermediates including CO/CO₂/H₂/H₂O under high pressures along with methanol going to the zeolite is yet to be resolved.

3.3.4. Summary and challenges

CO₂ to hydrocarbons has attracted a lot of attention in literature recently because of the potential it has for contributing to a circular carbon economy especially in terms of production of fuels and petrochemicals. Tandem catalysis appears to be the method of choice for this reaction as it offers several exciting prospects pertaining to tuning of the product composition as noted in Table 6.

Owing to the complexity of the process and the scarcity of fundamental investigations it is challenging to identify a specific set of properties which are ideal for a catalyst to be used in this process. This challenge is only magnified when tandem catalysts are brought into the picture since they tend to

have a higher degree of complexity as there are more parameters which require optimization. For example, product selectivity can be tuned by changing the type or different properties of zeolites (such as Si/Al ratio, pore size, and particle size). Additionally, more focus should be placed on understanding the reaction mechanism over the zeolite component. Moreover, very few zeolite types have been explored so far with H-ZSM-5 being the most common choice for aromatics production and SAPO-34 being the zeolite of choice for olefin synthesis (see Table 6). Hence, the exploration of other zeolite topologies also needs to be tackled.

Furthermore, since this is a multistep process, the precise control of the proximity of the active sites is a key factor for designing suitable tandem catalysts. In some cases, acidic sites of the zeolite can be poisoned by the alkaline functionalities of their counterpart due to close proximity and therefore dual bed configuration would be preferred in those cases. In fact, the spatial arrangement between the two phases of a tandem catalyst should be optimized based on the hydrogenation route followed (via CO₂-FT or MeOH).

Finally, there seems to be no clear front runner between the CO₂-FT route and the MeOH route. For the former, poor selectivity to target products remains an issue and is a big barrier for implementation requiring to be addressed. A potential solution would be to go beyond the zeolites typically reported in literature in order to uncover a possible winner as mentioned above. For the latter, hydrocarbon yields are a major obstacle due to the thermal incompatibility between a methanol synthesis catalyst and a zeolite. Methanol synthesis catalysts tend to function well at temperatures below 300 °C while zeolites typically need to reach temperatures of at least 350–400 °C in order to be effective. One possible solution to this problem is to uncover catalysts which are relatively efficient at producing methanol at higher temperatures (~350 °C). This option, however, is severely limited by thermodynamics. Another feasible option would be to house the methanol synthesis catalyst and the zeolite in separate reactors connected in series with individual temperature control thus overcoming their thermal incompatibility.

Table 6. A non-exhaustive list of catalytic concepts explored for the production of multi-carbon hydrocarbons from CO₂

Catalyst	Reaction conditions			Reaction route	Catalytic performance					Ref.
	<i>T</i>	<i>P</i>	GHSV (mL		<i>X</i> _{CO2}	Selectivity (%)				
	(°C)	(bar)	g _{cat} ⁻¹ h ⁻¹)		(%)	CO	CH ₄	C ₂ -C ₄ =	Arom.	
In ₂ O ₃ /HZSM-5	340	30	9000	MeOH	13.1	44.8	0.6	~2.0	8.2	6
Na-Fe ₃ O ₄ /HZSM-5	320	30	4000	CO ₂ -FT	~34	~15	~6.9	~3.4	~36.5	7
FeK/SWNTs	340	20	9000	CO ₂ -FT	52.7	9.6	13.5	22.5	-	217
FeK/MWNTs	340	20	9000	CO ₂ -FT	43.6	23.4	27.1	30.7	-	217
Red Mud + 2 wt% K	375	30	9600	CO ₂ -FT	45.0	26.0	19.0	36.0	-	221
ZnFeO _x -Na/HZSM-5	320	30	4000	CO ₂ -FT	36.2	11.0	7.3	2.8	53.4	223
Fe-K/HZSM-5	375	30	5000	CO ₂ -FT	47.4	13.7	14.9	11.8	23.4	236
Fe-K/MOR	375	30	5000	CO ₂ -FT	47.1	12.9	13.7	33.2	2.5	236
Fe-K/Ca-ZSM-5	375	30	5000	CO ₂ -FT	46.6	13.0	14.4	37.9	4.1	237
Fe-K/ZrS-SAPO-34	375	30	5000	CO ₂ -FT	49.0	13.0	~20	48.0	-	238
Zn-ZrO ₂ /Zn-SAPO-34	380	20	3600	MeOH	~18	~48	2.1	32.0	-	242
In-Zr/SAPO-34	380	30	9000	MeOH	26.2	63.9	0.7	26.9	-	244
ZnGa ₂ O ₄ /SAPO-34	370	30	5400	MeOH	13.0	~49.0	-	46.4	-	247
In-Zn-Zr/SAPO-34	380	30	9000	MeOH	17.0	53.4	0.6	39.4	-	257
K-Fe@Zn	320	30	7200	CO ₂ -FT	30.6	18.6	16.9	33.1	-	258
FeK-graphene/HZSM-5	340	20	26000	CO ₂ -FT	35.0	39.0	2.1	-	41.5	259

ZnO-ZrO ₂ /HZSM-5	340	40	7200	MeOH	16.0	34.3	0.2	4.3	49.9	260
NiCu-CeO ₂ /SAPO-34	375	20	12000	MeOH	15.3	65.0	0.7	26.8	-	261
Na-Fe@C/H-ZSM-5	320	30	9000	CO ₂ -FT	33.3	13.3	4.2	0.7	43.5	262

GHSV: gas hourly space velocity, X_{CO_2} : CO₂ conversion.

4. PROCESS DESIGN CONSIDERATIONS

In the previous sections, we have seen the advances made in catalyst design for the thermocatalytic conversion of CO₂. However, despite its importance, not a lot of effort has been dedicated to studying how these results will fit into a real process and their economic considerations.

Not surprisingly, most of the works in the field have been done in the methanol synthesis pathway where the commercial CuZn catalyst was mostly studied.²⁶³⁻²⁶⁷ It should be noted that the CuZn catalyst has been effectively commercialized with respect to the production of methanol from syngas. While it has proven to be quite active in the production of methanol from CO₂, multiple studies have been published with very different catalysts performing much better than the CuZn catalysts (see Table 3). However, due to the large amount of data available in open literature concerning this catalytic system owing to decades of study, it becomes the first choice for process modelling. Recently, Slotboom et al. compiled all results available for this system and refitted the kinetic model.²⁶⁷ This refitted model with only six parameters (and valid for pressures from 20 to 70 bar and temperatures from 450 to 530 K) showed that the rate determining steps are most likely to be the dissociation of the oxygen from formate and the CO₂ dissociation in the RWGS reaction. In addition to these works on the commercial CuZn catalyst, Chiavassa et al.²⁶⁸ and Ahmad et al.²⁶⁹ studied another promising system: the Ga based catalyst (Ga₂O₃-Pd/silica and Ga₃Ni₅, respectively). They discovered that the mechanism in this case is a competitive adsorption mechanism where adsorbed hydrogen occupies the same active sites as the oxygenated surface intermediates and H₂O, CO₂, CO and H₂ coverages are decisive.

Outside of the methanol pathway, only global final kinetic rate equations appear in the literature. Riedel et al. studied the CO₂ conversion to hydrocarbons on a K-promoted Fe catalyst in a fixed-bed microreactor.²⁷⁰ Despite the global kinetics used, their results showed that, in contrast to the traditional Fischer-Tropsch reaction (FTS), equilibrium limitations exist for CO₂ conversion. The experimental results reflect a two-step reaction mechanism with the RWGS CO₂ reduction to CO as the primary step (equilibrium-limited with kinetic control) followed by subsequent CO FTS reaction (with kinetic control). Willauer et al. performed a kinetic study on a similar catalyst system (Mn and K-promoted Fe catalyst) and observed that this second FTS step rate was much slower than the RWGS rate.²⁷¹ Their model was expanded to show the potential beneficial effects of water removal as the water formed under typical FTS conditions influences catalyst activity by re-oxidizing the catalyst. By removing water vapor on the catalyst surface, the equilibrium at the catalyst surface shifted to the production of desired intermediates and the predicted C₃H₆ yield increased from 27.5 to 63.3%. Finally, Saeidi et al. revised the mechanisms and kinetics of CO₂ hydrogenation to value-added products and proposed new mechanistic LHHW-type kinetic rates.²⁷² Moreover, they suggest a novel integrated dual reactor configuration with a water perm-selective component in the first reactor and a H₂ perm-selective component in the second that should greatly shift the equilibrium and enhance the overall CO₂ conversion (see Figure 33).

Figure 33. Schematic diagram of dual-type reactor with water and H_2 perm-selective membrane. Reproduced with permission from ref. 272. Copyright 2017 Elsevier.

Hence, despite being brief, the kinetic studies showed us a key factor: water removal could greatly help overcome thermodynamic limitations and increase the conversion levels. With this information in hand, research groups have started to develop reactor systems that can take advantage of water removal. Currently, the most popular reactor design is the membrane reactor²⁷³ where water is removed from the gaseous stream.²⁷⁴⁻²⁷⁷ Recently, Li et al. demonstrated that water conducting nanochannels could be created by assembling NaA zeolite crystals into a continuous, defect-free separation membrane (Figure 34).²⁷⁴ Water separation with high $\text{H}_2\text{O}/\text{CO}_2$ selectivity (~ 550) was the result of a gating effect of the Na^+ ions located in the 8-oxygen ring apertures that regulated their effective size. This highly efficient, in situ water removal through water-conducting nanochannels led to a substantial increase in CO_2 conversion (up to 61.4%, above the equilibrium conversion), resulting in a methanol space-time yield (STY) of $0.809 \text{ g g}_{\text{cat}}^{-1} \text{ h}^{-1}$ at GHSV of $10500 \text{ mL g}_{\text{cat}}^{-1} \text{ h}^{-1}$, 250°C and 35 bar, the highest value ever reported under similar conditions.

Figure 34. Schematics of the membrane reactor (MR) concept and catalytic performance of the MR. Reproduced with permission from ref. 274. Copyright 2020 The American Association for the Advancement of Science.

However, this promising concept has only been experimentally applied to the methanol synthesis pathway. Nevertheless, some revealing works can still be found in the literature outside this pathway. For instance, Li et al. studied a dual reactor in series with inter-stage water removal to enhance the liquefied petroleum gas (LPG) synthesis from CO_2 .²⁷⁸ They used a $\text{CuZnZrAl}/\text{Pd}-\beta$ bifunctional catalyst in the first reactor to synthesize DME-rich products and then a $\text{Pd}-\beta$ zeolite in the second stage to transform the DME into LPGs (see Figure 35). The removal of water enhanced the stability of the $\text{Pd}-\beta$ zeolite second component as the poisoning of acid sites by water molecules was suppressed. Guo et al. used a similar approach by removing water between two fixed bed reactors, although the catalyst was the same in both stages, a $\text{K-Co}/\text{Fe}$ catalyst highly selective to C_{5+} hydrocarbons.²³⁰ Owing to the water removal, the CO_2 conversion was increased from 35% up to 65% at similar catalyst overall loadings and reaction conditions. In a different approach, Kim et al. studied the effect of the reactor type on the CO_2 conversion to olefins by comparing a slurry, a fixed bed and a fluidized bed reactor.²⁷⁹ They found that temperature profiles are crucial in CO_2 hydrogenation as most of the intermediate reactions (i.e., CO_2 to methanol or hydrocarbon synthesis) are exothermic in nature. Hence, fixed-bed reactors are not optimal due to heat accumulation inside the reactor. This heat accumulation was recently studied by Cui et al. by comparing three fixed bed reactor types (the adiabatic, water-cooled and gas-cooled reactor).²⁸⁰ The simulation results showed that in the adiabatic and the gas-cooled reactor the hot spot temperatures inside the system can be within the typical operating temperature range for the catalyst and only the water-cooled system showed advantages in terms of efficient heat removal.

Figure 35. Diagram of improved two-stage process for LPG production. Reproduced with permission from ref. 278. Copyright 2015 Elsevier.

Finally, when looking at ASPEN process simulations, a similar trend is again observed²⁸¹⁻²⁸⁷ with most of the works being done in the methanol pathway field,²⁸¹⁻²⁸⁵ probably owing to the easier downstream separation of this process.²⁸⁶ Here, a typical process comprises an initial feed with pressurization steps followed by a fixed bed reactor. The subsequent unit operations consist of a flash separation where the liquid fraction is removed, a recycle stream of the water-free gases to the reactor, a small purge vent to avoid the accumulation of inert gases and a final distillation based separation unit to obtain the high purity product, typically methanol. Thanks to the recycle of the gaseous stream CO₂ conversions close to 100% can be achieved²⁸¹. Therefore, single pass conversion is not as critical as the high selectivity. However, we need to point out that despite the claim of using renewable H₂ from electrolysis, none of the models start with H₂ at atmospheric pressure and high pressure feeds (30 bar) are assumed. This will definitely hinder the overall economic viability of the process, as the costs associated with pre-compressing atmospheric H₂ are vast.

Summing up, thanks to the recycling stream and the water removal of certain reactor configurations, CO₂ conversions above the thermodynamic limitations can be achieved. Hence, focusing on water removal might have more impact on the overall process than developing complex and expensive catalytic systems. Nevertheless, as stated above, developing catalyst with low selectivity to undesired inert products (e.g., methane) is still crucial to minimize the vent purge and increase the recycle and, as a consequence, the overall conversion. Additionally, studies of how the components of this recycle stream (CO, CH₄, traces of C₂+, etc.) can affect the catalyst is a must. Moreover, very few studies have taken the trouble to analyze if the CO₂ removal levels of their processes are in fact significant.^{19, 288, 289} Last but not least, economic considerations should also be taken in consideration when developing a catalyst for the CO₂ conversion as, with the current green H₂ prices, the CO₂ conversion to hydrocarbons is economically hindered.²⁹⁰

5. CONCLUSIONS AND FUTURE DIRECTIONS

As has been concluded by multiple studies, addressing CO₂ emissions and the associated climate change challenges would require an assortment of innovative solutions. This can be likened to the principles of waste management (termed as waste hierarchy) which includes ‘Reduce, Reuse, Recycle, Recovery and

Disposal'. In this context, 'Reduce' would not only imply practices designed to minimize energy use but also, for example, designing engines and/or power plants that are more efficient so that more energy can be extracted from the same amount of fuel thus reducing the amount needed. 'Reuse', in the technical sense of the word, is not applicable to this situation since fuels and energy sources are ephemeral. 'Recycle' and 'Recovery' are combined into the concept of CCU or a circular carbon economy and finally 'Disposal' relates to CCS. Since the five terms of the waste hierarchy are ordered in terms of desirability, the mix of CO₂ abatement solutions can be considered in a similar fashion. However, based on the current state of the art, CCS is an easier solution to implement which could cause an appreciable impact in the short term. If the technical challenges associated with both DAC and production of renewable H₂ via water electrolysis could be addressed, then CCU has the potential to cause a significant impact in addressing climate change. Furthermore, for the effective implementation of CCU, proper catalyst and process design is required.

Based on the studies on catalyst design discussed here, it can be concluded that the current trend in CO₂ conversion research is towards the design of highly active and more selective catalysts. Different fundamental approaches have been adopted by researchers to identify the active sites and their interaction with reaction intermediates, which has helped in the design of better catalysts. Based on the active sites of catalysts, different reaction pathways were proposed and, in some cases, it was possible to select a more favorable pathway for a particular transformation just by tuning the catalyst composition and synthesis procedure. The majority of this review has discussed the role of various promoters to achieve improved activity and selectivity due to the improved adsorption ability of the modified catalysts. In most cases, it was observed that the use of promoters is necessary for initial activation of CO₂, which cannot otherwise be possible over simple active metal components without promotion. Integrated cascade pathways have been developed for the direct transformation of CO₂ into hydrocarbon fuels and/or useful aromatics/olefins and the associated catalysts were designed accordingly. However, the main challenge of these processes is associated with the low CO₂ conversion, poor product selectivity and dependence on cheap, renewable H₂, which is still an obstacle in CO₂-based refineries. Moreover, since CO₂ conversion mainly deals with reduction by H₂, water is always formed as an unavoidable byproduct. Thus, water removal becomes an important process design parameter because on the one hand, its removal allows the enhanced single pass conversion of CO₂ due to the shift in the reaction equilibrium but on the other hand, if a methanol/CO₂-FTS catalyst is paired with a zeolite for the production of chemicals or fuels, then the water generated in the first step might play a potentially helpful role in maintaining the overall composite catalyst stability.

Looking forward, there are many possibilities for CO₂ valorization in terms of deriving new renewable fine chemicals and fuels, but further attention needs to be paid to both catalyst design and process engineering. Nevertheless, despite all the difficulties, the state of the art is rapidly catching up and we foresee that the practical application of CO₂ derived products will undoubtedly take place in the near future.

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