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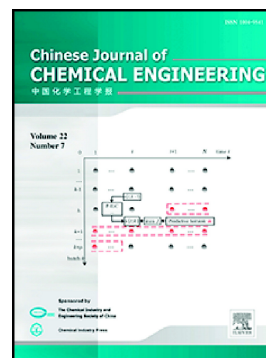
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Recent advances on the reduction of CO₂ to important C₂₊ oxygenated chemicals and fuels[☆]

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ABSTRACT: The chemical utilization of CO₂ is a crucial step for the recycling of carbon resource. In recent years, the study on the conversion of CO₂ into a wide variety of C₂₊ important chemicals and fuels has received considerable attention as an emerging technology. Since CO₂ is thermodynamically stable and kinetically inert, the effective activation of CO₂ molecule for the selective transformation to target products still remains a challenge. The well-designed CO₂ reduction route and efficient catalyst system has imposed the feasibility of CO₂ conversion into C₂₊ chemicals and fuels. In this paper, we have reviewed the recent advances on chemical conversion of CO₂ into C₂₊ chemicals and fuels with wide practical applications, including important alcohols, acetic acid, dimethyl ether, olefins and gasoline. In particular, the synthetic routes for C-C coupling and carbon chain growth, multifunctional catalyst design and reaction mechanisms are exclusively emphasized.

Keywords: CO₂; reduction; C₂₊; chemicals; fuels; catalysis

1. Introduction

For more than two centuries, utilization of carbon-rich fossil fuels such as coal, oil and natural gas, has greatly pushed the progressing of human civilization, economic and social development. However, the burning of fossil fuels lead to the concentration of CO₂ in the atmosphere and reached the highest level of ~400 ppm in recent years; Especially the increasing demand of energy results in the rapid increase level of CO₂ in atmosphere, which bring about adverse climate changes and increasing global temperatures, as a result build up an irreversible and uninhabitable planet for human beings [1-5].

Meanwhile, CO₂ is a ubiquitous and generally available C₁ feedstock in the world. Therefore, the need to simultaneously increase our energy supply while reducing CO₂ emissions is one of the major challenges facing our global society today. In this context, the chemical conversion of CO₂ from greenhouse gas into value-added products with the assistance of H₂ is highly desirable, which could reduce both the current CO₂ emission level and the dependence of chemical production on the depleting fossil fuels. Unfortunately, carbon is in its highest oxidation state in CO₂ and its transformation into other valuable chemicals requires high energy input. Up to now, the transformation of CO₂ to C₁ chemicals and some important products have been studied via chemical, electrochemical and photochemistry methods, such as methane [6,7], methanol [8] formic acid [9], alkyl carbamates [10], cyclic carbonates [11-13], dimethyl carbonate

[14], formic acid esters, urea, carbonic acid esters, decanoic acid esters, amino groups, salicylic acid and so on [15-19]. Our group has engaged in the valorization of CO₂ resources via the coupling reaction with the high-energy compounds into various chemicals and fuels, e.g. alcohols, carbonates, carbamates [20-24], in which processes the construction of C-O or C-N bonds were usually formed. The chemical utilization of CO₂ has also studied in cyclic carbonate synthesis via cycloaddition reaction, which shows promising application in industrial manufacture of cyclic carbonates from CO₂ and epoxides [25,26]. For C₂₊ chemicals (C₂₊ chemicals are compounds which include C-C bond with two or more carbon atoms) and fuels, the formations of new C-C bonds are inevitably involved. However, the formation of C-C bonds via CO₂ hydrogenation is a major challenge in the field of CO₂ chemistry [27]. As a very stable molecule ($\Delta_f G^\theta = -396 \text{ kJ}\cdot\text{mol}^{-1}$), the reduction of CO₂ needs high energy. To convert relatively simple CO₂ molecules into more complex and more active C₂₊ chemicals is a key issue [28]. What's more, it is also a challenge to accurately control carbon chain growth for obtaining desired C-ranged hydrocarbons and oxygenated chemicals. Recently, the advances on the direct conversion of CO₂ to more valuable feedstocks, such as higher alcohols, acetic acid, light olefins and gasoline have not been exclusively reviewed.

It is known that, CO₂ can be hydrogenated to hydrocarbons or oxygenates mainly via two routes. One is CO mediate route, also called CO₂-FTS, which refers to the conversion of CO₂ to CO by reverse water-gas shift (RWGS) reaction and followed by Fischer-Tropsch synthesis (FTS)---the hydrogenation of CO to hydrocarbons [29].

Another is methanol mediate route that is described as methanol that produced from CO₂ hydrogenation converted into other hydrocarbons [30]. In addition, some paper have reported that [31,32] water formed in the process suppressed the conversion of CO₂ and accelerated deactivation of catalyst, Therefore, proper catalyst that could catalyze both RWGS/methanol and C-C coupling reaction is crucial, and the active sites are needed to combine both RWGS/methanol intermediate and C-C coupling because of thermodynamic stability of CO₂.

Another important issue is that the source of H₂. Since the chemical conversion of CO₂ into valuable products should be under the assistance of H₂. Thus, the production of H₂ is quite important. However, hydrogen is unavailability in nature and its production could fall into two main categories, conventional and renewable methods, in accordance to feedstocks [33]. The first category accommodates the methods which produce hydrogen from fossil fuels, covering the methods of hydrocarbon reforming and pyrolysis [34]. For the second category, hydrogen could be produced from renewable resource such as water, wind [35], tidal [36], solar energy [37] and biomass [38-41]. In addition, multi-resources energies coupling is also a development trend for H₂ production.

In this review, we focused on stating current understanding of CO₂ chemical conversion into two-carbon and more than two-carbon (C₂₊) chemicals and fuels, which are usually reduction reactions. An overview of different routes is presented in Figure

2. Synthesis of alcohols

Various technologies are currently being taken to reduce the accumulation of CO₂ in the atmosphere. Among these CO₂ chemical transformation methods, the catalytic conversion of CO₂ into methanol, ethanol and higher alcohols is a potential approach from the viewpoint of high CO₂ conversion rates and high desired products selectivity. In addition, these alcohols can also be continuously converted to more value-added chemicals, such as high-octane gasoline and other feedstocks used for chemical industries.

Until now, much attention has been paid to CO₂ hydrogenation to methanol [42-45]. While ethanol and higher alcohols (C₂₊OH) are more desirable than methanol [46, 47] in many aspects, such as fuel additives, pure fuels and chemicals. However, it is a great challenge to break the high energy kinetic barriers for the formation of C-C bonds to synthesize C₂₊ alcohol. Thus, more efficient catalytic systems are required for the conversion of CO₂ to ethanol and other C₂₊ alcohol.

2.1 Synthesis of ethanol

Among varied value-added CO₂ hydrogenation alcohol products, ethanol is a renewable additive in the fuels and a well-known intermediate in the industries. Nevertheless, it is still a challenge to realize high selectivity to ethanol and only a few researches of direct CO₂ transformation to ethanol are reported, but low ethanol selectivity and yield limit its further application.

Table 1 shows a summary of CO₂ hydrogenation to C₂H₅OH over different catalysts.

Table 1. Results of CO₂ hydrogenation to C₂H₅OH over different catalysts.

Catalyst	Condition			CO ₂ conversion/%	Ethanol selectivity/%	Ref.
	<i>T</i> /K	<i>P</i> / MPa	H ₂ /CO ₂ molar ratio			
Rh-Li/SiO ₂	513	5	3	7.0	15.5	[48]
Rh-Fe/SiO ₂	533	5	3	26.7	16.0	[49]
Pd ₂ CuNPs/P25	473	-	-	-	92.0	[50]
CoMoS	613	10.4	3	32	5.5	[51]
MO ₂ C	473	4	3	10	16	[52]
Cu/MO ₂ C	473	4	3	10	14	[52]
Fe/MO ₂ C	473	4	3	10	16	[52]
CoAlO _x	413	4	3	-	92.1	[53]
α-MoC _{1-x}	473	2	5	3	1	[54]
β- MO ₂ C	473	2	5	6	1	[54]
K/Cu-Zn-Fe	573	7	3	44.4	19.5	[55]

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Kusama *et al.* [48,49] studied metal promoted Rh/SiO₂ catalysts on the hydrogenation of CO₂, and found that among more than 30 additives, Li was the most favorable to ethanol formation, Ethanol selectivity reached to 15.5% with 7.0% CO₂ conversion under optimized conditions. The CO intermediate route was verified by in situ FT-IR in their study. Furthermore, they studied Fe promoted Rh/SiO₂ catalysts [38], result showed that ethanol selectivity was influenced by the amount of Fe added, an ethanol selectivity of 16.0% with 16.7% CO₂ conversion were obtained. Mechanism research showed that Fe changed the electronic states of Rh and that Fe⁰ promoted methanation and prevented ethanol formation, as well as CO and methanol formation.

Inui *et al.* [56] used combined supported Rh catalyst, Fe based modified Fisher-Tropsch catalysts, and Cu-based modified methanol synthesis catalyst, which functioned as partial reduction of CO₂ to CO, C-C bond formation, and –OH group insertion, respectively, to synthesize ethanol via hydrogenation of CO₂. A very high ethanol space–time yields of 0.8–0.9 kg•L⁻¹•h⁻¹ under 30% CO₂ conversion level was obtained, which meant that these multi-functional catalytic routes had exhibited promising application to replace the traditional ethanol synthesis route from ethene hydration.

Tompson *et al.* [52] synthesized a series of M/MO₂C (M = Cu, Pd, Co and Fe) catalyst to evaluate CO₂ hydrogenation at relatively low temperatures of 135–200°C in 1,4-dioxane solvent. And the results showed that methanol was the major product at

135°C, while CH₃OH, C₂H₅OH and C₂₊hydrocarbons were produced at 200°C. Different from the deposition of Cu and Pd additives promoting the CH₃OH synthesis, the deposition of Co and Fe enhanced C–C coupling to produce C₂–C₄ hydrocarbons and ethanol. Mechanism study showed that CO was the intermediate for CO₂ hydrogenation, and Mo₂C had distinct sites for the alcohols and hydrocarbons production, and the metal deposition could alter the activities of these site.

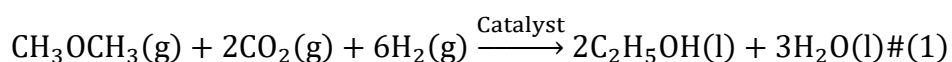
More recently, Pd-Cu nanoparticles (NPs) had been utilized towards producing C₂H₅OH from CO₂ by Huang *et al.* [50] After changing catalysts composition and support. They found Pd₂CuNPs/P25 showed high ethanol selectivity of 92.0% and turnover frequency (TOF) of 359.0 h⁻¹, which might result from charge transfer between Pd and Cu in the ordered pd-Cu NPs/P25, thus increasing the reducibility of surface oxide.

Xiao *et al.* [53] reported a kind of non-noble cobalt catalysts (CoAlO_x) for the selective hydrogenation of CO₂ to C₂H₅OH. Results presented that ethanol selectivity as high as 92.1% could be obtained at 140°C with catalyst reduced at temperature of 600°C. Operando FT-IR spectroscopy revealed that the high ethanol selectivity over the CoAlO_x catalyst might be due to the formation of acetate from formate by insertion of *CH_x, a key intermediate in the production of ethanol from CO₂ hydrogenation. Figure 2 gives obtained data for different catalysts at 140 and 200°C and the data confirmed the extraordinary catalytic performances of CoAlO_x, and Figure 3 gives the electron microscopy characterization of CoAlO_x. SEM showed the platelike morphology still

remained, and TEM showed Co particles highly dispersed on the amorphous Al₂O₃ support.

The hydrogenation of CO₂ to ethanol can be regarded as including the following steps i) reduction of CO₂ to CO. ii) C–C bond growth. iii) –OH group insertion to products [56]. It is generally believed that formate intermediates (*CO, *CH₃, *CO, *CH₃CO) are formed in the process of ethanol synthesis, which are hydrogenated into C₂H₅OH subsequently (proposed reaction mechanism is shown in Figure 4) [48]. And the conversion of *CO into *HCO may be the rate-determining step for CO₂ hydrogenated to ethanol [50].

In particular, Han *et al.* [57] created a new ethanol synthesis route, of which CO₂, H₂ and dimethyl ether (DME) were used as raw materials (Eq.1), catalyzed by a Ru–Co bimetallic catalyst with LiI as promoter. Ethanol selectivity reached to 94.1% in the liquid product as well as 71.7 C-mol% in total products. The proposed mechanism is shown in Figure 5. They speculated three reasons for this high efficiency reaction: 1) Direct involvement of DME in the process of ethanol formation could decrease undesired methane by-products. 2) Methanol produced could be used as a raw material for the production of DME that the selectivity of ethanol is improved. 3) Ru and Co worked well together to speed up the desired reaction synergistically.



$$\Delta H_{298}^{\theta} = -440.6 \text{ kJ/mol}, \Delta G_{298}^{\theta} = -158.3 \text{ kJ/mol}$$

Furtherly, Han *et al.* [58] developed another new synthesis route from

paraformaldehyde, CO₂ and H₂ (Eq. 2), which were accelerated over a Ru–Co bimetallic catalyst. The selectivity of ethanol reached to 50.9 C-mol%. They verified that the synergize of paraformaldehyde hydrogenation, RWGS reaction and methanol homologation contributed to the outstanding result of the reaction, which was also promoted by the cooperation of Ru and Co catalyst. Detailed mechanism is shown in Figure 6.



Another promising technique that utilizing CO₂ is via electroreduction way. Sun *et al.* [59] reported a high-efficiency metal-free catalyst (N-doped mesoporous carbon) for CO₂ electroreduction with almost 100% ethanol selectivity and 77% faraday efficiency. They speculated that high electricity density contributed to dimerization of CO* as well as formation of ethanol. The detailed reaction energy was shown in Figure 7.

As one of the important oxygenated chemicals, ethanol has wide applications in fuel additive and intermediate for synthetic chemistry. At present, the synthesis of ethanol from CO₂ has attracted growing interests and witnessed rapid progress both in the thermal and electrocatalysis routes. To make the production of ethanol from CO₂ into practice, more work should be done in the development of highly active and selective heterogeneous catalyst system. The precise design the non-noble catalysts with the functionalities of CO₂ activation and subsequent transformation towards ethanol, should be paid great attention. Moreover, the systematic study of the

mechanism for C-C bond formation is very helpful for understanding the pathway for selective formation of ethanol. Although great efforts still needed to be deserved, the breakthrough of ethanol synthesis from sustainable CO₂ in pilot scale is believed to be achieved in the near future.

2.2 Synthesis of higher alcohols (C₂₊OH).

Up to now, research progress is mainly focus on the synthesis of methanol and ethanol. Higher alcohols (C₂₊OH) are more desirable in many cases, especially as fuels and fuel additives. However, the synthesis of C₂₊OH via CO₂ hydrogenation is obviously a challenge. The main difficulty of this process is concentrated on the catalyst [60]. Heterogeneous catalysts have the disadvantages of low activity, low C₂₊OH selectivity and high reaction temperature [61]. Therefore, new catalysts with high catalytic performance are needed to be developed.

Han et al. [61] studied the synthesis of C₁₋₅OH from CO₂ hydrogenation via Ru–Rh bimetallic homogeneous catalyst promoted by LiI in DMI solvent. They found the catalyst system could work effectively and the C₂₊ alcohols could be obtained at 160°C, which is the lowest temperature reported so far for producing C₂₊ alcohols via CO₂ hydrogenation. Under the optimized conditions, the alcohols selectivity reached to as high as 96.4%. Noteworthy to say that the alcohols generated by their catalytic system included not only the linear but also branched alcohols, which suggested the reaction pathway is different from the reported CO₂ hydrogenation in the literature.

Han *et al.* [60] reported $\text{Ru}_3(\text{CO})_{12}\text{-Co}_4(\text{CO})_{12}$ homogeneous bimetallic catalyst with bis (triphenylphosphoranylidene) ammonium chloride (PPNCl) as co-catalyst and LiBr as the promoter for the CO_2 hydrogenation. Under this bromide promoted catalytic system, alcohols selectivity achieved as high as 90.8%. This outstanding performance of the catalytic system resulted from the synergize effect of Ru, Co, PPNCl, and LiBr. The bromide promoted Ru catalyst catalyzed the methanol to produce ethanol, Co behaved as accelerating the C_{2+} alcohols. The coordination between the active Ru center (Ru^*) and Cl^- from PPNCl enhanced the electron density of the metal center, which would facilitate the oxidative addition step as well as the hydrogenation step.

$\text{Pt/Co}_3\text{O}_4$ heterogeneous catalysts were also applied to convert CO_2 into higher alcohols by some researchers. Han *et al.* [62] firstly used $\text{Pt/Co}_3\text{O}_4$ catalyst on CO_2 hydrogenation to produce higher alcohols ($\text{C}_2\text{-C}_4$), and the effect of water was investigated. Results showed that, 88.1% alcohol selectivity could be reached under $\text{Pt/Co}_3\text{O}_4$ catalyst at 220°C with water as solvent and DMI (1,3-dimethyl-2-imidazolidinone) as co-solvent. They discovered that water took part in the reaction by providing a hydrogen source, and the C_{2+} alcohols are formed via methanol intermediate route. Li *et al.* [63] paid more attention to morphology effect of Co_3O_4 on higher alcohol synthesis from CO_2 hydrogenation. They found that the Co_3O_4 with both of the nanoplates and nanorods structure performed relative higher selectivity during 50h under mild reaction condition. The highest selectivity of C_{2+}OH is 26.7% at

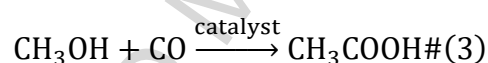
190 °C. The Pt/Co₃O₄-p was much easier reduced, part Co₃O₄ was reduced to CoO and metallic Co in the reaction condition, formed new activate site (Pt-Co/Co₃O_{4-x}).

From the mechanism point of view, in the process of higher alcohol synthesis, methanol is generally considered to form in the first step, which is further converted into ethanol. And these small alcohols act as intermediate to generate larger alcohols subsequently [61]. Han *et al.* [60] considered CO was also formed during the first step, and they put forward the proposed mechanism as shown in Figure 8. Ru catalyst catalyzed the CH₃OH to generate C₂H₅OH, and Co catalyst ([Co]) mainly enhanced the production of C₂₊OH in the reaction.

Electrocatalytic reduction of CO₂ to prepare carbon-based chemical feedstock is an effective way to solve the long-term storage of renewable energy. However, since the reaction involves the transfer of multiple CO₂ molecules and more than 12 electrons, the electrochemical reduction of CO₂ to produce multi-carbon alcohol is still full of challenges. Sargent *et al.* [64] reported a class of core-shell vacancy engineering catalysts that utilize sulfur atoms in the nanoparticle core and copper vacancies in the shell to achieve efficient electrochemical CO₂ reduction to propanol and ethanol (Figure 9). Results showed that the alcohol-to-ethylene ratio increased more than sixfold compared to that of bare-copper nanoparticles, and achieved C₂₊ alcohol production rate of (126±5) mA·cm⁻² with a selectivity of (32±1)% Faradaic efficiency. Their research provided new ideas for the selective production of high energy density liquid alcohol fuels, *e.g.* engine fuels.

3. Synthesis of acetic acid

Carboxylic acids are important basic chemicals in industry and human life. Great progress had been made in formic acid synthesis from CO₂ hydrogenation. The carboxylic acids with two or more C atoms (C₂₊) are more useful in many cases. However, synthesis of C₂₊ carboxylic acids using CO₂ as raw material is challenging. The reported routes suffered from obvious disadvantages, such as low selectivity, low activity, higher reaction temperature and use of expensive and/or toxic reactants. Acetic acid is a significant bulk substance, which is commonly produced by methanol carbonylation. In this process, methanol reacted with carbon monoxide to produce acetic acid according to the Eq.3 [65]:



While, acetic acid generated directly from CO₂ and CH₄ is another route developed in recent years in view of chemical utilization of CO₂. The chemical reaction equation is shown in Eq.6. Although this reaction possessed 100% atom efficiency, it is thermodynamically unfavorable. Thus, it is necessary to find efficient catalytic system to activate these two molecules for this reaction. Actually, some researchers have already conducted research work on catalytic system, for example, zeolite catalytic system, which has uniform molecular size pores, acid catalytic activity, good thermal stability and hydrothermal stability, and can catalyze many reactions with high activity and high selectivity. Huang et al. first reported the co-conversion of CH₄ and CO₂ to acetic acid using the Cu/Co-based metal oxide heterogeneous catalyst. However, the

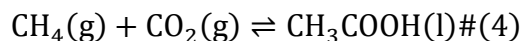
selectivity for acetic acid was only 28% and the product distribution was broad.

Wang *et al.* [66] further reported a co-conversion of methane and CO₂ to produce acetic acid over the bifunctional Zn/H-ZSM-5 catalyst (zinc-modified H-ZSM-5 zeolite) at the range of 523-773K, and also explored the mechanism. Results showed that zinc methyl species ($-\text{Zn}-\text{CH}_3$) were formed by activation of CH₄ from zinc site and followed with inserting of Zn-C bond into CO₂. The final acetic acid formation was through transfer of proton, where Brønsted acid sites played the vital role and the zeolite framework served as a platform for stabilizing and transferring these Brønsted protons.

Park *et al.* [67] reported a synthesis method of CH₃COOH from CO₂ and CH₄ over Cu-M⁺-ZSM-5 catalyst (M⁺ = Li⁺, Na⁺, K⁺ and Ca⁺⁺) which is continuously fed in flow micro-reactor system. They demonstrated that cation ZSM-5 catalysts loaded with Cu nanoparticles could simultaneously activate both methane and CO₂. Acetic acid sustained a yield of 395 $\mu\text{mol} \cdot (\text{g cat})^{-1} \cdot \text{h}^{-1}$ for 10h. Accordingly, the formation rate of CH₃COOH was obtained in the order of K > Na > Ca > Li.

Curet-Arana *et al.* [68] studied the mechanism of co-conversion of CH₄ and CO₂ into acetic acid systematically over MFI zeolite exchanged with Be, Co, Cu, Mg, Mn, and Zn using density functional theory (DFT). Calculations and the results are shown in Fig.10. The whole process could be explained as below: activation of CH₄ led to the formation of ($-\text{Cu}-\text{CH}_3$), while the activation of CO₂ helped the formation of surface carbonate species over cations site (Steps 1–3): insertion of CO₂ into the ($-\text{Cu}-\text{CH}_3$)

produced surface acetate species ($-\text{Cu}-\text{OOCCH}_3$) as a reaction intermediate which abstracted the proton to form acetic acid (Steps 4–5).



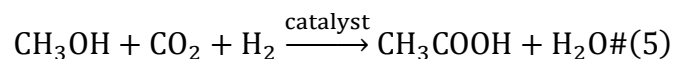
$$\Delta H_{298}^{\theta} = -13.3 \text{ kJ/mol}, \Delta G_{298}^{\theta} = 58.1 \text{ kJ/mol}$$

Recently, Han's group reported a significant progress in synthesizing acetic acid from methanol, CO_2 and hydrogen (Eq.5) over Ru-Rh bimetallic catalysts using imidazole as ligand and LiI as promoter in 1,3-dimethyl-2-imidazolidinone (DMI) solvent [69]. Outstanding yield of 77.0% acetic acid with 22.5 h^{-1} TOF was obtained under 200°C and 12h. More recently, they explored a monometallic catalytic system including $\text{Rh}_2(\text{CO})_4\text{Cl}_2$, 4-methylimidazole (4-MI), LiCl, and LiI, which had advantages of low corrosiveness and easy preparation compared with previously Ru-Rh bimetallic catalysts system [70]. The TOF as well as yield of acetic acid under $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ system reached to 26.2 h^{-1} and 81.8%, respectively, which is more effective than the bimetallic system.

They also conducted experiments to clarify the mechanism, and the results indicated that the reaction did not proceed via the CO route and CO_2 took part in the reaction directly. As shown in Figure 11, LiI reacted with methanol to form CH_3I , then CH_3I was oxidative added to the Rh active species, then CO_2 inserted into CH_3RhI to form the CH_3COORhI ; at last, acetic acid was formed by reductive elimination from CH_3COORhI with H_2 , and LiOH reacted with HI to form LiI and H_2O . In this reaction, LiI promoted acetic acid formation, and LiCl activated catalyst and contributed to the

stability of the catalyst, meanwhile $\text{Rh}_2(\text{CO})_4\text{Cl}_2$ and 4-MI were applied as the ligand.

During this process, CO_2 was directly inserted into the intermediate [69, 70].

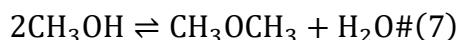
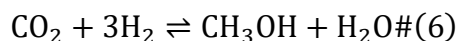


In short summary, the synthesis of acetic acid from CO_2 in the current reports generally employed homogeneous catalyst system. Iodide compounds usually were involved in the reaction system, which has imposed serious equipment corrosion during reaction process. In terms of the production cost, sustainability and safety, heterogeneous catalyst system needed to be developed for this important route. Alternatively, with the depletion of fossil energy, the chemical valorization of CO_2 into acetic acid will exhibit promising application in industrial scale owing to the atom efficiency, abundant carbon source and environmental friendliness.

4. Synthesis of dimethyl ether(DME)

Dimethyl ether (DME) is an important chemical and has received significant attention as a clean fuel source because of its lower NO_x emission and its near-zero smoke evolution compared to traditional diesel fuels. Generally speaking, there are two technologies for the production of DME from CO_2 : 1) a two-step process (dehydration of methanol that produced from CO_2 hydrogenation), as shown in Eqs. (6-7) [71-75]. 2) One-step process: a single step using bifunctional catalyst for both methanol synthesis and methanol dehydration in one reactor [76].

Methanol intermediate route:



Two step route is mainly focused on the catalyst for CO_2 hydrogenation and methanol dehydrogenation. According to current researches, Cu-Zn-Al(CZA) based catalysts are commonly used for methanol synthesis. And different additives are used to modify the conversion rate of CO_2 [77-79]. While for the second step, dehydrogenation of methanol to DME is usually catalyzed by acid catalysts, such as, γ -alumina [73, 75], ZSM-5 [74] and so on.

Figure 12.

Compared with two-step method, the one-step method has remarkable result because of low methanol concentration in the reactor, which could change thermodynamic equilibrium of the reaction [76]. One-step synthesis of DME from CO_2 hydrogenation can break the thermodynamic restriction that exists for methanol synthesis and consequently improve the CO_2 conversion. Moreover, the direct method is more economical compared to the indirect one because of eliminating the cost of methanol purification and higher conversion of methanol. Therefore, one-step process is the development trend of catalytic synthesis of DME from CO_2 [80].

Up to now, the one-step process focuses on $\text{CuO-ZnO-Al}_2\text{O}_3$ /HZSM-5, CuO-ZnO-ZrO_2 / γ -alumina, $\text{CuO-Fe}_2\text{O}_3$ - ZrO_2 /HZSM-5 and so on. The process adopted bifunctional catalysts composed of both methanol synthesis active site and a methanol dehydration active site [81].

Wu *et al.* [82] used CuO–ZnO–Al₂O₃/HZSM-5 catalysts to conduct reaction of one-step producing DME from CO₂. CuO–ZnO–Al₂O₃ catalysts were made by urea–nitrate combustion, which were merged together with HZSM-5 subsequently. Results showed that the amount of urea had a great influence on the structure of the catalyst. With 40% stoichiometry of urea added, CuO–ZnO–Al₂O₃/HZSM-5 (40CZAH) catalyst with smaller CuO and Cu grain size, higher BET and copper surface areas, and lower reduction temperatures were obtained, which resulted in 15% DME yield and 30.6% CO₂ conversion.

Mota *et al.* [83] prepared impregnated catalysts (Cu·ZnO supported on γ -alumina) to study one-step DME synthesis from CO₂ and the highest selectivity reached to 35%, under the operating conditions of higher than 270 °C and 50 bar. They deduced that formation of DME is mainly controlled by catalyst's metal activity instead of the acid function.

It is worth to mention that Ateka *et al.* [84] used CuO–ZnO–ZrO₂ (CZZr)/SAPO-18 and CuO–ZnO–MnO (CZMn)/SAPO-18 to replace conventional CZA/ γ -Al₂O₃ catalyst to produce DME from CO₂. They found CZZr and CZMn metal functionalities exhibited similar behavior during the methanol synthesis step and showed higher DME yield and selectivity compared with CZA. Thereby, favoring the valorization of CO₂ under moderate conditions (3 MPa and H₂/CO_x=3). These results are promising for future studies that focus on optimizing the operating conditions with the objective of CO₂ valorization.

Qin *et al.* [85] reported synthesis of DME from CO₂ over Cu–Fe–Zr/HZSM-5 catalyst in the range of 240 °C–280 °C. The highest CO₂ conversion obtained was around 30% at 260 °C, 3.0 MPa. They put forward that methanol synthesis was the speed control of the reaction and the proposed mechanism was shown in Figure 13. They illustrated that the formation of H₂CO was rate control steps of methanol synthesis. The process model was considered to be an accurate description of intrinsic kinetic of DME synthesis from carbon addition.

5. Synthesis of olefins

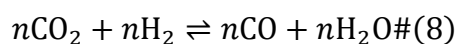
5.1 Light olefins (C₂–C₄)

Another promising route to exploit CO₂ is the hydrogenation to high value added light olefins (C₂–C₄), which are one of the most important intermediates in organic chemical process and are essential feedstocks in petrochemical industry. Currently, they are mainly produced by hydrocarbon fluid catalytic cracking (FCC) and steam cracking of petroleum [86], as well as by alkanes dehydrogenation [87]. The constantly growing demand of light olefins, which has caused the global production capacity to double over the past 15 years, asks for new synthesis processes based on low-cost feedstock.

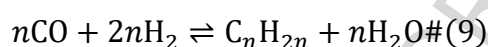
Among numerous studies, the production of light olefins by the hydrogenation of CO₂, would be highly desirable from the viewpoint of CO₂ utilization. However, until now, only few studies have been reported on the selective hydrogenation of CO₂ to C₂–C₄ olefins. The conversion of CO₂ to lower olefins (C₂–C₄) also include two routes:

1) Fischer–Tropsch pathway (RWGS reaction (Eq.8) and the CO hydrogenation to olefins (FTO, Fischer-Tropsch to olefins. Eq.9). and 2) methanol mediated process (MTO, Methanol to olefins Eq.2 and Eq.10).

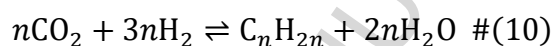
RWAS:



FTO:



Combined reaction:



Iron-based catalysts are valid on RWGS and in favor of CO hydrogenation to olefins. Han *et al.* [88] studied dynamic structure of Fe-based catalyst (α -Fe₂O₃ and γ -Fe₂O₃) for CO₂ hydrogenation using a combination of operando Raman spectroscopy and X-ray Diffraction coupled with online gas chromatography. Results indicated that the structure of iron oxides went through a process of α -Fe₂O₃ (γ -Fe₂O₃) \rightarrow α -Fe₃O₄ (γ -Fe₃O₄) \rightarrow α -Fe (γ -Fe) \rightarrow χ -Fe₅C₂ (θ -Fe₃C) during activation process. And both iron carbides of χ -Fe₅C₂ and θ -Fe₃C showed high activities. χ -Fe₅C₂ exhibited higher selectivity to lower olefins because of its higher effective barrier, but weak alkenes hydrogenation ability. However, θ -Fe₃C showed stronger chain growth probability than χ -Fe₅C₂ because of its strong CO₂ adsorption, which could enhance the chain-growth of adsorbed carbonaceous species. Figure 14 gives the detailed structure performance.

In addition, many researchers have studied various supporters, such as K-OMS-2

nanofiber [89], potassium [90-92], ZIF-8 [93], MIL-53(Al) [93], to modify iron based catalyst.

Suib *et al.* [89] developed a new kind of porous cryptomelane-type octahedral molecular sieve manganese oxide (K-OMS-2) supported Fe nonocatalysts for light olefin production in both CO₂ and CO hydrogenation. High selectivities to light olefins (C^{2-}/C^{-} :1.8–13.4) and catalytic activities (87.2% CO conversion and 45% CO₂ conversion) at temperature of 593K in both CO and CO₂ hydrogenation are owing to the synergistic effect of iron carbides, potassium promoters, and manganese oxide supports.

Song *et al.* [90] also adopted K to promote Fe-based catalysts (Fe–Co/Al₂O₃) for the CO₂ hydrogenation to olefin. They found lower olefins were the majority among C₂₊ hydrocarbons when the atomic ratio of K/Fe was 1. Adding K would diminish the weakly adsorbed hydrogen on the metal surface while increased absorbed CO₂ over catalyst surface which led to a decrease in further hydrogenation of desired produced olefins and thus increased in the light olefins. In addition, they also found Fe-Co bimetallic catalyst showed better property than Fe-Mn catalyst when both of them were promoted by K under the same conditions (573 K ,1.0 MPa). Pathway analysis showed that the light olefins were formed via CO or CO-liked intermediate in CO₂ hydrogenation.

Visconti *et al.* [91] focused on the morphology of K-promoted bulk Fe-based catalyst. They prepared catalysts via ammonium glycolate complexes decomposing,

potassium carbonate impregnating, drying and calcinating. They found that a careful control of the calcination process allowed to achieve high surface area and spinel structure that facilitated its reduction and carburization. The K-Fe catalyst with maximum surface area as well as greatest spinel structure fraction, could lead to majority of light olefins in the products pool (300°C, 0.5Mpa, H_2/CO_2 inlet ratio=3, GHSV=2700cm³·h⁻¹·(g cat)⁻¹). This good result could be ascribed to the maximization of type II sites (active in CO activation and C–C bond formation) instead of type I sites (active in WGS/RWGS process).

Wang *et al.* [92] found CO₂ could react with hydrogen to form methane and C₂-C₄ olefins catalyzed by an Fe/ZrO₂ catalyst. Afterwards they used Na⁺, K⁺, or Cs⁺ to modify Fe/ZrO₂ catalyst, and K⁺ with a proper concentration (0.5wt%–1.0 wt%) showed the best performance to lower olefins with 12% C₂-C₄ yield. The possible reason might be the production of χ -Fe₅C₂ active phase facilitated by K⁺, which was good for light alkenes.

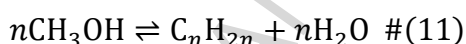
Hu *et al.* [93] also used metal organic frameworks (MOF) with different sizes and morphologies to support Fe-based catalyst. They found that the larger crystals of ZIF-8 supporter performed lower selectivity of olefins, due to the influence of secondary hydrogenation reaction in the process of internal diffusion.

The direct CO₂ hydrogenation to hydrocarbons proceeds via a modified Fischer-Tropsch synthesis process. However, this process favors the hydrogenation of surface adsorbed intermediates, resulting in the ready formation of methane with a

decrease in chain growth, Thus, it remains a grand challenge to simultaneously achieve high selectivity for lower olefins and low selectivity for CH₄

The indirect route of lower olefins production from CO₂ includes conversion of CO₂ into methanol and olefins production from CH₃OH (MTO) (Eq.11). Until now, MTO route have attracted attention from many researchers. While the water formed in the process of methanol synthesis will impede the reaction seriously as well as the activity of catalyst [94]. Thus, there is a need to find high efficiency catalyst to enhance catalytic activity and stability.

MTO:



SAPO-34 is a promising industrial catalyst mainly because of its high selectivity to C₂H₄ and C₃H₆. Liu *et al.* (2017a)[95] and Sun *et al.* (2017b) [96] reported a bifunctional catalyst composed of In-Zr oxide for CO₂ activation and SAPO-34 zeolites for C-C coupling, which could convert CO₂ to C₂-C₄ olefins with 80%-90% selectivity. The design of this bifunctional catalyst could break through the thermodynamic limitations in the process of methanol synthesis, because of the equilibrium shift resulted from methanol consumed [95]. The adding of zirconium was in favor of methanol formation from CO₂ hydrogenation because of the new building vacancies as well as resisting sintering of oxide particles. Additionally, no significant deactivation of catalyst was observed within 150 hours, which was potential for application in industry[96].

Li *et al.* [97] also produced ZnZrO/SAPO tandem catalyst to catalyze MTO reaction. CH_xO species (not only methanol) via CO₂ hydrogenation were generated firstly over ZnZrO, which were transferred onto SAPO zeolite subsequently.

Wang *et al.* [98] employed a bifunctional catalyst consisting of SAPO-34 and ZnGa₂O₄ to catalyze CO₂ to lower olefins, with 86% selectivity and 13% CO₂ conversion at 370 °C. They gave the possible reaction mechanism shown in Figure 15. and speculated the oxygen vacancies on the surface of ZnGa₂O₄ were used to activate CO₂ to form formate and methoxide species, which were formed into methanol intermediate subsequently.

In addition to chemical routes to use CO₂, electrochemical reduction of CO₂ to desired products also studied by many researchers. For example, Sargent *et al.* [99] reported CO₂ electroreduction to ethylene over copper electrocatalyst reaching to 70% faradaic efficiency at -0.55 volts versus a reversible hydrogen electrode (RHE) (Figure 16). Recently, Bell *et al.* [100] reported copper catalyst for electrochemical reduction of CO₂. Specially, they substituted pure copper for CuAg bimetallic electrodes, which was found to show higher selectivity to multi-carbon products. Higher selectivity was on account of selective inhibition of hydrogen evolution. And it was caused by compressive strain in the process of CuAg surface alloy formation. A small quantity of Ag could promote the selectivity to multi-carbon oxygenated Cu surface in the reaction of CO₂ electroreduction. Cu nanocatalyst has advantages in the electrocatalytic reduction of CO₂ to C₂₊ products due to good ability of C-C coupling.

Karen *et al.* [101] developed a metal-ion battery recycling method to regulate the crystal surface of Cu nanocatalysts based density functional theory(DFT). And a highly selective electrocatalytic reduction of CO₂ to produce C₂₊ products could be achieved. They also constructed a copper-ion battery with the highest faraday efficiency of 60%, an H₂ ratio of less than 20% in the product, as well as a C₂₊ current density of about 40 mA•C•m⁻². Gewirth *et al.* [102] developed a method of converting CO₂ into multi-carbon hydrocarbons and oxygenates. When the alloy film contained 6% Ag, CO₂ electroreduction showed the better performance, and the Faradaic efficiency of ethylene and ethanol reached to 60% and 25%, respectively. In addition, Minteer *et al.* [103] studied bioelectrochemical CO₂ reduction to produce ethylene and propene over a metalloenzyme.

In summary, there are two synthesis routes of lower olefins (C₂-C₄) process via CO₂ hydrogenation. One is Fischer–Tropsch pathway (RWGS reaction (Eq.1) and the CO hydrogenation to olefins (FTO, Fischer-Tropsch to olefins. Eq.10). In this route, Fe based catalysts show good performance. Another important process is methanol mediated process (MTO, Methanol to olefins Eq.2 and Eq.11). Zeolites are often employed into this route. For electrochemical route to utilize CO₂, copper electrode and alloy are often employed as electrodes.

5.2 Higher olefins

It is worth to mention that Guo *et al.* [82] created a bio-promoters-modified

catalyst for CO₂ hydrogenation into alkenes. The catalyst was composed of iron carbides as well as alkali promoters from corncob, based on the synergistic catalysis occurring in biomass enzyme. Compared with chemical promoters, potassium derived from bio-accelerator showed a stronger migration ability during CO₂ hydrogenation, because of enriched K⁺ on the surface facilitate carbides formation, which increase C-C coupling activity. The specific reaction mechanism was shown in Figure 17. The experimental results showed alkenes selectivity of 72% and 50.3% C₄–18 alkenes selectivity.

6. Synthesis of gasoline

Gasoline (C₅–C₁₁ hydrocarbons), is a significant transportation fuel used widely all over the world [28]. C₅–C₁₁ hydrocarbons are generally obtained in three ways: 1) by refining petroleum 2) from syngas by FTS process; 3) MTG (methanol to gasoline) process [104]. Converting CO₂ to fuels not only contribute to CO₂ emission reduction, but also provide valuable fuels. However, because of the chemical inert and thermodynamically stable of CO₂, it is a challenge to transform CO₂ to long chain product, as C₅–C₁₁ hydrocarbons.

CO₂ can be hydrogenated to hydrocarbons by either direct or indirect route. the direct CO₂ hydrogenation (CO₂-FT) is often described as the combination of the reduction of CO₂ to CO via reverse water-gas shift (RWGS) reaction and subsequent hydrogenation of CO to hydrocarbons via Fischer-Tropsch synthesis (FTS).

Sun *et al.* [105] succeeded in direct hydrogenation of CO₂ to produce fuels using multifunctional Na-Fe₃O₄/HZSM-5 catalyst which provided three types of active sites Fe₃C₄, Fe₅C₂ and acid sites, that catalyzed RWGS, olefins synthesis and oligomerization isomerization aromatization respectively (Figure 18). Results showed that 22% CO₂ conversion with 78% gasoline selectivity, and 4% methane selectivity were obtained. Changing zeolite type and/or catalyst's integration manner would lead to different gasoline composition. What was worth mentioning is that low ratio of H₂/CO₂ in feed gas was permitted by this multifunctional catalyst, which decreased hydrogen cost. Moreover, the catalyst showed stability for 1000 hours. These meant that CO₂-gasoline route over Na-Fe₃O₄/HZSM-5 catalyst had broad application prospects.

However, the indirect route is generally performed via using different reactors with syngas, and/or forming intermediate of methanol [105]. Sun *et al.* [28] reported a bifunctional catalyst consisting of In₂O₃ and HZSM-5, which could convert CO₂ into C₅₊ hydrocarbons with 78.6% selectivity and only 1% CH₄ selectivity at 13.1% CO₂ conversion. They speculated methanol formed from CO₂ hydrogenation at the site of oxygen vacancy over the surface of indium oxides catalyst, which was subsequently transformed into hydrocarbons inside HZSM-5 (Figure 19). In addition, the number of active vacancies determine the activity of catalyst. That meant using a proper support and/or introducing modifiers could enhance catalytic activity. Industry test also showed a good results of pellet catalyst, which meant a potential application in the industries.

In contrast, the direct route is more economic and environmentally benign since the direct route usually produce CO and light paraffins as major products owing to weak CO hydrogenation activity and over-hydrogenation of olefins. Gasoline-range hydrocarbons are generally produced from refining of petroleum, or from syngas via FTS process, or from methanol-to-gasoline (MTG) process¹⁹. So far, there has been no report on highly selective synthesis of gasoline from direct CO₂ hydrogenation. The key to this process is to search for a highly efficient catalyst.

7. Conclusion

Undoubtedly, the chemical utilization of CO₂ has received significant and increasingly attention worldwide as an important carbon source with the gradual depletion of fossil energy. The utilization of CO₂ is being developed towards the environment friendly, diversified and efficient processes. The reduction of CO₂ to C₂₊ chemicals and fuels, e.g. alcohols, acetic acid, dimethyl ether, olefins and gasoline, has witnessed rapid growth in recent years. Definitely, the new emerging green catalytic technology will play an important role in the efficient utilization of CO₂ as cheap and easily available carbon oxygen sources. In order to improve the efficiency of the catalytic process, new catalytic material with high efficiency is needed to be developed. The CO₂ conversion was restrained by reaction thermodynamics, the intrinsic catalytic activity must be excellent, simultaneously the selectivity should be improved. Additionally, the lifetime of the catalyst also could be long enough to meet the

requirement of the industrialization. The development of the reduction catalyst with the good activity and durability is the prerequisite of the industrialization. Meanwhile, the in-depth understanding of the reaction mechanisms relevant to C=O bond activation and C-C bond on the catalyst surface are crucial for developing more effective catalyst system. Besides the development of catalyst with remarkable activity and stability, the design of specific reactor is inevitable for the enlargement of the technology.

In some extent, the chemical utilization of CO₂ to chemicals and fuels is beyond the scope of the field of CO₂ chemistry, the feasibility of the practical application of this route is dominantly depending on the source of cheap hydrogen. From a practical view-points, the comprehensive and economical assessment of varied production routes via hydrogenation of diverse CO₂ resources as raw materials should be clarified. It should be noted the storage and remote transfer of hydrogen is difficult so far. In particular, the reduction transformation of CO₂ with H₂ into readily stored and transported chemicals and fuels is highly desired. The integration of multiple sources of energy, e.g. solar energy, wind energy and nuclear energy, could potentially provide abundant and complementary H₂ for CO₂ reduction. Importantly, CO₂-free H₂ source is beneficial for neat CO₂ mitigation, which could be realized together with the development of renewable energy or atomic energy in the future.

The transformations of CO₂ to important chemicals and fuels have demonstrated enormous potential and now are considered as an important route for CO₂ chemical utilization on large scale. At present, most of the new-developed technologies are still

in the stage of laboratory study and engineering demonstration. The comprehensive evaluation of the catalyst efficiency, durability, cost and energy integration on the industrial demonstration scale has great significance for the practical applications.

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Figure captions

Figure 1. Overview of the CO₂ conversion routes to C₂+ chemicals.

Figure 2. The performance of various catalysts in CO₂ hydrogenation. Reaction conditions: catalyst (20 mg), H₂O (2 mL), initial pressure 4.0 MPa (H₂/CO₂=3:1), 15 h, 140 °C (a) or 200 °C (b). The yields and selectivities are based on the number of moles of carbon [53].

Figure 3. Electron microscopy characterization of CoAlO_x - 600. a) SEM image. b) TEM image (inset: size distribution of the Co NPs). c) HAADF - STEM image. d–f) EDX elemental maps for CoAlO_x - 600 (d), Al (e), and Co (f). g, h) HRTEM images. i) FFT image of the Co NPs corresponding to the HRTEM image in (h). j) EELS result. The pink circles highlighted the cobalt particles [53].

Figure 4. The proposed reaction mechanism of ethanol synthesis from CO₂+H₂ [48].

Figure 5. The proposed mechanism of ethanol synthesis from CO₂, H₂ and CH₃OCH₃ [57].

Figure 6. The synergy of the reactions for ethanol synthesis from paraformaldehyde, CO₂ and H₂. Ru* and Co* represent the active species of Ru and Co, respectively [58].

Figure 7. Calculated reaction energy diagrams for the electroreduction of CO₂ to ethanol over the pyridinic and pyrrolic N sites [59].

Figure 8. Proposed mechanism of C₂+OH synthesis from CO₂ hydrogenation [60].

Figure 9. Catalyst design and structural characterization. a) Preparation of ethanol and propanol by electrochemical reduction of CO₂ using Cu₂S-Cu-V core-shell-vacancy

copper. b-c) Structural characterization of V-Cu₂S. d-g) Structure Characterization of Cu₂S-Cu-V.

Figure 10. An ostensible mechanism for the Co-Conversion of CH₄ and CO₂ into acetic acid over Cu-M⁺-ZSM-5 Zeolite: (Steps 1–3) activation of CH₄ leads to the formation of (–Cu–CH₃), while the activation of CO₂ helps in the formation of surface carbonate species over cations site. (Steps 4–5): insertion of CO₂ into the (–Cu–CH₃), produces surface acetate species (–Cu–OOCCH₃) as a reaction intermediate which abstracts the proton to form acetic acid [68].

Figure 11. Proposed mechanism of the reaction over the Rh-based catalytic system [70].

Figure 12. General DME synthesis scheme.

Figure 13. The process simulation of the methanol synthesis reaction from CO₂ hydrogenation on Cu(111) via the formate pathway(brown, Cu; gray, C; red, O; white, H) [85].

Figure 14. Scheme of structure - performance relationship of α -Fe₂O₃ and γ -Fe₂O₃ catalysts for CO₂ hydrogenation during activation and reaction processes [88].

Figure 15. A possible reaction mechanism for the conversion of CO₂ into methanol on the Zn–Ga–O catalyst [98].

Figure 16. Structure and performance of the polymer-based gas diffusion electrode. (A) Schematic illustration of the graphite/carbon NPs/Cu/PTFE electrode. (B)

Cross-sectional SEM image of a fabricated graphite/carbon NPs/Cu/PTFE electrode.

(C) SEM image of Cu nanoparticles sputtered on the PTFE membrane. (D) Comparison of ethylene faradaic efficiencies on graphite/carbon NPs/Cu/PTFE and graphite/Cu/PTFE electrodes for CO₂-RR in 7 M KOH electrolyte. Values are means, and error bars indicate SD (n = 3 replicates) [99].

Figure 17. Reaction scheme for CO₂ hydrogenation to α -olefins. The existences of biopromoters weaken secondary hydrogenation of olefins and strengthen the reaction activity of C–C coupling [82].

Figure 18. Reaction scheme for CO₂ hydrogenation to gasoline-range hydrocarbons. The CO₂ hydrogenation reaction over Na–Fe₃O₄/Zeolite multifunctional catalyst takes place in three steps: (1) an initially reduced to CO intermediate via RWGS, (2) a subsequent hydrogenation of CO to α -olefins intermediate via FTS and (3) the formation of gasoline-range hydrocarbons via the acid-catalysed oligomerization, isomerization and aromatization reactions [105].

Figure 19. Molecular-level mechanism for CO₂ hydrogenation into hydrocarbons. a) Energy profile from DFT calculations for CO₂ hydrogenation to CH₃OH on the In₂O₃(110) surface (D and P stand for defective and perfect surfaces with and without the oxygen vacancy, respectively). b) Schematic of the hydrocarbon-pool mechanism for CH₃OH conversion into hydrocarbons inside HZSM-5. c) Schematic for the formation of CH₃OH from CO₂ at the oxygen vacancy site on the In₂O₃ catalyst surface, which involve four major steps: (1) CO₂ adsorption at the oxygen-vacancy site, (2) sequential hydrogenation of the adsorbed CO₂ species to CH₃OH, (3) CH₃OH

desorption, which leads to the surface without the oxygen vacancy, and (4) hydrogenation of the surface to regenerate the oxygen-vacancy site. d) Schematic for hydrocarbon formation from CH_3OH at the acidic site inside the pores of the HZSM-5 catalyst via the hydrocarbon-pool mechanism [28].

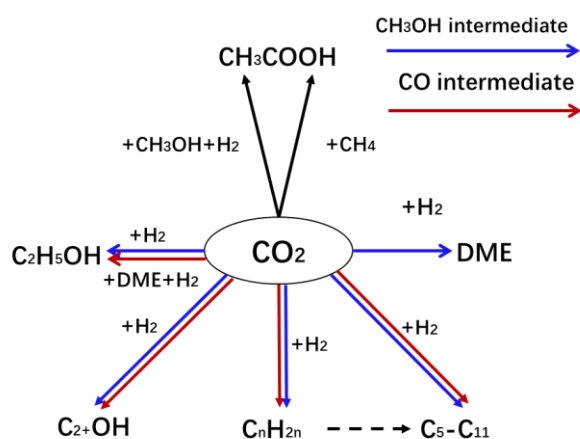


Figure 1. Overview of the CO_2 conversion routes to C_2+ chemicals.

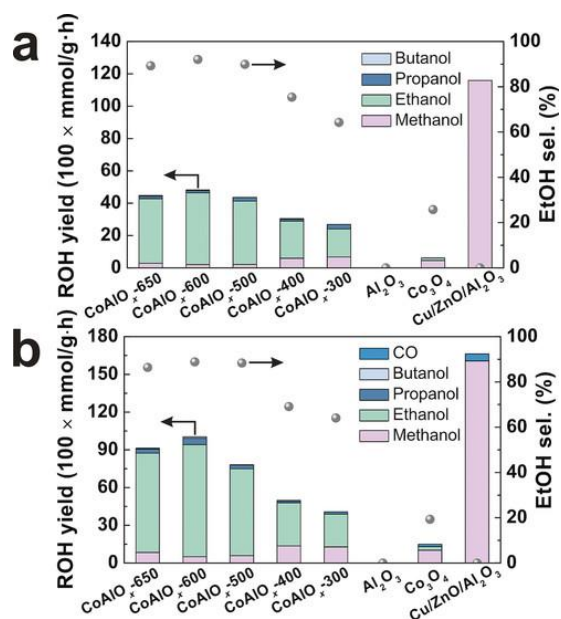


Figure 2. The performance of various catalysts in CO₂ hydrogenation. Reaction conditions: catalyst (20 mg), H₂O (2 mL), initial pressure 4.0 MPa (H₂/CO₂=3:1), 15 h, 140 °C (a) or 200 °C (b). The yields and selectivities are based on the number of moles of carbon [53].

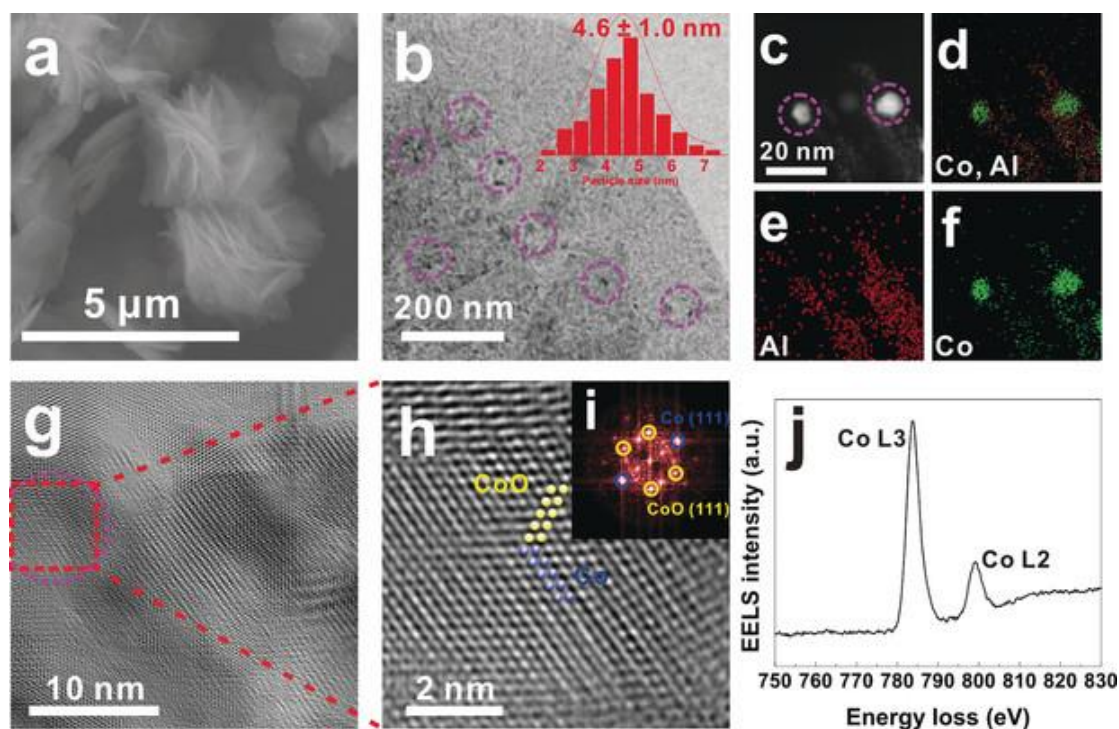


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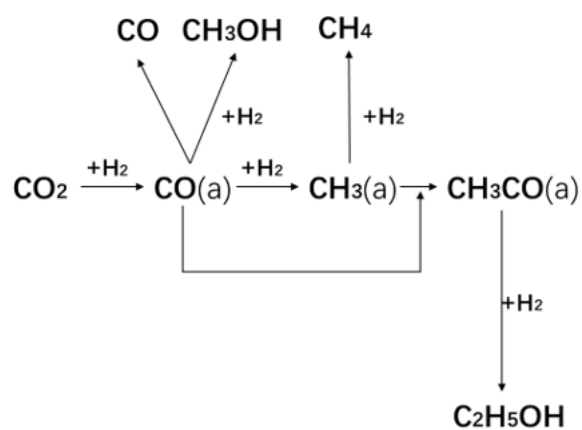


Figure 4. The proposed reaction mechanism of ethanol synthesis from $\text{CO}_2 + \text{H}_2$ [48].

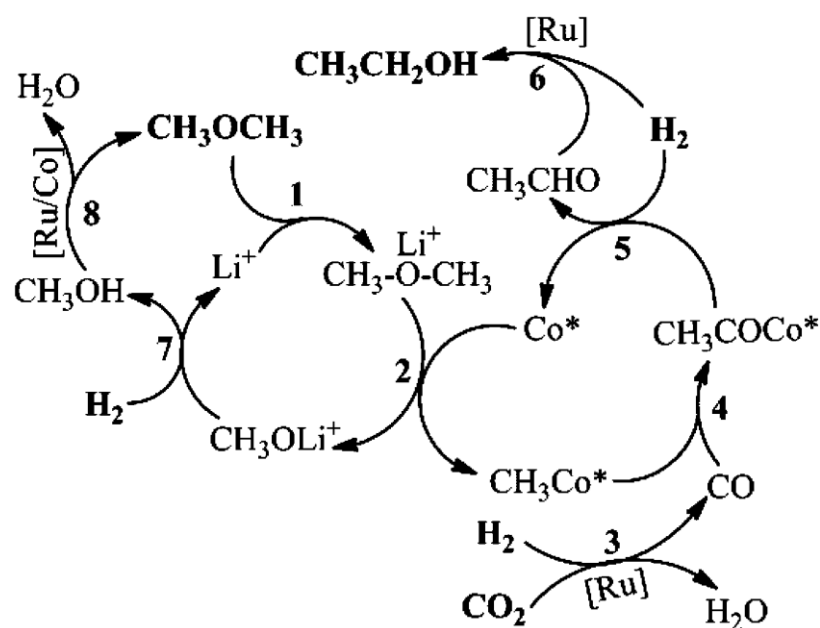


Figure 5. The proposed mechanism of ethanol synthesis from CO_2 , H_2 and CH_3OCH_3

[57].

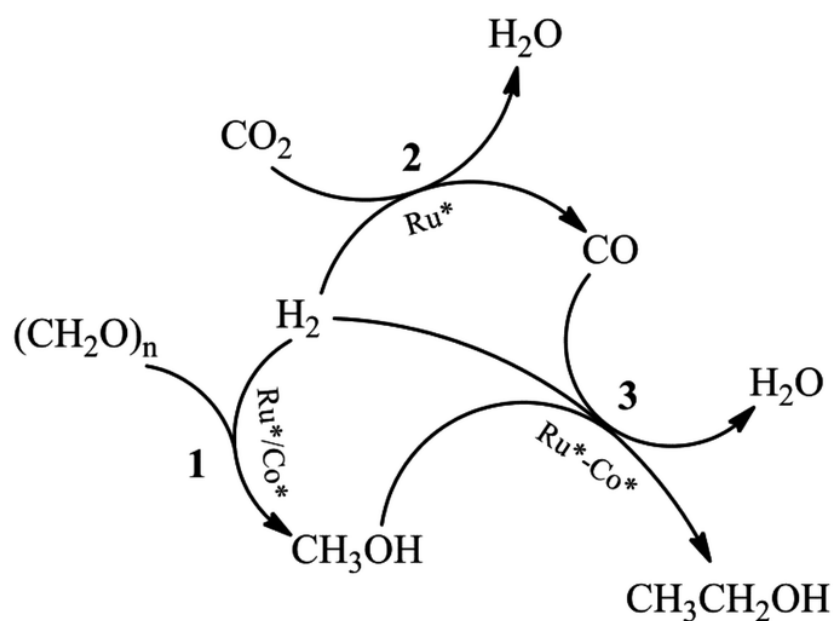


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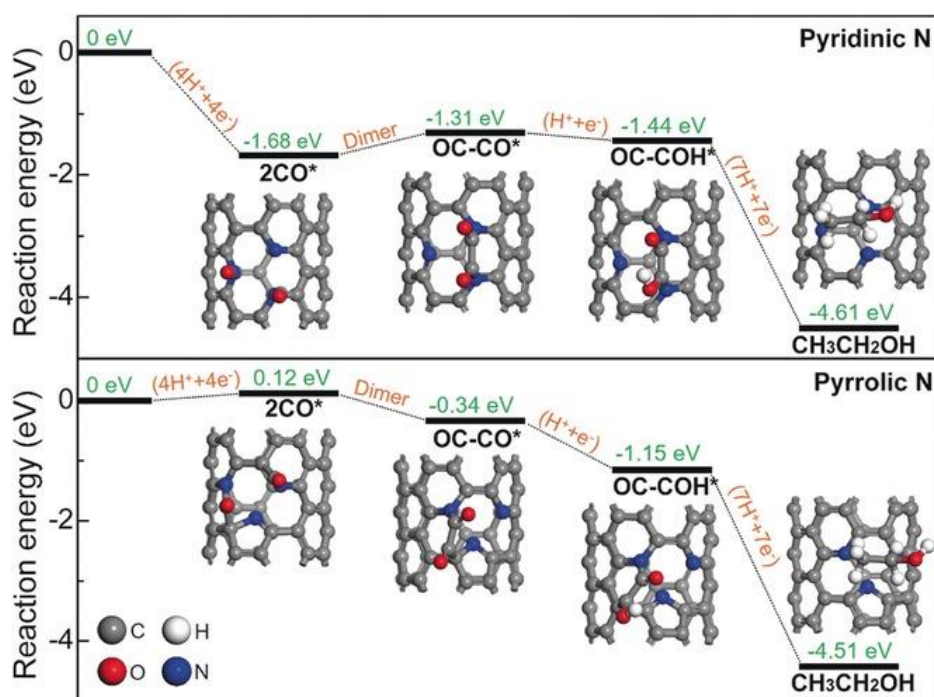


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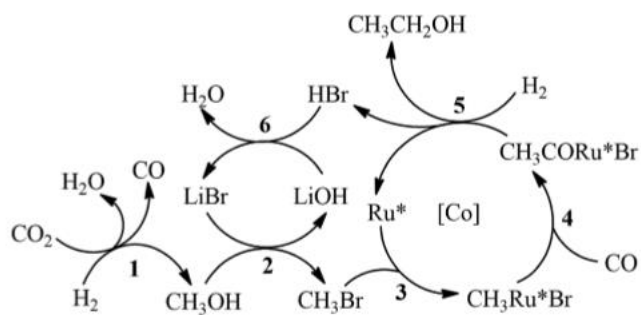


Figure 8. Proposed mechanism of C_2^+OH synthesis from CO_2 hydrogenation [60].

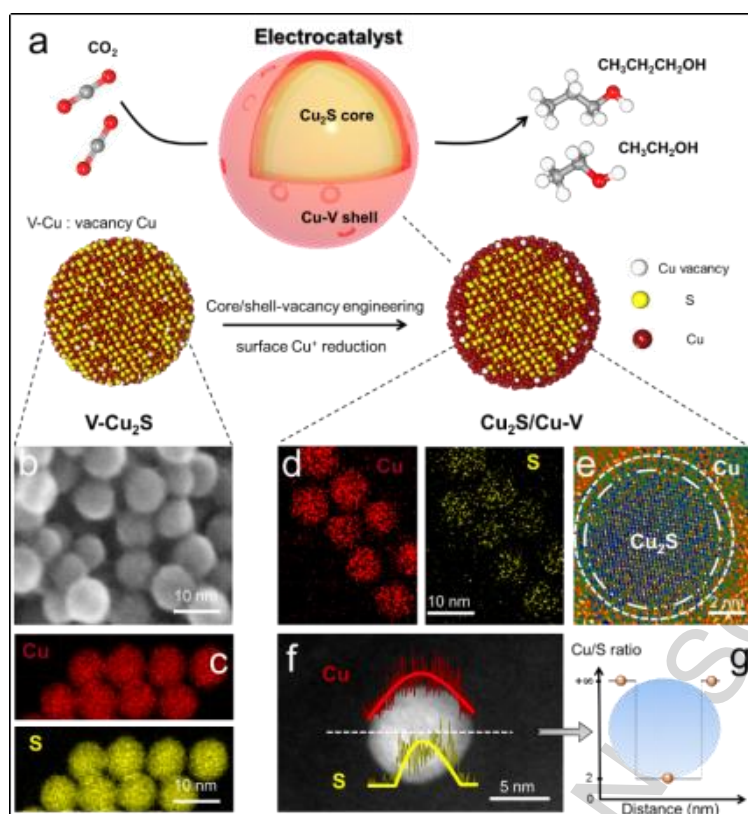


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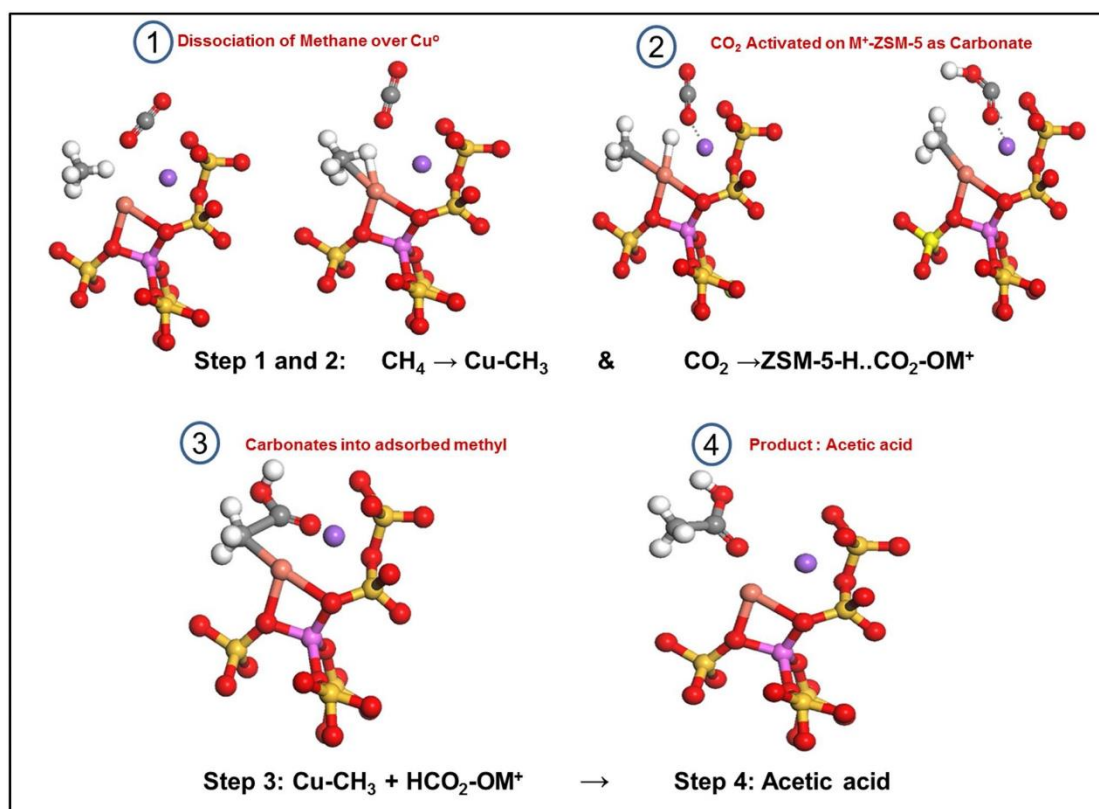


Figure 10. An ostensible mechanism for the Co-Conversion of CH_4 and CO_2 into acetic acid over $\text{Cu-M}^+\text{-ZSM-5}$ Zeolite: (Steps 1–3) activation of CH_4 leads to the formation of (-Cu-CH_3) , while the activation of CO_2 helps in the formation of surface carbonate species over cations site. (Steps 4–5): insertion of CO_2 into the (-Cu-CH_3) , produces surface acetate species (-Cu-OOCCH_3) as a reaction intermediate which abstracts the proton to form acetic acid [68].

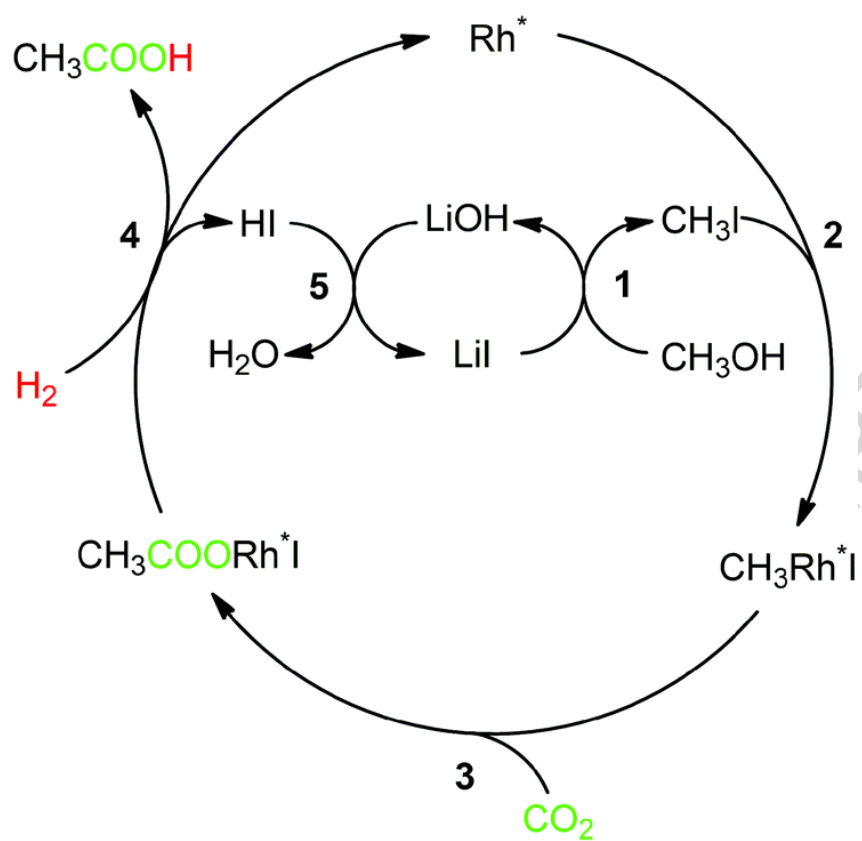


Figure 11. Proposed mechanism of the reaction over the Rh-based catalytic system [70].

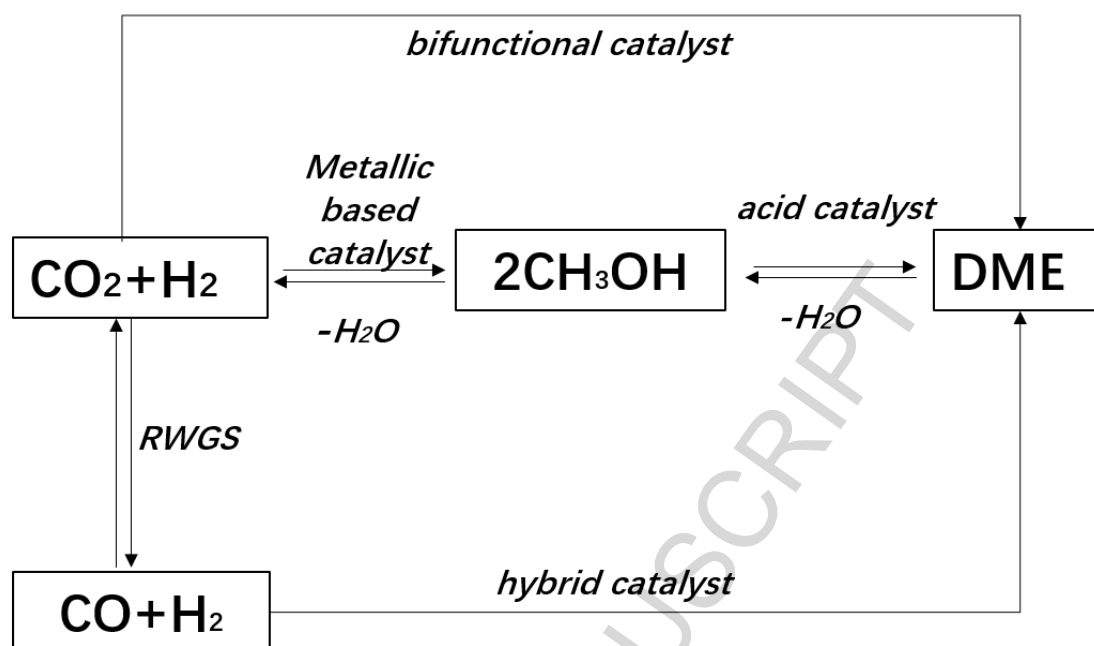


Figure 12. General DME synthesis scheme.

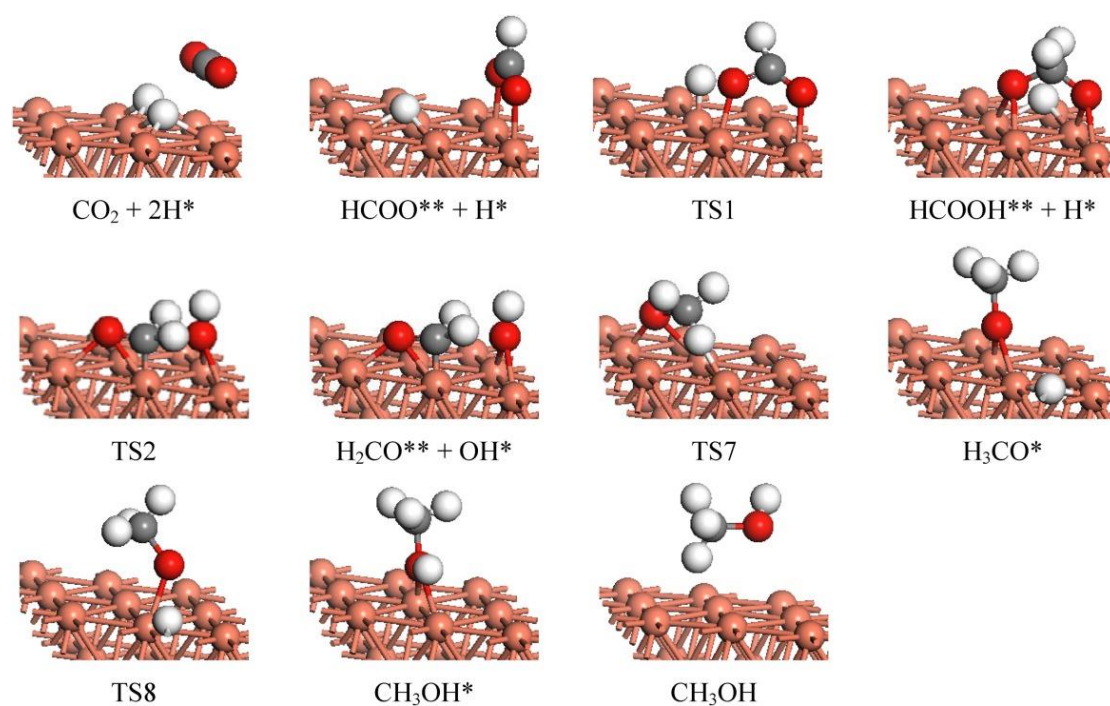


Figure 13. The process simulation of the methanol synthesis reaction from CO_2 hydrogenation on $\text{Cu}(111)$ via the formate pathway (brown, Cu; gray, C; red, O; white, H) [85].

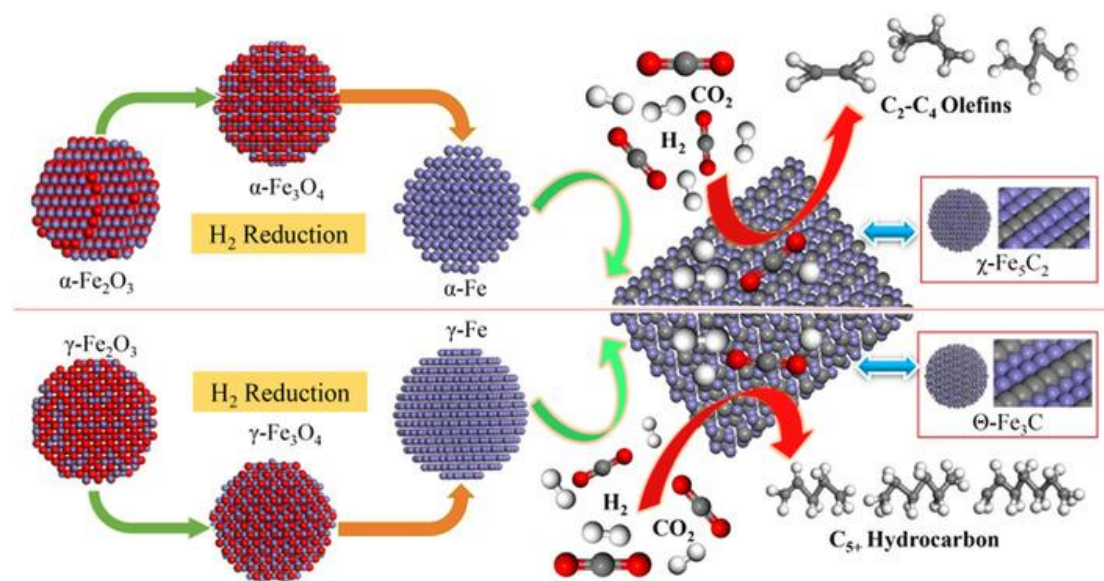


Figure 14. Scheme of structure-performance relationship of α -Fe₂O₃ and γ -Fe₂O₃ catalysts for CO₂ hydrogenation during activation and reaction processes [88].

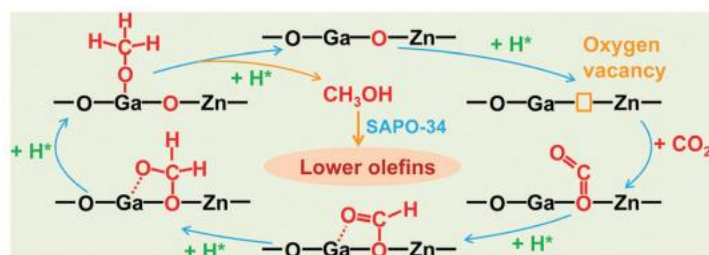


Figure 15. A possible reaction mechanism for the conversion of CO₂ into methanol on the Zn–Ga–O catalyst [98].

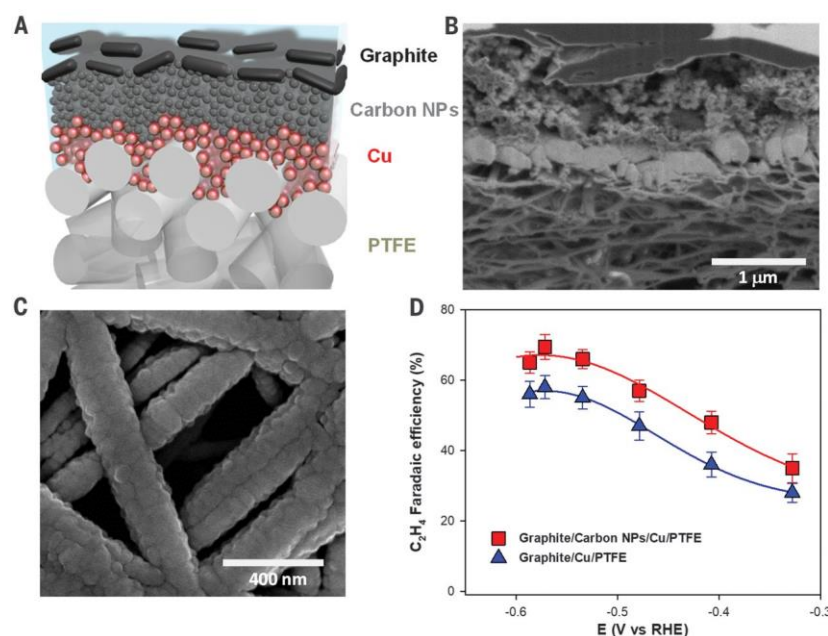


Figure 16. Structure and performance of the polymer-based gas diffusion electrode.

(A) Schematic illustration of the graphite/carbon NPs/Cu/PTFE electrode. (B) Cross-sectional SEM image of a fabricated graphite/carbon NPs/Cu/PTFE electrode. (C) SEM image of Cu nanoparticles sputtered on the PTFE membrane. (D) Comparison of ethylene faradaic efficiencies on graphite/carbon NPs/Cu/PTFE and graphite/Cu/PTFE electrodes for CO_2 -RR in 7 M KOH electrolyte. Values are means, and error bars indicate SD ($n = 3$ replicates) [99].

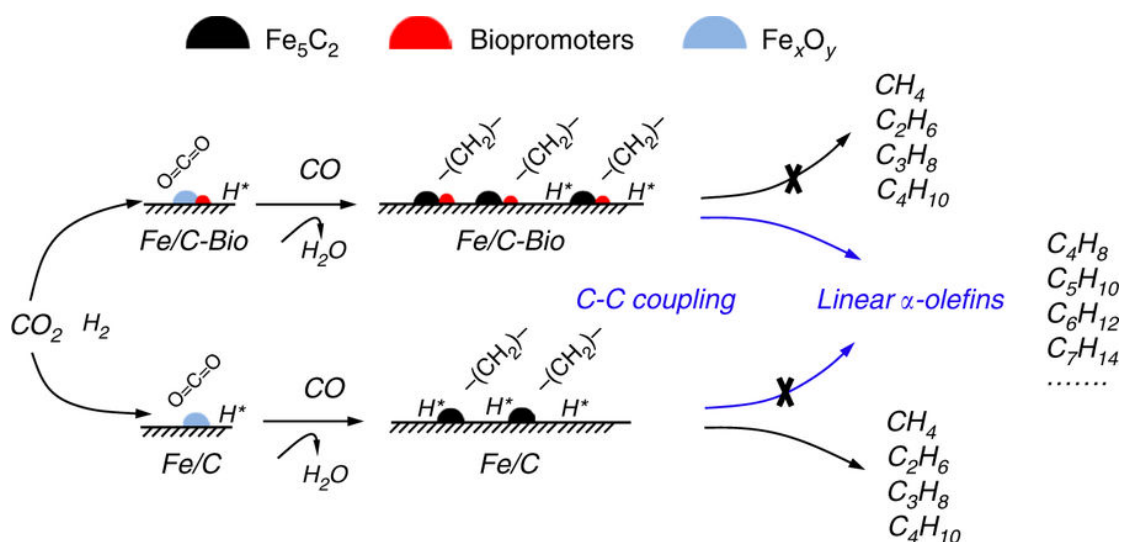


Figure 17. Reaction scheme for CO₂ hydrogenation to α-olefins. The existences of biopromoters weaken secondary hydrogenation of olefins and strengthen the reaction activity of C–C coupling [82].

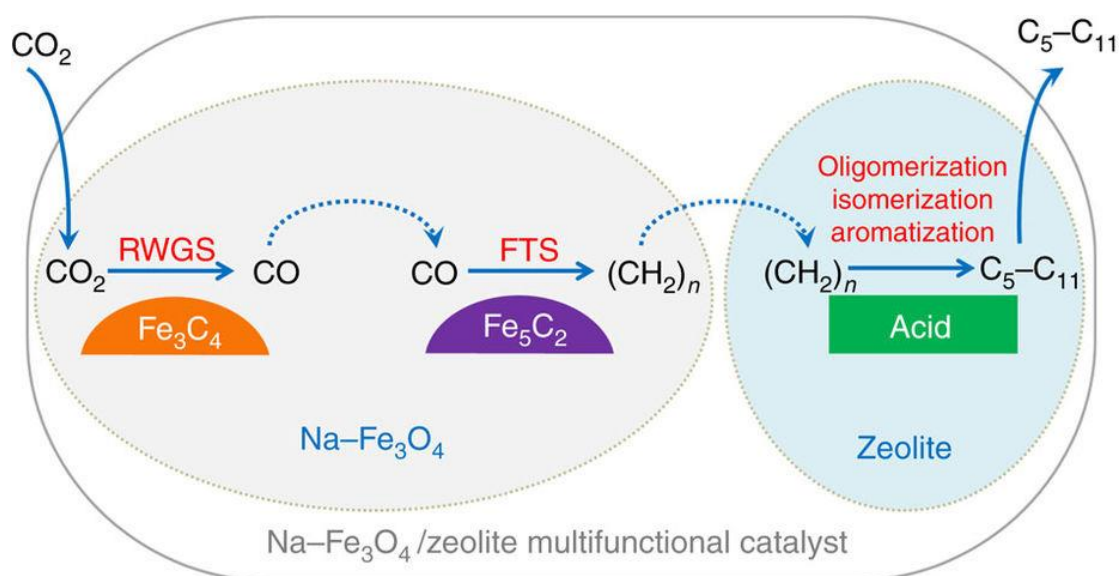


Figure 18. Reaction scheme for CO₂ hydrogenation to gasoline-range hydrocarbons.

The CO₂ hydrogenation reaction over Na-Fe₃O₄/Zeolite multifunctional catalyst takes place in three steps: (1) an initially reduced to CO intermediate via RWGS, (2) a subsequent hydrogenation of CO to α -olefins intermediate via FTS and (3) the formation of gasoline-range hydrocarbons via the acid-catalysed oligomerization, isomerization and aromatization reactions [105].

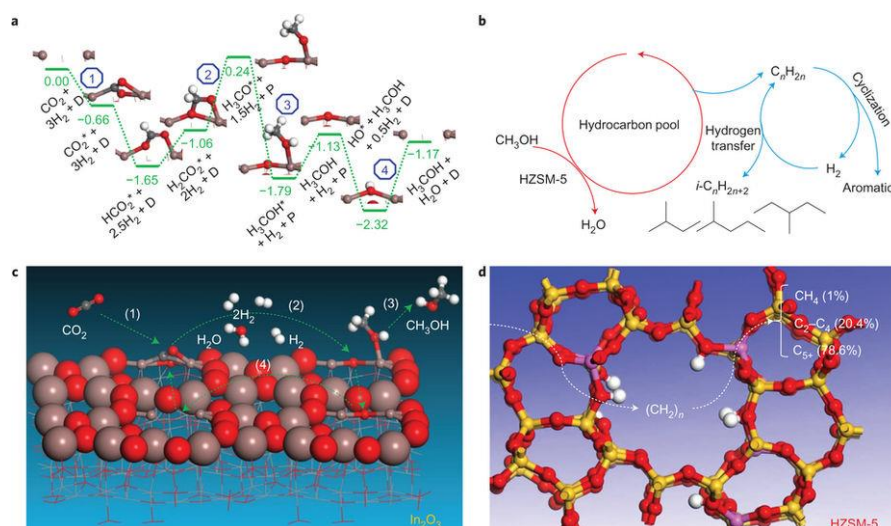
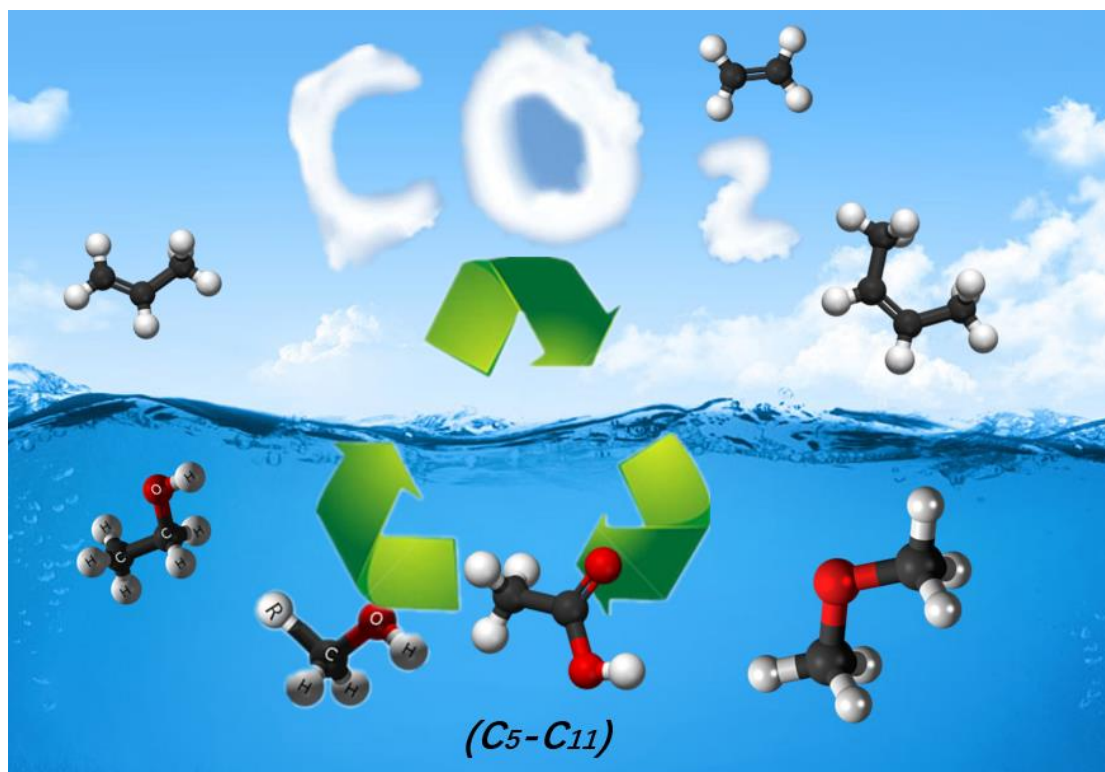


Figure 19. Molecular-level mechanism for CO₂ hydrogenation into hydrocarbons. a) Energy profile from DFT calculations for CO₂ hydrogenation to CH₃OH on the In₂O₃(110) surface (D and P stand for defective and perfect surfaces with and without the oxygen vacancy, respectively). b) Schematic of the hydrocarbon-pool mechanism for CH₃OH conversion into hydrocarbons inside HZSM-5. c) Schematic for the formation of CH₃OH from CO₂ at the oxygen vacancy site on the In₂O₃ catalyst surface, which involve four major steps: (1) CO₂ adsorption at the oxygen-vacancy site, (2) sequential hydrogenation of the adsorbed CO₂ species to CH₃OH, (3) CH₃OH desorption, which leads to the surface without the oxygen vacancy, and (4) hydrogenation of the surface to regenerate the oxygen-vacancy site. d) Schematic for hydrocarbon formation from CH₃OH at the acidic site inside the pores of the HZSM-5 catalyst via the hydrocarbon-pool mechanism [28].



Graphical abstract