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Recent advances on the reduction of CO_2 to important C_{2+} oxygenated chemicals and fuels☆

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ABSTRACT: The chemical utilization of CO_2 is a crucial step for the recycling of carbon resource. In recent years, the study on the conversion of CO_2 into a wide variety of C_{2+} important chemicals and fuels has received considerable attention as an emerging technology. Since CO_2 is thermodynamically stable and kinetically inert, the effective activation of CO_2 molecule for the selective transformation to target products still remains a challenge. The well-designed CO_2 reduction route and efficient catalyst system has imposed the feasibility of CO_2 conversion into C_{2+} chemicals and fuels. In this paper, we have reviewed the recent advances on chemical conversion of CO_2 into C_{2+} 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: CO_2; reduction; C_{2+}; 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 CO_2 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 CO_2 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, CO_2 is a ubiquitous and generally available C_1 feedstock in the world. Therefore, the need to simultaneously increase our energy supply while reducing CO_2 emissions is one of the major challenges facing our global society today. In this context, the chemical conversion of CO_2 from greenhouse gas into value-added products with the assistance of H_2 is highly desirable, which could reduce both the current CO_2 emission level and the dependence of chemical production on the depleting fossil fuels. Unfortunately, carbon is in its highest oxidation state in CO_2 and its transformation into other valuable chemicals requires high energy input. Up to now, the transformation of CO_2 to C_1 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 CO_2 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 CO_2 has also studied in cyclic carbonate synthesis via cycloaddition reaction, which shows promising application in industrial manufacture of cyclic carbonates from CO_2 and epoxides [25,26]. For C_{2+} chemicals (C_{2+} 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 CO_2 hydrogenation is a major challenge in the field of CO_2 chemistry [27]. As a very stable molecule ($\Delta_f G^{\theta}$ = –396 kJ•mol^{-1}), the reduction of CO_2 needs high energy. To convert relatively simple CO_2 molecules into more complex and more active C_{2+} 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 CO_2 to more valuable feedstocks, such as higher alcohols, acetic acid, light olefins and gasoline have not been exclusively reviewed.

It is known that, CO_2 can be hydrogenated to hydrocarbons or oxygenates mainly via two routes. One is CO mediate route, also called CO_2-FTS, which refers to the conversion of CO_2 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 CO_2 hydrogenation converted into other hydrocarbons [30]. In addition, some paper have reported that [31,32] water formed in the process suppressed the conversion of CO_2 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 CO_2.

Another important issue is that the source of H_2. Since the chemical conversion of CO_2 into valuable products should be under the assistance of H_2. Thus, the production of H_2 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 H_2 production.

In this review, we focused on stating current understanding of CO_2 chemical conversion into two-carbon and more than two-carbon (C_{2+}) chemicals and fuels, which are usually reduction reactions. An overview of different routes is presented in Figure 1.

2. Synthesis of alcohols

Various technologies are currently being taken to reduce the accumulation of CO_2 in the atmosphere. Among these CO_2 chemical transformation methods, the catalytic conversion of CO_2 into methanol, ethanol and higher alcohols is a potential approach from the viewpoint of high CO_2 conversion rates and high desired products selectivity. In addition, these alcohols can also be continuous 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 CO_2 hydrogenation to methanol [42-45]. While ethanol and higher alcohols ($C_{2+}OH$) 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 C_{2+} alcohol. Thus, more efficient catalytic systems are required for the conversion of CO_2 to ethanol and other C_{2+} alcohol.

2.1 Synthesis of ethanol

Among varied value-added CO_2 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 CO_2 transformation to ethanol are reported, but low ethanol selectivity and yield limit its further application.

Table 1 shows a summary of CO_2 hydrogenation to C_2H_5OH over different catalysts.

Table 1. Results of CO_2 hydrogenation to C_2H_5OH over different catalysts.

Catalyst	Condition			CO_2 conversion/%	Ethanol selectivity/%	Ref.
	T/K	*P*/ 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_2CuNPs/P25	473	-	-	-	92.0	[50]
CoMoS	613	10.4	3	32	5.5	[51]
MO_2C	473	4	3	10	16	[52]
Cu/MO_2C	473	4	3	10	14	[52]
Fe/MO_2C	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_2C	473	2	5	6	1	[54]
K/Cu-Zn-Fe	573	7	3	44.4	19.5	[55]

(0.08/1-1-3)						

Kusama *et al.* [48,49] studied metal promoted Rh/SiO_2 catalysts on the hydrogenation of CO_2, 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% CO_2 conversion under optimized conditions. The CO intermediate route was verified by in situ FT-IR in their study. Furthermore, they studied Fe promoted Rh/SiO_2 catalysts [38], result showed that ethanol selectivity was influenced by the amount of Fe added, an ethanol selectivity of 16.0% with 16.7% CO_2 conversion were obtained. Mechanism research showed that Fe changed the electronic states of Rh and that Fe^0 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 CO_2 to CO, C-C bond formation, and –OH group insertion, respectively, to synthesize ethanol via hydrogenation of CO_2. A very high ethanol space–time yields of 0.8–0.9 $kg•L^{-1}•h^{-1}$ under 30% CO_2 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 serious of M/MO_2C (M = Cu, Pd, Co and Fe) catalyst to evaluate CO_2 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 CH_3OH, C_2H_5OH and C_{2+}hydrocarbons were produced at 200°C. Different from the deposition of Cu and Pd additives promoting the CH_3OH synthesis, the deposition of Co and Fe enhanced C –C coupling to produce C_2-C_4 hydrocarbons and ethanol. Mechanism study showed that CO was the intermediate for CO_2 hydrogenation, and Mo_2C 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 C_2H_5OH from CO_2 by Huang *et al.* [50] After changing catalysts composition and support. They found Pd_2CuNPs/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 CO_2 to C_2H_5OH. 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 CO_2 hydrogenation. Figure 2 gives obtained data for different catalysts at 140 and 200℃ 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 Al_2O_3 support.

The hydrogenation of CO_2 to ethanol can be regarded as including the following steps i) reduction of CO_2 to CO. ii) C–C bond growth. iii) –OH group insertion to products [56]. It is generally believed that formate intermediates (*CO, *CH_3, *CO, *CH_3CO) are formed in the process of ethanol synthesis, which are hydrogenated into C_2H_5OH subsequently (proposed reaction mechanism is shown in Figure 4) [48]. And the conversion of *CO into *HCO may be the rate-determining step for CO_2 hydrogenated to ethanol [50].

In particular, Han *et al.* [57] created a new ethanol synthesis route, of which CO_2, H_2 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.

$$CH_3OCH_3(g) + 2CO_2(g) + 6H_2(g) \xrightarrow{\text{Catalyst}} 2C_2H_5OH(l) + 3H_2O(l) \#(1)$$

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

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

paraformaldehyde, CO_2 and H_2 (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.

$$(CH_2O)_n + CO_2 + H_2 \xrightarrow{\text{Catalyst}} C_2H_5OH + H_2O \#(2)$$

Another promising technique that utilizing CO_2 is via electroreduction way. Sun *et al*. [59] reported a high-efficiency metal-free catalyst (N-doped mesoporous carbon) for CO_2 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 CO_2 has attracted growing interests and witnessed rapid progress both in the thermal and electrocatalysis routes. To make the production of ethanol from CO_2 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 CO_2 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 CO_2 in pilot scale is believed to be achieved in the near future.

2.2 Synthesis of higher alcohols ($C_{2+}OH$).

Up to now, research progress is mainly focus on the synthesis of methanol and ethanol. Higher alcohols ($C_{2+}OH$) are more desirable in many cases, especially as fuels and fuel additives. However, the synthesis of $C_{2+}OH$ via CO_2 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 $C_{2+}OH$ 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 $C_{1\text{-}5}OH$ from CO_2 hydrogenation via Ru–Rh bimetallic homogeneous catalyst promoted by LiI in DMI solvent. They found the catalyst system could work effectively and the C_{2+} alcohols could be obtained at 160°C, which is the lowest temperature reported so far for producing C_{2+} alcohols via CO_2 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 CO_2 hydrogenation in the literature.

Han *et al*. [60] reported $Ru_3(CO)_{12}$–$Co_4(CO)_{12}$ 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.

Pt/Co_3O_4 heterogeneous catalysts were also applied to convert CO_2 into higher alcohols by some researchers. Han et al. [62] firstly used Pt/Co_3O_4 catalyst on CO_2 hydrogenation to produce higher alcohols (C_2-C_4), and the effect of water was investigated. Results showed that, 88.1% alcohol selectivity could be reached under Pt/Co_3O_4 catalyst at 220 ℃ 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℃. The Pt/Co_3O_4-p was much easier reduced, part Co_3O_4 was reduced to CoO and metallic Co in the reaction condition, formed new activate site (Pt-Co/Co_3O_{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 CH_3OH to generate C_2H_5OH, and Co catalyst ([Co]) mainly enhanced the production of $C_{2+}OH$ in the reaction.

Electrocatalytic reduction of CO_2 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 CO_2 molecules and more than 12 electrons, the electrochemical reduction of CO_2 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 CO_2 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 C_{2+} alcohol production rate of (126±5) $mA \cdot cm^{-2}$ 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 CO_2 hydrogenation. The carboxylic acids with two or more C atoms (C_{2+}) are more useful in many cases. However, synthesis of C_{2+} carboxylic acids using CO_2 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]:

$$CH_3OH + CO \xrightarrow{\text{catalyst}} CH_3COOH \#(3)$$

While, acetic acid generated directly from CO_2 and CH_4 is another route developed in recent years in view of chemical utilization of CO_2. 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 CH_4 and CO_2 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 CO_2 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 (−Zn−CH_3) were formed by activation of CH_4 from zinc site and followed with inserting of Zn−C bond into CO_2. 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 CH_3COOH from CO_2 and CH_4 over Cu-M^+-ZSM-5 catalyst (M^+= Li^+, Na^+, K^+ and Ca^{++}) which is continuouly feeded in flow micro-reactor system. They demonstrated that cation ZSM-5 catalysts loaded with Cu nanoparticles could simultaneously activate both methane and CO_2. Acetic acid sustained a yield of 395 μmol • $(g\ cat)^{-1}$• h^{-1} for 10h. Accordingly, the formation rate of CH_3COOH was obtained in the order of K > Na > Ca > Li.

Curet-Arana *et al.* [68] studied the mechanism of co-conversion of CH_4 and CO_2 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 CH_4 led to the formation of (−Cu−CH_3), while the activation of CO_2 helped the formation of surface carbonate species over cations site(Steps 1–3).: insertion of CO_2 into the (−Cu−CH_3)

produced surface acetate species (−Cu−$OOCCH_3$) as a reaction intermediate which abstracted the proton to form acetic acid(Steps 4–5).

$$CH_4(g) + CO_2(g) \rightleftharpoons CH_3COOH(l) \#(4)$$

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

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-imidazolidinoe (DMI) solvent [69]. Outstanding yield of 77.0% acetic acid with 22.5 h^{-1} TOF was obtained under 200℃ and 12h. More recently, they explored a monometallic catalytic system including $RH_2(CO)_4Cl_2$, 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 $Rh_2(CO)_4Cl_2$ 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 $Rh_2(CO)_4Cl_2$ and 4-MI were applied as the ligand. During this process, CO_2 was directly inserted into the intermediate [69, 70].

$$CH_3OH + CO_2 + H_2 \xrightarrow{\text{catalyst}} CH_3COOH + H_2O\#(5)$$

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:

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O\#(6)$$

$$2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O\#(7)$$

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 exits 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 CuO-ZnO-Al_2O_3 /HZSM-5, CuO-ZnO-ZrO_2/γ-alumina, CuO-Fe_2O_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–Al_2O_3/HZSM-5 catalysts to conduct reaction of one-step producing DME from CO_2. CuO–ZnO–Al_2O_3 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–Al_2O_3/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% CO_2 conversion.

Mota *et al.* [83] prepared impregnated catalysts (Cu·ZnO supported on γ-alumina) to study one-step DME synthesis from CO_2 and the highest selectivity reached to 35%, under the operating conditions of higher than 270℃ 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–ZrO_2 (CZZr) /SAPO-18 and CuO–ZnO–MnO (CZMn)/SAPO-18 to replace conventional CZA/γ-Al_2O_3 catalyst to produce DME from CO_2. 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 CO_2 under moderate conditions (3 MPa and H_2/CO_x=3). These results are promising for future studies that focus on optimizing the operating conditions with the objective of CO_2 valorization.

Qin *et al*. [85] reported synthesis of DME from CO_2 over Cu–Fe–Zr/HZSM-5 catalyst in the range of 240℃-280℃. The highest CO_2 conversion obtained was around 30% at 260℃, 3.0MPa. 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 H_2CO 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 CO_2 is the hydrogenation to high value added light olefins (C_2-C_4), 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 CO_2, would be highly desirable from the viewpoint of CO_2 utilization. However, until now, only few studies have been reported on the selective hydrogenation of CO_2 to C_2-C_4 olefins. The conversion of CO_2 to lower olefins (C_2-C_4) 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:

$$n\mathrm{CO_2} + n\mathrm{H_2} \rightleftharpoons n\mathrm{CO} + n\mathrm{H_2O} \#(8)$$

FTO:

$$n\mathrm{CO} + 2n\mathrm{H_2} \rightleftharpoons \mathrm{C}_n\mathrm{H}_{2n} + n\mathrm{H_2O} \#(9)$$

Combined reaction:

$$n\mathrm{CO_2} + 3n\mathrm{H_2} \rightleftharpoons \mathrm{C}_n\mathrm{H}_{2n} + 2n\mathrm{H_2O} \ \#(10)$$

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-Fe_2O_3 and γ-Fe_2O_3) for CO_2 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-Fe_2O_3 (γ-Fe_2O_3)⟶ α-Fe_3O_4 (γ-Fe_3O_4) ⟶α-Fe (γ-Fe) ⟶χ-Fe_5C_2 (θ-Fe_3C) during activation process. And both iron carbides of χ-Fe_5C_2 and θ-Fe_3C showed high activities. χ-Fe_5C_2 exhibited higher selectivity to lower olefins because of its higher effective barrier, but weak alkenes hydrogenation ability. However, θ-Fe_3C showed stronger chain growth probability than χ-Fe_5C_2 because of its strong CO_2 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 mangnese oxide (K-OMS-2) supported Fe nonocatalysts for light olefin production in both CO_2 and CO hydrogeneration. High selectivities to light olefins (C^{2-}/C^{-}:1.8–13.4) and catalytic activities (87.2% CO conversion and 45% CO_2 conversion) at temperature of 593K in both CO and CO_2 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/Al_2O_3) for the CO_2 hydrogenation to olefin. They found lower olefins were the majority among C_{2+} 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 CO_2 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 CO_2 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=2700$cm^3 \cdot h^{-1} \cdot (g\ cat)^{-1}$). 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 CO_2 could react with hydrogen to form methane and C_2-C_4 olefins catalyzed by an Fe/ZrO_2 catalyst. Afterwards they used Na^+, K^+, or Cs^+ to modify Fe/ZrO_2 catalyst, and K^+ with a proper concentration (0.5wt%–1.0 wt%) showed the best performance to lower olefins with 12% C_2-C_4 yield. The possible reason might be the production of χ-Fe_5C_2 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 CO_2 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 CH_4

The indirect route of lower olefins production from CO_2 includes conversion of CO_2 into methanol and olefins production from CH_3OH (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:

$$n\mathrm{CH_3OH} \rightleftharpoons \mathrm{C}_n\mathrm{H}_{2n} + n\mathrm{H_2O} \quad \#(11)$$

SAPO-34 is a promising industrial catalyst mainly because of its high selectivity to C_2H_4 and C_3H_6. Liu *et al*. (2017a)[95] and Sun *et al*. (2017b) [96] reported a bifunctional catalyst composed of In−Zr oxide for CO_2 activation and SAPO-34 zeolites for C-C coupling, which could convert CO_2 to C_2-C_4 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 CO_2 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 CO_2 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 $ZnGa_2O_4$ to catalyze CO_2 to lower olefins, with 86% selectivity and 13% CO_2 conversion at 370℃. They gave the possible reaction mechanism shown in Figure 15. and speculated the oxygen vacancies on the surface of $ZnGa_2O_4$ were used to activate CO_2 to form formate and methoxide species, which were formed into methanol intermediate subsequently.

In addition to chemical routes to use CO_2, electrochemical reduction of CO_2 to desired products also studied by many researchers. For example, Sargent *et al.* [99] reported CO_2 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 CO_2. 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 CO_2 electroreduction. Cu nanocatalyst has advantages in the electrocatalytic reduction of CO_2 to C_{2+} 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 CO_2 to produce C_{2+} products could be achieved. They also constructed a copper-ion battery with the highest faraday efficiency of 60%, an H_2 ratio of less than 20% in the product, as well as a C_{2+} current density of about 40 $mA•C•m^{-2}$. Gewirth *et al.* [102] developed a method of converting CO_2 into multi-carbon hydrocarbons and oxygenates. When the alloy film contained 6% Ag, CO_2 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 CO_2 reduction to produce ethylene and propene over a metalloenzyme.

In summary, there are two synthesis routes of lower olefins (C_2-C_4) process via CO_2 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 CO_2, 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 CO_2 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 CO_2 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 (C_5–C_{11} hydrocarbons), is a significant transportation fuel used widely all over the world [28]. C_5–C_{11} 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 CO_2 to fuels not only contribute to CO_2 emission reduction, but also provide valuable fuels. However, because of the chemical inert and thermodynamically stable of CO_2, it is a challenge to transform CO_2 to long chain product, as C_5-C_{11} hydrocarbons.

CO_2 can be hydrogenated to hydrocarbons by either direct or indirect route. the direct CO_2 hydrogenation (CO_2-FT) is often described as the combination of the reduction of CO_2 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 CO_2 to produce fuels using multifunctional Na–Fe_3O_4/ HZSM-5 catalyst which provided three types of active sites Fe_3C_4, Fe_5C_2 and acid sites, that catalyzed RWGS, olefins synthesis and oligomerization isomerization aromatization respectively (Figure 18). Results showed that 22% CO_2 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 H_2/ CO_2 in feed gas was permitted by this multifunctional catalyst, which decreased hydrogen cost. Moreover, the catalyst showed stability for 1000 hours. These meant that CO_2-gasoline route over Na–Fe_3O_4/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 In_2O_3 and HZSM-5, which could convert CO_2 into C_{5+} hydrocarbons with 78.6% selectivity and only 1% CH_4 selectivity at 13.1% CO_2 conversion. They speculated methanol formed from CO_2 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) process[19]. So far, there has been no report on highly selective synthesis of gasoline from direct CO_2 hydrogenation. The key to this process is to search for a highly efficient catalyst.

7. Conclusion

Undoubtedly, the chemical utilization of CO_2 has received significant and increasingly attention worldwide as an important carbon source with the gradual depletion of fossil energy. The utilization of CO_2 is being developed towards the environment friendly, diversified and efficient processes. The reduction of CO_2 to C_{2+} 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 CO_2 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 CO_2 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 CO_2 to chemicals and fuels is beyond the scope of the field of CO_2 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 CO_2 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 CO_2 with H_2 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 H_2 for CO_2 reduction. Importantly, CO_2-free H_2 source is beneficial for neat CO_2 mitigation, which could be realized together with the development of renewable energy or atomic energy in the future.

The transformations of CO_2 to important chemicals and fuels have demonstrated enormous potential and now are considered as an important route for CO_2 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

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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.

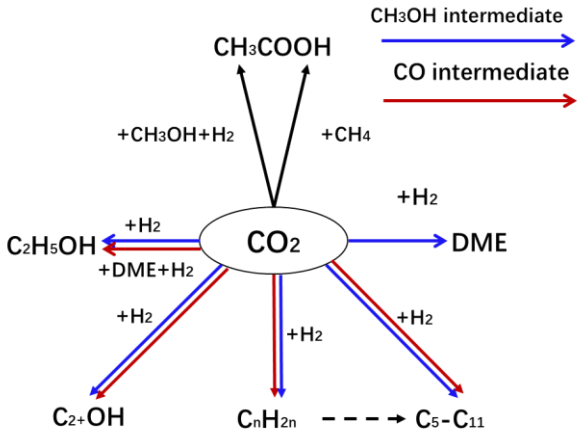
(C) SEM image of Cu nanoparticles sputtered on the PTFE membrane. (D) Comparison of ethylene faradaic efficiencies on graphite/carbon NPs/Cu/PTFE and graphite/Cu/PTFE electrodes for CO2-RR in 7 M KOH electrolyte. Values are means, and error bars indicate SD (n = 3 replicates) [99].

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 CH3OH at the acidic site inside the pores of the HZSM-5 catalyst via the hydrocarbon-pool mechanism [28].



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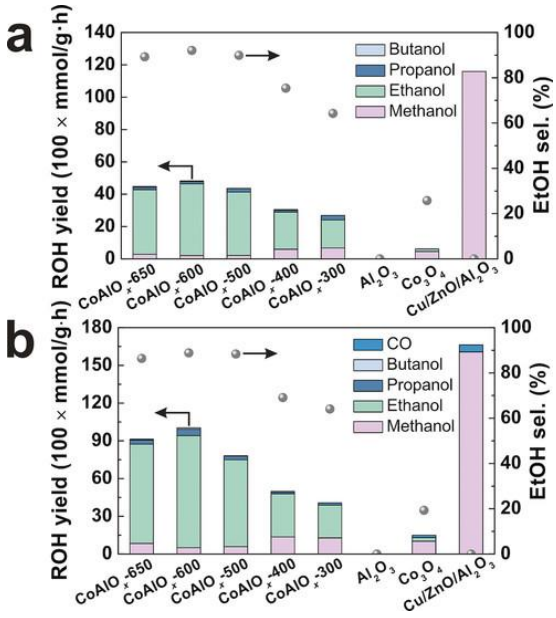

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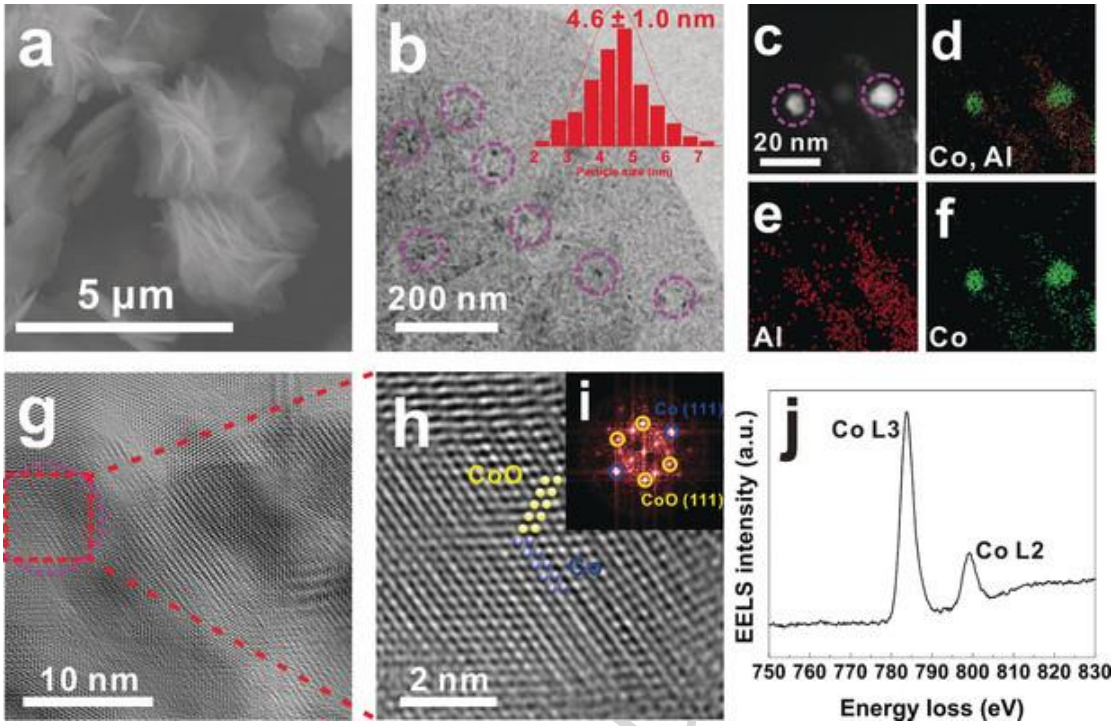

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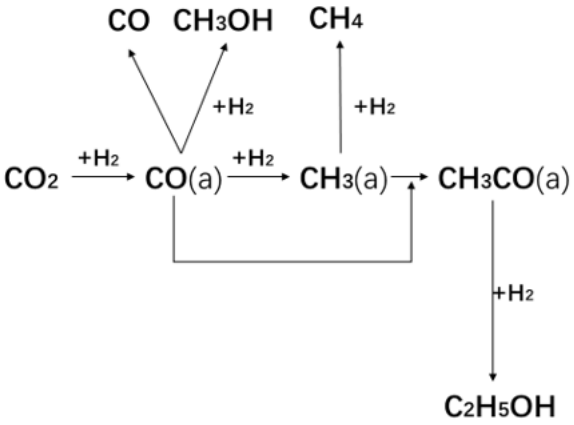

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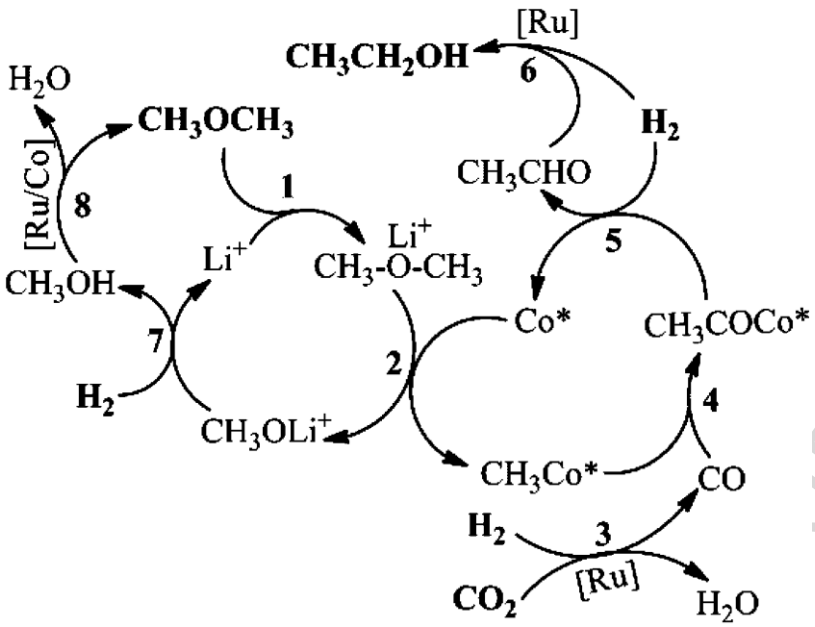

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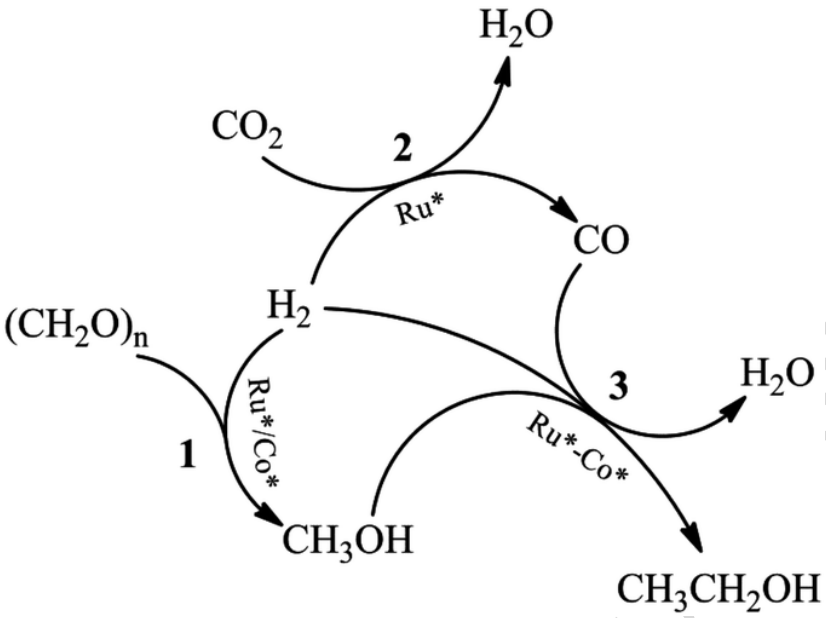

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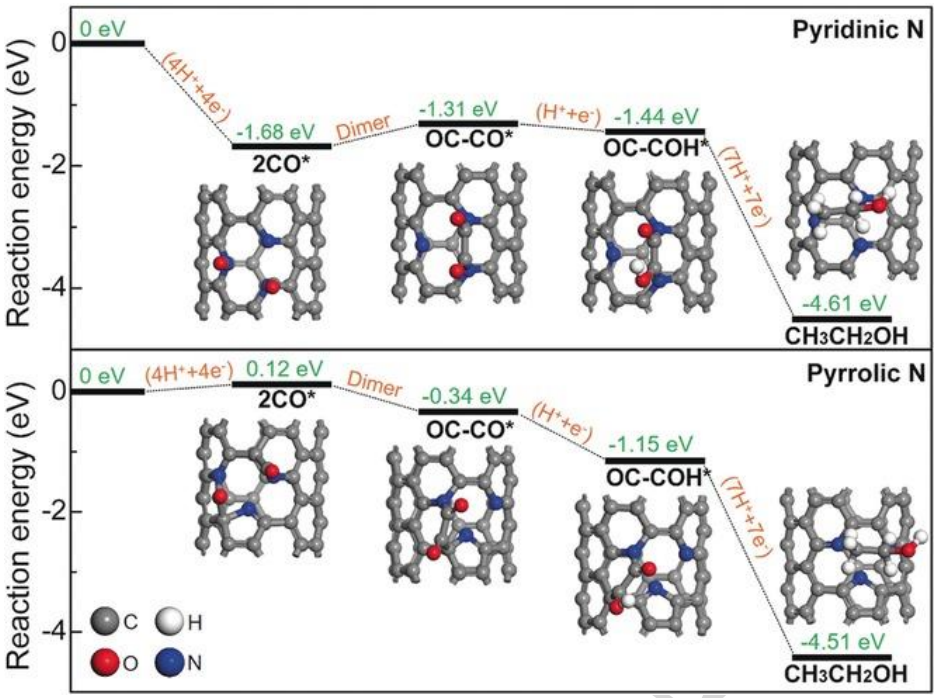

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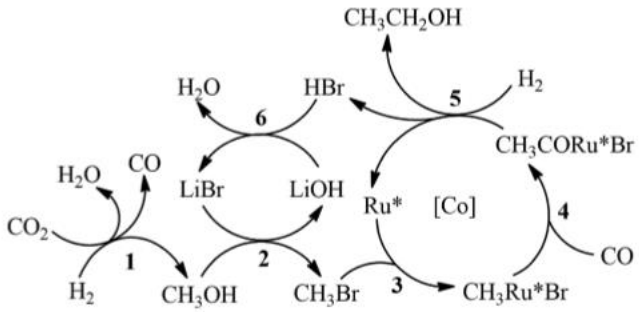

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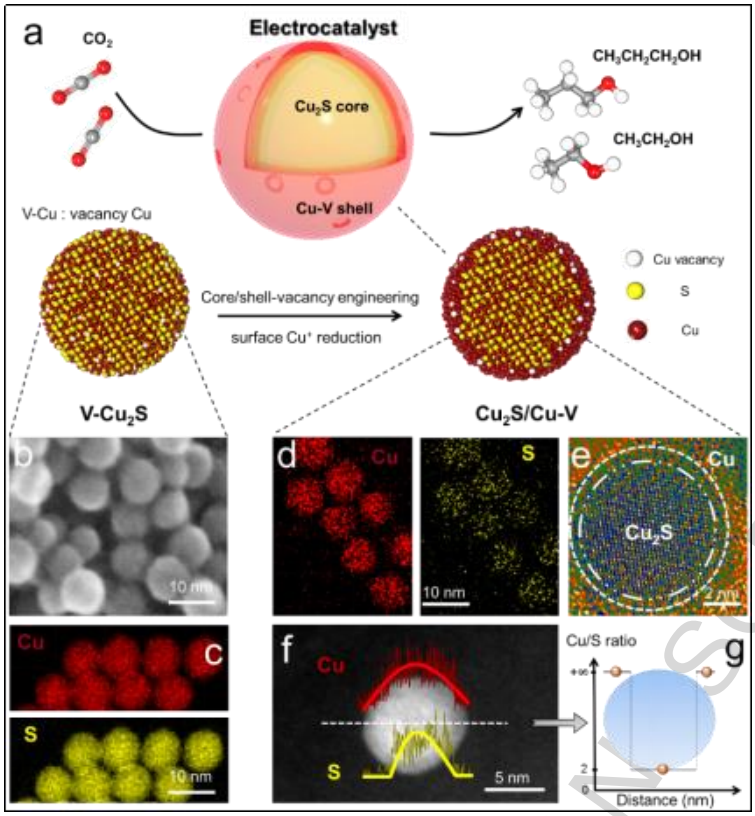

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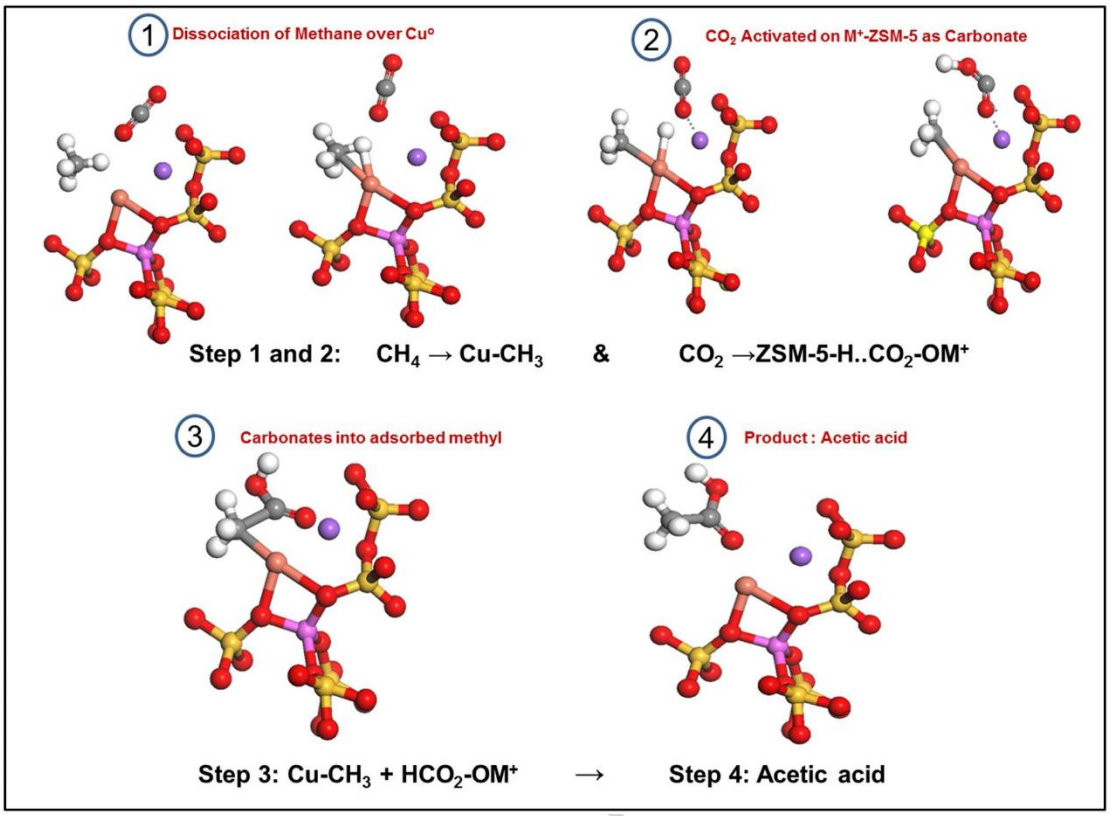

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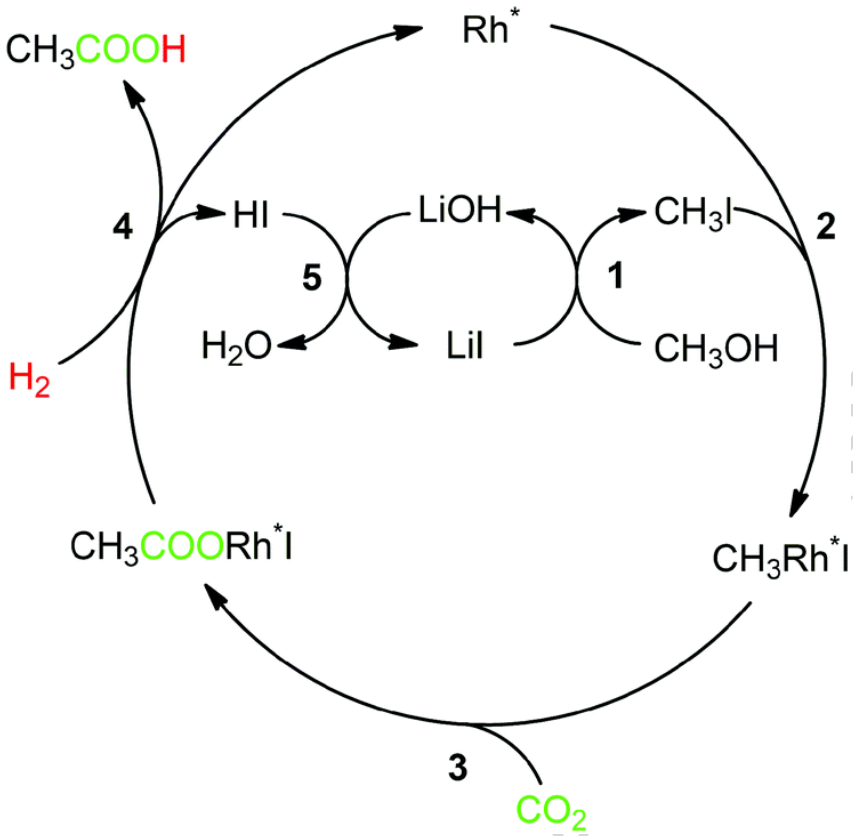

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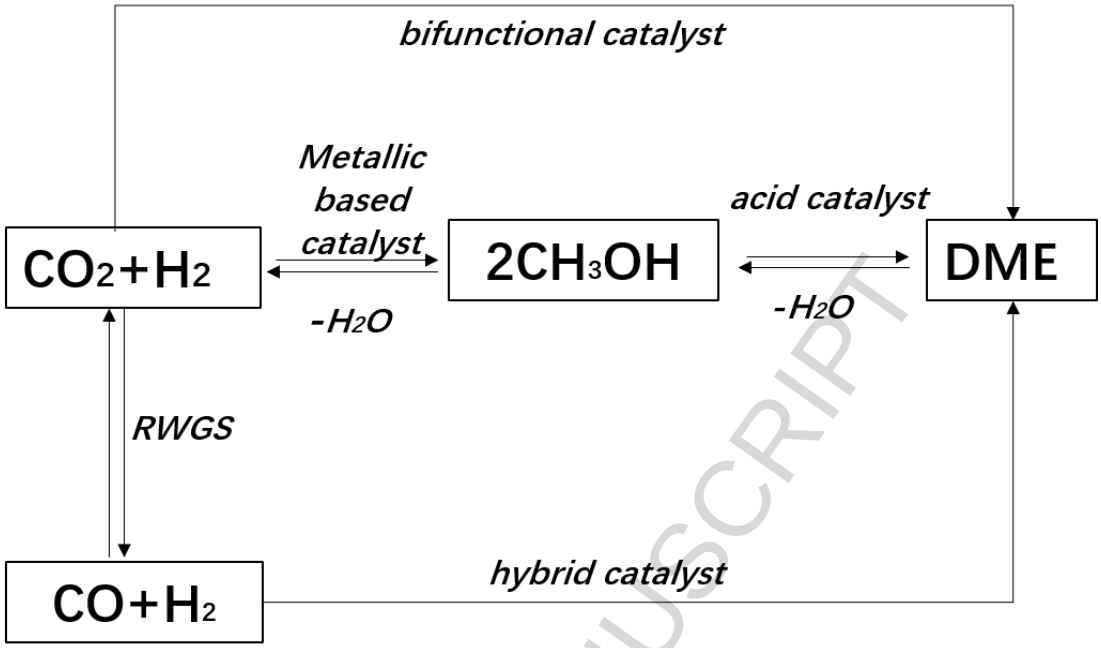

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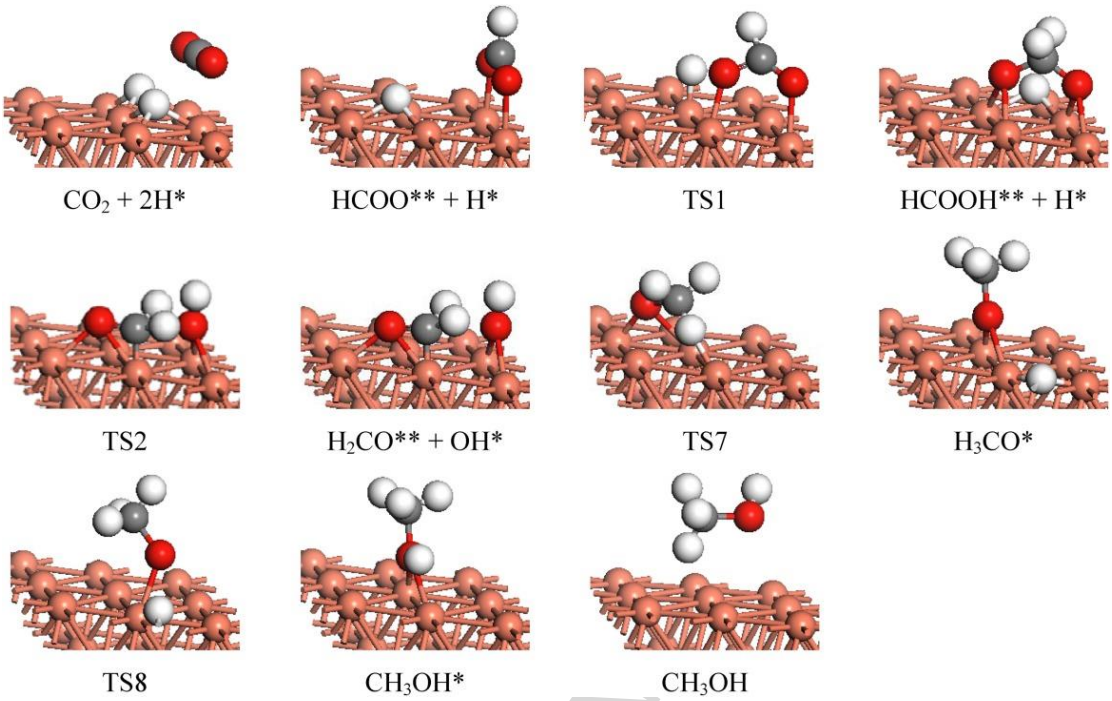

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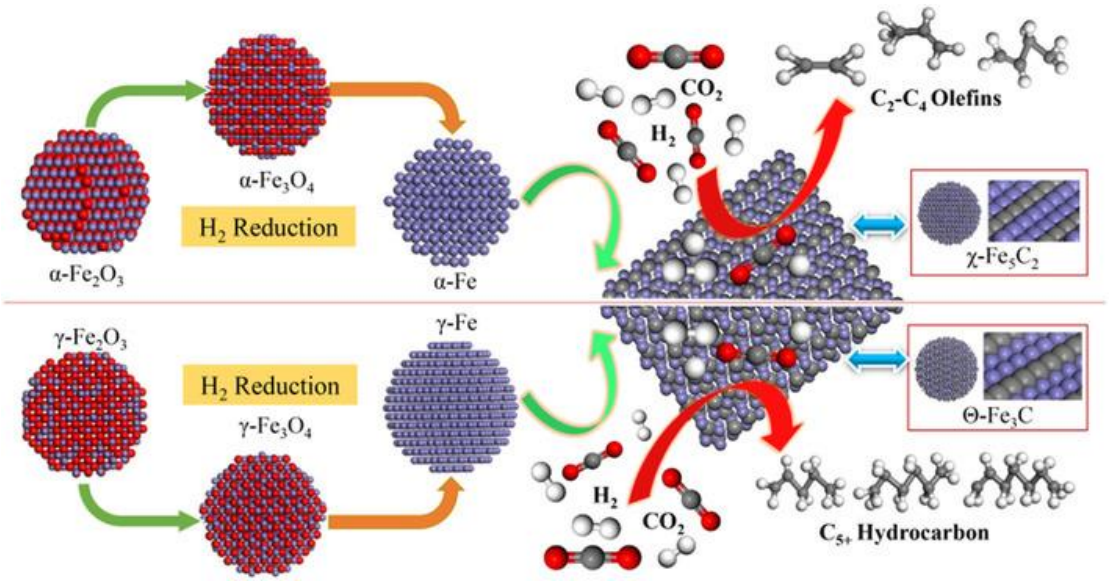


Figure 14. Scheme of structure-performance relationship of α-Fe_2O_3 and γ-Fe_2O_3 catalysts for CO_2 hydrogenation during activation and reaction processes [88].

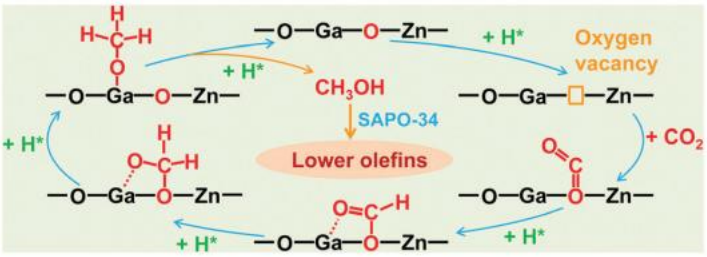


Figure 15. A possible reaction mechanism for the conversion of CO_2 into methanol on the Zn–Ga–O catalyst [98].

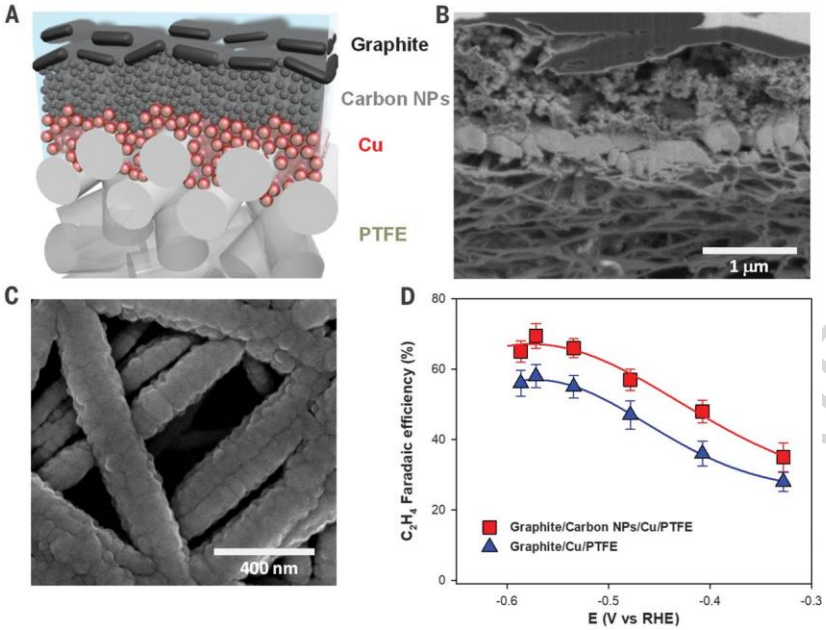


Figure 16. Structure and performance of the polymer-based gas diffusion electrode. (A) Schematic illustration of the graphite/carbon NPs/Cu/PTFE electrode. (B) Cross-sectional SEM image of a fabricated graphite/carbon NPs/Cu/PTFE electrode. (C) SEM image of Cu nanoparticles sputtered on the PTFE membrane. (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].

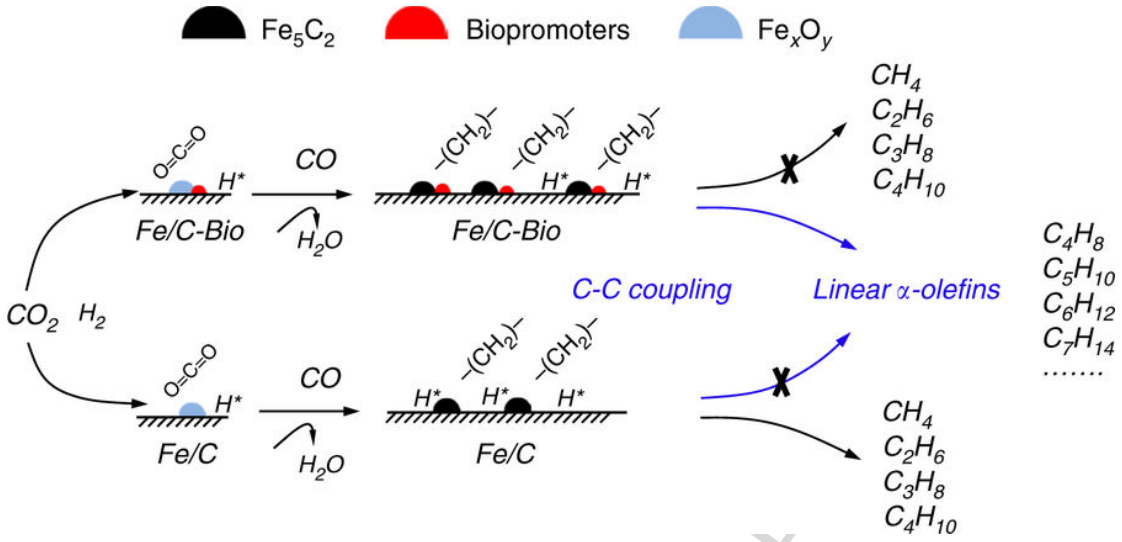


Figure 17. Reaction scheme for CO_2 hydrogenation to α-olefins. The existences of biopromoters weaken secondary hydrogenation of olefins and strengthen the reaction activity of C–C coupling [82].

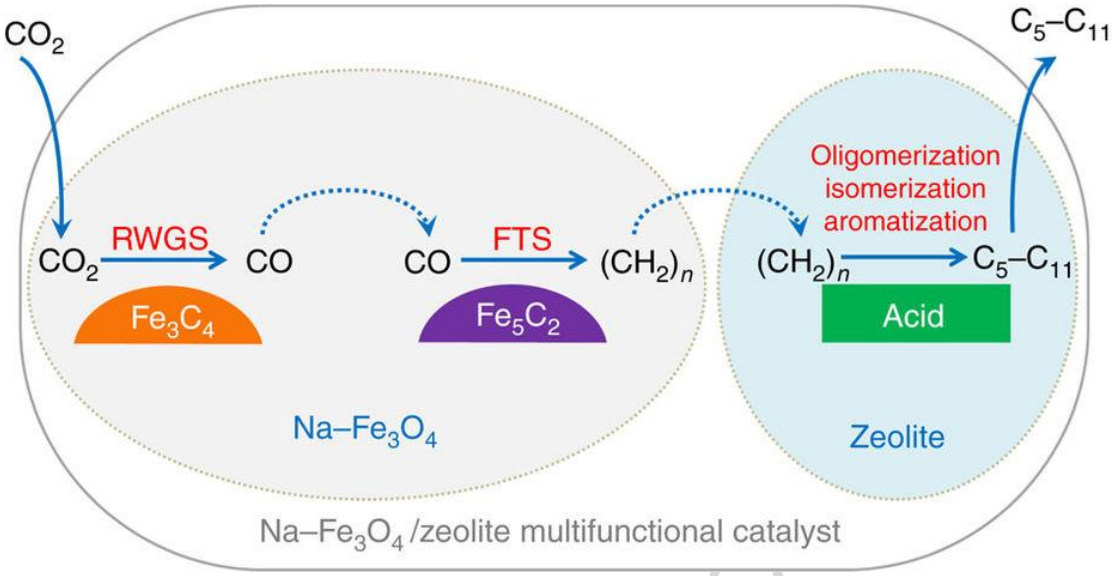


Figure 18. Reaction scheme for CO_2 hydrogenation to gasoline-range hydrocarbons. The CO_2 hydrogenation reaction over Na–Fe_3O_4/Zeolite multifunctional catalyst takes place in three steps: (1) an initially reduced to CO intermediate via RWGS, (2) a subsequent hydrogenation of CO to α-olefins intermediate via FTS and (3) the formation of gasoline-range hydrocarbons via the acid-catalysed oligomerization, isomerization and aromatization reactions [105].

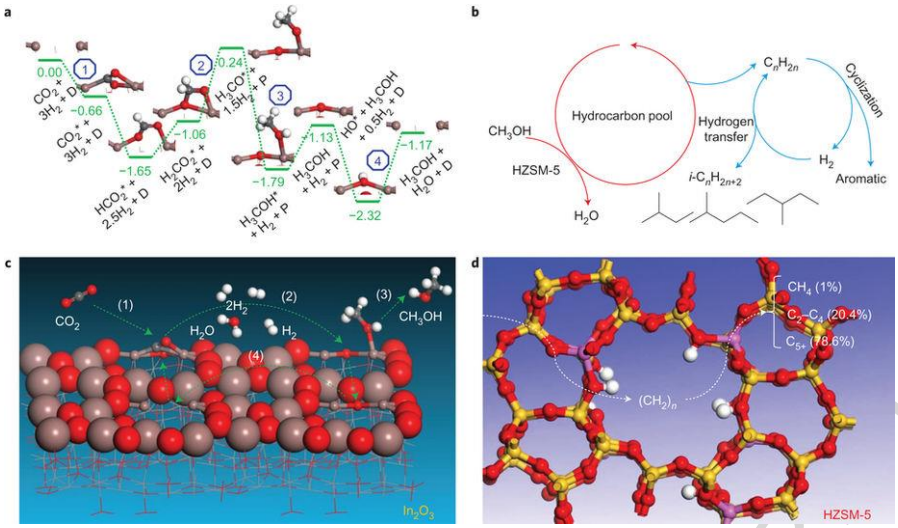
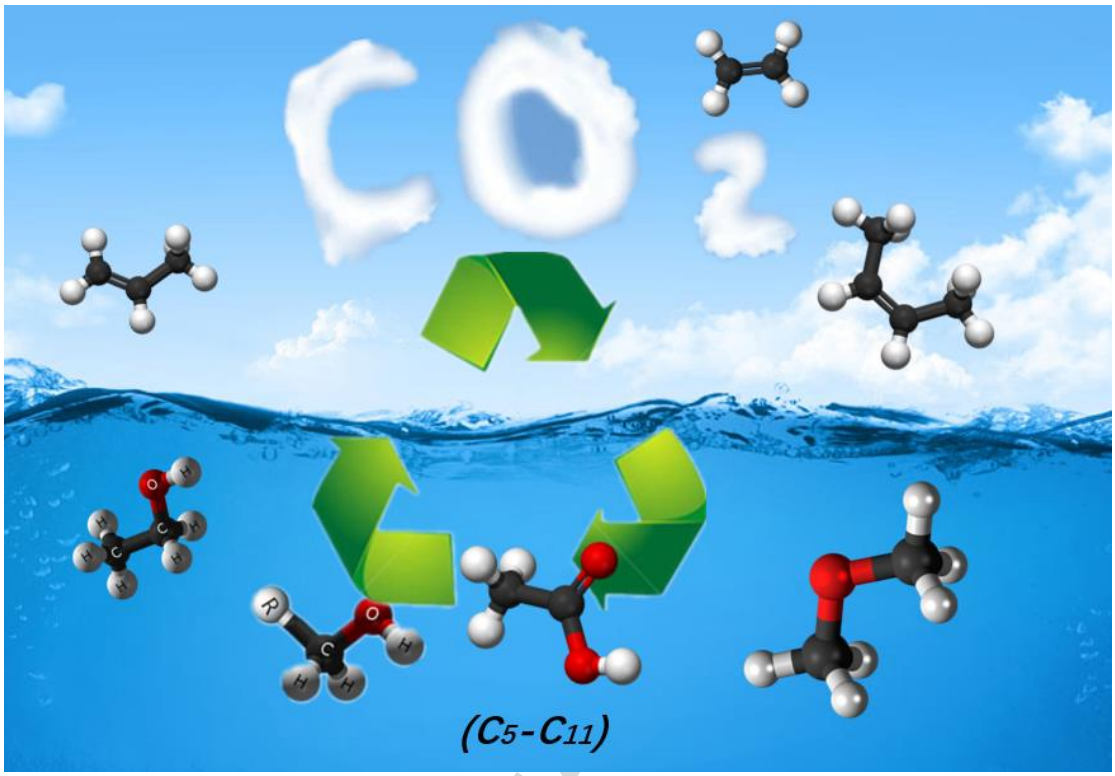


Figure 19. Molecular-level mechanism for CO_2 hydrogenation into hydrocarbons. a) Energy profile from DFT calculations for CO_2 hydrogenation to CH_3OH on the $In_2O_3(110)$ surface (D and P stand for defective and perfect surfaces with and without the oxygen vacancy, respectively). b) Schematic of the hydrocarbon-pool mechanism for CH_3OH conversion into hydrocarbons inside HZSM-5. c) Schematic for the formation of CH_3OH from CO_2 at the oxygen vacancy site on the In_2O_3 catalyst surface, which involve four major steps: (1) CO_2 adsorption at the oxygen-vacancy site, (2) sequential hydrogenation of the adsorbed CO_2 species to CH_3OH, (3) CH_3OH 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].



Graphical abstract