Novel Heterogeneous Catalysts for CO₂ Hydrogenation to Liquid Fuels

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ABSTRACT: Carbon dioxide (CO₂) hydrogenation to liquid fuels including gasoline, jet fuel, diesel, methanol, ethanol, and other higher alcohols via heterogeneous catalysis, using renewable energy, not only effectively alleviates environmental problems caused by massive CO₂ emissions, but also reduces our excessive dependence on fossil fuels. In this Outlook, we review the latest development in the design of novel and very promising heterogeneous catalysts for direct CO₂ hydrogenation to methanol, liquid hydrocarbons, and higher alcohols. Compared with methanol production, the synthesis of products with two or more carbons (C₂+) faces greater challenges. Highly efficient synthesis of C₂+ products from CO₂ hydrogenation can be achieved by a reaction coupling strategy that first converts CO₂ to carbon monoxide or methanol and then conducts a C−C coupling reaction over a bifunctional/multifunctional catalyst. Apart from the catalytic performance, unique catalyst design ideas, and structure−performance relationship, we also discuss current challenges in catalyst development and perspectives for industrial applications.

INTRODUCTION

The catalytic conversion of captured carbon dioxide (CO₂) to liquid fuels can ameliorate global climate change and reduce our excessive dependence on fossil fuels. Since carbon in CO₂ is in its highest oxidation state, its reduction and transformation need a large energy input. As a high-energy material, hydrogen is generally used for the large-scale catalytic transformation of CO₂ to value-added products.1,2 At present, the hydrogen source mainly comes from syngas, petrochemical plants, methane steam reforming, chlorine alkali plants, and coke oven gas.3 Renewable energies such as solar, wind, geothermal, and hydro can be used along with CO₂ and water to produce green liquid fuels. In 2017, Shih et al. proposed the “liquid sunshine” concept that employs solar energy to produce stable, easily transportable, energy dense liquid products.4 In Europe, power-to-liquid (PTL) fuels obtained from surplus renewable electricity via water electrolysis-derived H₂ and CO₂ have received much attention, and a number of PTL-related studies were recently reported.5−9

Liquid hydrocarbon (C₅+) fuels including gasoline (C₅−11), jet fuel (C₈−10), and diesel (C₁₀−20) play an instrumental role in the global energy supply chain and are widely used as transportation fuels around the world. Besides, alcohols such as methanol, ethanol, and other higher alcohols (C₂+OH) are clean and multipurpose fuels.4,10,11 In both academic research and industrial practices, great progress has been made in the synthesis of C₁ molecules such as methanol (CH₃OH) from CO₂ hydrogenation. Currently, the largest plant, Carbon Recycling International (CRI)’s CO₂-to-renewable-methanol plant in Iceland, is capable of producing 4000 t/year of methanol by converting about 5500 t/year of CO₂.12 However, direct reduction of CO₂ to C₂+ products is still a grand challenge due to the lack of efficient catalysts with high stability, as the activity of C−C coupling is low and the formation of byproduct water can easily deactivate the various catalysts for CO₂ conversion.2,13−15 Syngas (CO/H₂) and CH₃OH are the most important C₁ platform molecules, and their conversions to value-added products via the Fischer−Tropsch synthesis (FTS) and methanol to hydrocarbons (MTH) processes, respectively, were extensively applied in industry.16−19 Therefore, combining the reverse water−gas shift (RWGS) with FTS and combining high-temperature methanol synthesis with MTH over bifunctional/multifunctional catalysts are two efficient strategies for direct CO₂ hydrogenation to C₂+ hydrocarbons. Moreover, the synthesis of C₂+ alcohols is even more
challenging than 

\[ C_2 \text{H}_4 \] hydrocarbons either in CO\textsubscript{2} or CO hydrogenation, which requires more precise control of the C–C coupling.\textsuperscript{20–22}

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In this Outlook, we will discuss recent developments in designing heterogeneous catalysts for direct CO\textsubscript{2} hydrogenation to liquid fuels including methanol, liquid hydrocarbons, and higher alcohols, focusing on new structures, smart design, and exciting performance of novel materials. One efficient route of \( C_2 \text{H}_4 \) hydrocarbons synthesis is based on the methanol intermediate. Advances in methanol synthesis will strongly promote the development of this process and the understanding of related reaction mechanisms. Therefore, we mainly introduce the work of highly selective conversion of CO\textsubscript{2} to CH\textsubscript{3}OH, as there have been many excellent recent reviews on methanol synthesis via heterogeneous catalysis.\textsuperscript{12,23–27}

## \( \text{CO}_2 \) HYDROGENATION TO METHANOL

During CO\textsubscript{2} hydrogenation, the formation of the undesired CO through RWGS is a competitive reaction to methanol synthesis. Decreasing the reaction temperature favors the exothermic methanol synthesis reaction, and raising the space velocity decreases the CO selectivity because of the lower RWGS reaction rate.\textsuperscript{28} However, the low temperature and/or high space velocity usually result in low single pass CO\textsubscript{2} conversion. Thus, it remains a great challenge to simultaneously obtain high CO\textsubscript{2} conversion and high methanol selectivity. Very recently, significant progress has been made in developing more efficient catalysts for CO\textsubscript{2} hydrogenation to CH\textsubscript{3}OH, including metal-supported catalysts, bimetallocatalytic systems, and reducible metal oxides.

Industrial methanol production from CO\textsubscript{2}-containing syngas uses the well-known Cu–ZnO-Al\textsubscript{2}O\textsubscript{3} catalysts. Currently, CH\textsubscript{3}OH synthesis from catalytic CO\textsubscript{2} hydrogenation has been implemented at the pilot-plant level by Lurgi, Mitsui, and CR1, among others.\textsuperscript{12,29} These processes mainly used modified Cu–ZnO-Al\textsubscript{2}O\textsubscript{3} catalysts and were carried out under conditions similar to syngas-based methanol synthesis. Therefore, supported copper materials have attracted much attention and have been extensively investigated for CO\textsubscript{2} hydrogenation to CH\textsubscript{3}OH. The methanol synthesis reaction is known to show strong support effects. Using a suitable support material can enhance CH\textsubscript{3}OH selectivity, attributed to structural, electronic, and chemical promotional effects. For example, CH\textsubscript{3}OH selectivity is usually high (\( \geq 70\% \)) at 200–260 °C when ZrO\textsubscript{2} is used as the support.\textsuperscript{30–32} Recently, several works have clarified the origin of the promotional effect of the ZrO\textsubscript{2} support that is unknown before. Larmier et al. confirmed that the Cu/ZrO\textsubscript{2} interface can promote the conversion of the formate intermediates to methanol by combined experimental and computational investigations.\textsuperscript{30} Tada et al. found that the interfacial sites on Cu–ZrO\textsubscript{2} (\( \alpha; \) amorphous) are favored for methanol production compared to those on tetragonal and monoclinic ZrO\textsubscript{2} supported Cu.\textsuperscript{31} Additionally, the oxygen vacancies on tetragonal ZrO\textsubscript{2} were proposed to play a crucial role in enhancing the activity of methanol formation by stabilizing the Cu\textsuperscript{+} active sites adjacent to them.\textsuperscript{32} Lam et al. suggested that the surface Lewis acid Zr(IV) sites with Cu particles in the vicinity are responsible for improving CH\textsubscript{3}OH activity and selectivity on the Cu/ZrO\textsubscript{2}-based catalysts.\textsuperscript{33} Apart from conventional metal oxides, researchers recently also explored other supports such as TiO\textsubscript{2} nanotubes\textsuperscript{34} and Mg–Al layered double hydroxide (LDH)\textsuperscript{35} to promote methanol formation.

To simultaneously improve the intrinsic activity and catalyst stability, researchers directly used Cu–Zn-based LDH as the precursor to synthesize an efficient methanol synthesis catalyst with a confined structure, in which the active metallic Cu phase is highly dispersed and partially embedded in the remaining oxide matrix.\textsuperscript{36–39} Li et al. prepared ultrathin Cu–Zn–Ga LDH nanosheets by the aqueous miscible organic solvent treatment method and further increased Cu surface areas and dispersion of the resulting Cu-based catalysts (Figure 1A).\textsuperscript{37} The CH\textsubscript{3}OH space time yield (STY) is 0.59 g\textsubscript{MeOH}g\textsubscript{cat}\textsuperscript{−1} h\textsuperscript{−1} with selectivity of \( \sim 49\% \) at CO\textsubscript{2} conversion of \( \sim 20\% \). On the other hand, scientists also tried to use silica and metal–organic frameworks to confine small Cu nanoparticles and developed highly efficient Cu-based catalysts for CO\textsubscript{2} hydrogenation.\textsuperscript{40–44} For example, Liu et al. synthesized three-dimensional porous Cu@ZrO\textsubscript{2} framework catalysts using the Cu@UiO-66 precursor, which displays CH\textsubscript{3}OH STY of 0.796 g\textsubscript{MeOH}g\textsubscript{cat}\textsuperscript{−1} h\textsuperscript{−1} and a long-term stability for 105 h with a selectivity of 78.8% and conversion of 13.1% at 260 °C, 4.5 MPa, 21 600 mL H\textsubscript{2}/CO\textsubscript{2} = 3.\textsuperscript{43}

Recently, several groups have developed novel cobalt (Co)-based catalytic systems that display a promising performance for methanol synthesis from CO\textsubscript{2} hydrogenation.\textsuperscript{45–48} Co catalysts are widely used and extensively studied for FTS and can easily catalyze the CO methanation reaction.\textsuperscript{49–52} The high performance for CH\textsubscript{3}OH synthesis over Co-based catalysts was attributed to the formation of a new active phase, rather than the conventional metallic Co phase. Li et al. reported MnO\textsubscript{2} nanoparticles supported on a mesoporous Co\textsubscript{3}O\textsubscript{4} for methanol production at low pressure (0.1–0.6 MPa).\textsuperscript{45} They showed the importance of the CoO phase and revealed the strong interaction between MnO\textsubscript{2} nanoparticles and Co@CoO core–shell grains, which enhances the performance of CO\textsubscript{2} hydrogenation to CH\textsubscript{3}OH. Li et al. ascribed the increased CH\textsubscript{3}OH selectivity to the oxygen defects on the surface of Co@Co\textsubscript{3}O\textsubscript{4} core–shell active species supported on the nitrogen-doped carbon material, which is derived from zeolitic imidazolate framework precursors.\textsuperscript{53} Wang et al. also inferred that the cobalt oxide phase on silica supported Co catalyst with Co–O–SiO\textsubscript{2} linkages via Co phyllosilicates could suppress the CO and CH\textsubscript{4} formation and promote methanol production (Figure 1B).\textsuperscript{48} This novel Co catalyst shows CH\textsubscript{3}OH STY of 0.096 g\textsubscript{MeOH}g\textsubscript{cat}\textsuperscript{−1} h\textsuperscript{−1} (3.0 mmol H\textsubscript{2}/CO\textsubscript{2} = 1 h\textsuperscript{−1}) with a selectivity of 70.5% at 8.6% conversion at 320 °C. Because the H\textsubscript{2} splitting ability of cobalt oxide is lower than the metallic Co phase, the activities of these Co-based methanol synthesis catalysts are to be further enhanced. Moreover, the mechanism of this new active site inhibiting the
Figure 1. (A) TEM images of Cu–Zn–Ga catalysts derived from conventional hydroxyl-carbonate phases and ultrathin LDH (left) as well as their performance (right).37 Reaction conditions: 270 °C, 4.5 MPa, 18 000 mL g⁻¹ h⁻¹, and H₂/CO₂ = 3. (B) Synthesis and catalysis strategies (left) as well as CO₂ hydrogenation performance (right) of Co@Six catalysts.48 Reaction conditions: 260–380 °C, 2.0 MPa, 6000 mL g⁻¹ h⁻¹ and H₂/CO₂ = 3. (C) HAADF-STEM images and corresponding EDX maps (top) of indium (blue) and palladium (green) for the spent coprecipitated (CP, left) and dry impregnated (DI, right) Pd–In₂O₃ catalysts with 0.75 wt % Pd as well as illustration for the distinct role of Pd in equilibrated CP and DI catalysts with pure In₂O₃ as a reference.84 The thickness of the arrows qualitatively suggests the methanol and CO formation rates. Reprinted with permission from refs 37, 48, and 84. Copyright 2018 American Chemical Society and Copyright 2019 and 2020 Springer-Nature.
CO₂ methanation and RWGS reactions needs to be further clarified.

Various bimetallic materials including Pd–Cu,\(^{53–55}\) Pd–Ga,\(^{56,57}\) Pd–In,\(^{58–60}\) Pd–Zn,\(^{61}\) Ni–Ga,\(^{52–66}\) In–Rh,\(^{67}\) In–Cu,\(^{68,69}\) In–Co,\(^{70}\) In–Ni,\(^{71,72}\) and Ni–Cu,\(^{55,73}\) have also been examined for methanol production from CO₂ hydrogenation. Among these catalysts, some non-noble metal-based bimetallics were designed for efficient CO₂ hydrogenation to CH₃OH at low pressure. Compared with the benchmark Cu–ZnO–Al₂O₃, Ni–Ga₃ intermetallic compounds exhibited a higher CH₂OH synthesis activity and a much lower CO selectivity at ambient pressure.\(^{62}\) The Ga-rich and Ni-rich sites are responsible for methanol synthesis and RWGS, respectively, and poisoning of the Ni sites by adsorbed CO suppress the RWGS reaction. Gallo et al. further suggested that the formation of an amorphous Ga₂O₃ shell over the metallic Ni–Ga₃ during the catalysis after low temperature reduction promoted CO₂ activation.\(^{63}\) The Ni₅In₃.₅Al/SiO₂ catalyst with 15% metal loading via a phyllosilicate precursor also shows a higher conversion and a better stability, while yielding lower CH₂OH selectivity than the conventional Cu–ZnO–Al₂O₃ catalyst at ambient pressure.\(^{72}\) The optimized metal composition and well-dispersed metal particles can be achieved by partial decomposition of the phyllosilicate, which enhances the activity for CO₂ hydrogenation. For the GaPd₂/SiO₂ system, a much higher intrinsic activity and CH₂OH selectivity than Cu–ZnO–Al₂O₃ have been observed at above 200 °C and atmospheric pressure.\(^{73}\) However, under high reaction pressure (above 3.0 MPa), the performance advantage of the bimetallic catalyst is not obvious, even lower than conventional Cu-based catalysts.

In recent years, reducible oxides have received considerable attention due to their excellent performance with high CH₂OH selectivity in a wide range of temperatures (200–320 °C). Nearly 100% selectivity can be attained over cubic In₂O₃ nanomaterial and In₂O₃ supported on monoclinic ZrO₂ at CO₂ conversions of less 5.5% under 300 °C, 5.0 MPa, 20,000 mL g⁻¹ h⁻¹ and H₂/CO₂ = 4.\(^{74}\) The surface oxygen vacancies surrounded by indium atoms are considered as the active sites for CO₂ activation and hydrogen splitting, and methanol formation from CO₂ hydrogenation follows the cycle between generation and annihilation of vacancies.\(^{75,76}\) Researchers have clearly demonstrated the structure sensitivity of the In₂O₃ catalyst in terms of both the phase and the exposed facet by combined computational and experimental studies.\(^{77,78}\) Dang et al. reported a successful work of computer-aided rational design of more efficient In₂O₃ catalysts for CO₂ hydrogenation to CH₂OH.\(^{79}\) On the basis of density functional theory (DFT) calculations, they designed and synthesized a highly efficient hexagonal In₂O₃ catalyst with a high proportion of the exposed {104} surface. CH₂OH selectivity is as high as 92.4% with a CO₂ conversion of more than 17% under 300 °C, 5.0 MPa, 9000 mL g⁻¹ h⁻¹, H₂/CO₂ = 6. For the In₂O₃/ZrO₂ catalyst system, the ZrO₂ support remarkably boosted the activity of the In₂O₃ catalyst and prevented its sintering.\(^{79}\) It was suggested that synergic effects between In₂O₃ and ZrO₂ carriers favorably tuned CH₂OH selectivity by changing the reaction pathway.\(^{80}\) Frei et al. also investigated the electronic, geometric, and interfacial phenomena related to the peculiar promotional effects of the monoclinic ZrO₂ carrier on In₂O₃.\(^{81}\)

Less-pronounced lattice mismatching between In₂O₃ and ZrO₂ favors the formation of more surface oxygen vacancies on In₂O₃, which is beneficial for methanol synthesis. Because of the lower H₂ splitting ability of In₂O₃ compared with metal catalyst, palladium (Pd) was introduced to enhance H₂ activation and facilitate oxygen vacancy formation and thereby substantially promote the activity of In₂O₃.\(^{82,83}\) CO₂ conversion over In₂O₃ supported highly dispersed Pd nano-catalyst reached above 20% with CH₃OH selectivity of ~70% and STY up to 0.89 gMeOH gcat⁻¹ h⁻¹,\(^{83}\) which is about 2–5 times higher than pure In₂O₃ under similar reaction conditions. Moreover, the incorporation of Pd atoms in the In₂O₃ matrix forming low-nuclearity Pd clusters can simultaneously increase the activity, selectivity and long-term stability (Figure 1C).\(^{84}\)

Different from dry impregnated Pd–In₂O₃, this nanostructure can effectively avoid Pd clustering and minimize In₂O₃ sintering; thus, CH₂OH STY dropped slightly from 1.01 to 0.96 gMeOH gcat⁻¹ h⁻¹ after time-on-stream of 500 h at 280 °C, 5.0 MPa, 48,000 mL g⁻¹ h⁻¹, and H₂/CO₂ = 4. The addition of Pt, Au, Cu, Co, or Ni can also benefit the generation of active hydrogen species.\(^{85–89}\) For the Au₆₄–In₉ catalyst, the strong Au–In₂O₃ interaction is responsible for the promising methanol synthesis performance.\(^{89}\) Shi et al. found that the Cu₉In₉ phase is formed by controlled reduction of CuInO₃ mixed oxides, and the synergy between Cu₉In₉ and In₂O₃ gives a CH₂OH STY of 0.2 gMeOH gcat⁻¹ h⁻¹ with a selectivity of 80.5% at CO₂ conversion of 11.4% under 280 °C, 3.0 MPa, 7500 mL g⁻¹ h⁻¹, and H₂/CO₂ = 3.\(^{69}\) Bavykina et al. combined Co and In₂O₃ to prepare In@Co catalysts, which significantly enhanced methanol productivity due to the formation of Co-supported In₂O₃ films. The CH₂OH STY is as high as 0.86 gMeOH gcat⁻¹ h⁻¹ with above 80% selectivity and ~12% conversion at 300 °C, 5.0 MPa, 27 500 mL g⁻¹ h⁻¹, and H₂/CO₂ = 4.\(^{86}\)

The ZnO–ZrO₂ solid solution is another reducible oxide system efficient for methanol synthesis from CO₂ hydrogenation. It gives a CH₂OH STY of 0.73 gMeOH gcat⁻¹ h⁻¹ at CH₂OH selectivity of 86% and CO₂ conversion of 10% with high stability over 500 h on stream under 320 °C, 5.0 MPa, 24,000 mL g⁻¹ h⁻¹ and H₂/CO₂ = 3.\(^{60}\) Under similar reaction conditions, a high selectivity of more than 80% is obtained over CdZrO₂ and GaZrO₂ solid-solution catalysts with a conversion of 12.4% and 4.3%, respectively.\(^{91}\) The ZnO–ZrO₂ solid solution catalyst also exhibits high resistance to sulfur-containing species in the feed gas up to 50 ppm, which makes the catalyst industrially viable in methanol production processes.\(^{60}\)

Compared with Cu-based catalysts, the biggest advantage of the reducible metal oxides (In₂O₃-based oxides or ZnO–ZrO₂ solid solution catalysts) is that it can effectively inhibit the undesired RWGS reaction even if the reaction temperature is as high as 320 °C. However, additional works are needed to further clarify the origin of this promotional effect by identifying the active sites and understanding the reaction mechanisms for both methanol and CO formations, which will promote the rational design of more efficient CO₂-to-methanol oxide catalysts. In₂O₃ is very suitable as a model catalyst to study the structure–activity relationship and the reaction mechanism because it can achieve efficient methanol synthesis from CO₂ hydrogenation by itself without using any promoters and supports. This is one of the reasons why In₂O₃ has received such great attention for the CO₂ hydrogenation reactions.
CO$_2$ HYDROGENATION TO LIQUID HYDROCARBONS

As CO$_2$ can be easily converted to CO via RWGS, modified CO-FTS catalysts were widely used for direct CO$_2$ hydrogenation to long-chain (C$_{5+}$) hydrocarbons. Methane and gaseous hydrocarbons (C$_{2-4}$) are also formed through this classical CO-FTS reaction. Compared with CO-FTS, more H$_2$ is usually needed in CO$_2$-based FTS, and the concentration of the CO intermediates is also lower during CO$_2$ hydrogenation, which results in a higher H/C ratio on the catalyst surface. As CO$_2$ can be directly hydrogenated to CH$_4$, the high H/C ratio favors methane formation and leads to a decrease in the chain growth probability. Therefore, CO$_2$-FTS catalysts to be

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Figure 2. Detail hydrocarbon product distribution obtained over (A) well-defined mesoporous carbon (MPC) supported Fe−K in the range of C$_{15-27}$, (B) Fe−Cu, (C) Na−Fe$_2$O$_4$ (middle), Na−Fe$_2$O$_4$/HZMS-5 (left), and Na−Fe$_2$O$_4$/HZM-5 (right), (D) ZnFeO$_{4.25}$Na (left) and ZnFeO$_{4.25}$Na/HZSM-5 (right) under the reaction conditions of 320 °C, 3.0 MPa, H$_2$/CO$_2$ = 3, and 4000 mL g$^{-1}$ h$^{-1}$, as well as (E) FeK1.5/HSG/HZSM-5 (SiO$_2$/Al$_2$O$_3$ molar ratio of HZSM-5 = 50) catalysts during the CO$_2$ hydrogenation reaction. Reprinted with permission from refs 95, 98, 105, 107, 109, and 110. Copyright 2017 and 2020 Elsevier, Copyright 2017 Springer-Nature, and Copyright 2018 and 2019 American Chemical Society.
developed should have high activity for both RWGS and FTS reactions but inhibit the CO₂ methanation reaction. Iron (Fe)- and Co-based catalysts are industrially adopted CO-FTS catalysts, though Co has little activity for RWGS, and thus a second component is needed for CO₂ conversion to CO. The combined selectivity of CH₄ and light hydrocarbons are usually very high (>55%), but the introduction of promoters such as Cu, Mo, and alkali metals to the Co catalyst enhances the selective formation of C₅+, hydrocarbons from CO₂ hydrogenation.\(^{52,93}\) For example, the optimized Na₂C₁−Mo/SiO₂−TiO₂ catalyst shows the C₅+ selectivity of 27.3% with CH₄ selectivity of 40% at CO₂ conversion of 26.9% under the very mild reaction condition of 200 °C and 0.1 MPa.\(^{92}\) Neverthele...
reaction intermediate (Figure 3A). The C5+ selectivity among all hydrocarbons is as high as 78.6% with only 1% CH4 at CO2 conversion of 13.1%. Because the C–C coupling from methanol occurs on zeolites at high temperature (>320 °C), HZSM-5 combined with other active components, which can achieve highly selective CO2 hydrogenation to methanol at above 320 °C, is also suitable for direct liquid hydrocarbons production from CO2 hydrogenation via bifunctional catalysis. The C5+ hydrocarbons selectivity of 70–80% with CH4 selectivity of 0.3–2% is obtained over various bifunctional catalysts containing HZSM-5 zeolites and ZnAlOx, ZnZrOx, ZnCrOx, ZnGaOx, or Cr2O3 oxides (Figure 3B,C). Similar to the CO2 activation mechanism on In2O3, the activity and formation rates of the methanol intermediate are dominated by the amount of oxygen vacancies on these oxide surfaces. Additionally, many studies have demonstrated that the C5–C11 isoparaffin/ aromatic ratio depends on the nature of oxides and zeolites and the proximity of the two components. For the oxide/zeolite catalyst system, the CO2 conversion is still low (<20%), and the selectivity of byproduct CO is usually >30%. As mentioned above, the introduction of highly dispersed metals can improve the CO2-to-methanol performance of In2O3. This strategy can help to increase the bifunctional catalytic activity for CO2 hydrogenation to liquid hydrocarbons via the methanol intermediates and reduce CO selectivity, while the origin of the enhancement effect of the bifunctional catalysis needs further studies. In addition, the introduction of CO in the feed gas can inhibit the undesired RWGS reaction. For example, the CO selectivity over Cr2O3/HZSM-5 decreased to only 11.4% with the addition of 5.42 vol % CO into the feed gas. Inspired by the CO2 hydrogenation to gasoline process over the multifunctional catalyst comprised of Fe3O4, Fe5C2, and zeolite acid sites, the introduction of iron carbide active sites into oxide/zeolite bifunctional catalysts to promote the further conversion of the generated CO may also be an effective strategy to decrease CO selectivity.

■ CO2 HYDROGENATION TO HIGHER ALCOHOLS

The selective conversion of CO2 and H2 into higher alcohols remains a much greater challenge than that into C2+ hydrocarbon products due to the existence of many parallel and consecutive reactions and usually higher energy barriers for CO insertion compared with CHx hydrogenation. Noble metal (Au, Pd)-based catalysts were developed for direct synthesis of ethanol from CO2 hydrogenation with high selectivity in a batch reactor. Han’s group reported water promoted CO2 hydrogenation to C2–4 alcohols, and the selectivity over Pt/Co3O4 is up to 88.1% at 220 °C and 8.0 MPa in the water/1,3-dimethyl-2-imidazolidinone mixed solvent. Recently, non-noble metal-based catalysts were found to also enable highly efficient liquid-phase ethanol
synthesis from direct CO₂ hydrogenation. The Co−Al LDH derived CoAlOₓ catalyst gives an ethanol selectivity of 92.1% and an ethanol time yield of 0.444 mmol g⁻¹ h⁻¹ at 140 °C. In addition, the introduction of nickel species into the CoAlOₓ catalyst accelerates the formation of the relatively stable CHₓ intermediates, which enables Co₀.5₂Ni₀.4₈AlOₓ to achieve excellent performance for the selective conversion of CO₂ to ethanol.

In an autoclave reactor, very high C₂+OH selectivity (especially for ethanol) was usually obtained over the above-mentioned catalysts at relatively low reaction temperatures (140−220 °C). Some researchers have recently explored a new strategy to fabricate practical catalysts for direct CO₂ hydrogenation to C₂+OH in a fixed-bed reactor at a relatively high reaction temperature (>250 °C). Gong’s group developed TiO₂ nanorods supported Rh−Fe−Li catalysts for higher alcohol synthesis (HAS) from CO₂ hydrogenation and demonstrated that high density of hydroxyl groups on the support is responsible for the highly selective formation of ethanol. Rh−Fe−Li/TiO₂ displays a high ethanol selectivity of 32% among all carbon-containing products at around 15% CO₂ conversion at 250 °C and 3.0 MPa. Zhang et al. found that supported Co₂C catalysts enable 62.8% ethanol selectivity in the alcohol distribution at CO₂ conversion of around 18% at 250 °C and 5.0 MPa. They suggested that CO can form via RWGS at Co₂C sites and then insert into the CHₓ intermediates to produce ethanol. Xu et al. reported Cs-modified Cu−Fe−Zn catalysts for HAS from CO₂ hydrogenation, which exhibit a CO₂ conversion of 36.6%, C₂,OH selectivity of 19.8%, 93.8% C₂,OH fraction in the alcohol distribution, and C₂,OH STY of 73.4 mg g⁻¹ h⁻¹ at 330 °C and 5.0 MPa. It was suggested that Fe₇C₃ and Cu are responsible for CO dissociation to form CHₓ species and CO nondissociative adsorption, respectively, and a good balance between them enables Cs₃Cu₀.₈Fe₁.₀Zn₁.₀ catalysts to have the best performance among the catalysts with different metal compositions (Figure 4). Although the high C₂,OH fraction in the alcohol distribution seems to be easily obtained over these modified FTS catalysts, the alcohol selectivity among all products is very low (<40%), and the main products are still hydrocarbons and CO.

Very recently, Ding’s group reported the Cu@Na-Beta catalyst with Cu nanoparticles enclosed in the Na-Beta zeolite crystal particles that enables highly selective conversion of CO₂...
to ethanol in a fixed-bed reactor due to the synergistic effects among irregular Cu nanoparticles and surrounding of zeolitic frameworks (Figure 5A). Ethanol and CO are the only products, and no hydrocarbons and methanol are formed. The ethanol yield is up to ~14% with CO selectivity of 21% at CO₂ conversion of ~18% at 2.1 MPa (Figure 5B). They also found that the CH₃COO* species are the most important intermediates for ethanol production from CO₂, which are formed by bonding between CO₂* and CH₄* at the step sites of Cu nanoparticles. It is usually difficult to obtain C₂+ products at a single Cu site. The subtlety of this work is the use of 3D zeolitic frameworks to confine and regulate Cu nanoparticles in unique shapes to achieve precise C−C coupling on the Cu surface.

In the field of CO hydrogenation, new routes using multifunctional catalysts have been developed for higher alcohol synthesis (HAS) from syngas with high selectivity. Sun’s group combined Co−Mn oxides (FTS catalyst) with Cu−Zn−Al−Zr oxides (methanol synthesis catalyst) and markedly increased the oxygenates selectivity to 58.1 wt % with the C₂O,OH fraction of 92.0 wt %. The Cu−Zn−Al−Zr oxides could provide more CH₃O* species and selectively promote the CO*−(or CH₂O*) insertion reaction, which benefits the oxygenates formation. A similar strategy by using multifunctional catalysts composed of Mo-based sulfides and Zn−Cr−Al oxides has been reported for HAS. The alcohol selectivity was enhanced to 60.4% with >72.7% C₂O* selectivity in alcohols. Wang’s group proposed relay catalysis using a three-component catalytic system that enables syngas-to-methanol/dimethyl ether (DME), methanol/DME carboxylation, and acetic acid hydrogenation reactions in one reactor. Ethanol selectivity reaches 64% at a CO conversion of around 10%. Inspired by these effective strategies, the development of a new catalyst with different functions for CO₂ hydrogenation with high alcohol selectivity is highly attractive but also very challenging.

### SUMMARY AND PERSPECTIVE

In the past few decades, heterogeneous CO₂ hydrogenation to methanol via thermal catalysis has received great attention and has seen enormous progress. As a result, various highly efficient and novel catalysts (such as Cu, Co, bimetallic systems, and reducible metal oxides) have been developed with their active sites revealed and their reaction mechanisms understood to some extent. Considering the catalytic performance, catalyst cost, scale-up preparation feasibility, and other factors, Cu-based catalysts still hold the greatest prospect for large-scale industrial applications of methanol synthesis from pure CO₂. Very recently, more researchers are considering the direct synthesis of value-added C₂+ liquid products from CO₂ hydrogenation. Direct CO₂ hydrogenation to oxygenates possesses a better atom economy and also a higher efficiency in hydrogen utilization than hydrocarbon production. On the other hand, worldwide consumption of liquid hydrocarbon fuels is greater, due to their higher energy content. Currently, high selectivity of gasoline fuels (above 75%) can be achieved over Na−Fe/HZSM-5 and In₂O₃/HZSM-5 bifunctional catalyst systems albeit via different reaction mechanisms. The modified FTS catalysts are expected to be more suitable for the synthesis of heavier hydrocarbons (such as jet fuels and diesel) and C₂O,OH alcohols from CO₂ due to the great C−C coupling ability. For CO₂ hydrogenation to liquid hydrocarbons over Fe-based catalysts, better understanding of the iron carbide active sites is required for further improving the stability and decreasing the selectivity of light hydrocarbons as well as the industrial implementation of this process. To further enhance the performance of the Co-based CO₂−FTS catalyst, it is necessary to introduce a highly active low-temperature RWGS site. For the production of higher alcohols, catalyst development is still at a very early stage, where the problem of low alcohol yield remains to be solved. In addition to learning from the new strategy using multifunctional catalysts in HAS from syngas, using the confinement or modulation effects of zeolites on the reactive centers is an effective strategy to increase the selectivity of higher alcohols in CO₂ hydrogenation.

If the CO₂ source is coal- or biomass-combustion flue gas, the CO₂ conversion process becomes more complicated due to the copresence of CO, O₂, SOₓ, and/or NOₓ. Cost associated with cleaning the flue gas especially via deep desulfurization will decrease the economic viability of CO₂ conversion. In this regard, the ZnO−ZrO₂ catalyst mentioned above is more suitable due to its excellent sulfur tolerance. Although little attention has been paid to the effect of sulfur-containing molecules on the CO₂ hydrogenation reaction, it can be speculated that other oxide catalyst systems with the oxygen vacancy as the active site also have good sulfur resistance owing to their similar reaction mechanism. Therefore, for CO₂ sources from flue gas, partially reduced oxides and oxides/zeolites bifunctional catalysts are industrially more relevant for methanol production and liquid hydrocarbons synthesis via the methanol intermediate, respectively. The In₂O₃-based catalysts have received especially great attention due to their high performance and relatively simple active site structures. In addition, these catalyst systems usually show excellent selectivity and high stability, although their single-pass CO₂ conversions are usually much lower than those over supported metal catalysts (such as Cu- and Fe-based catalysts) and are generally below 20% even with noble metal modifiers and at relatively high reaction temperature (＞280 °C). A very high recycle ratio of the unconverted gas is needed in industrial applications of CO₂ hydrogenation, which may decrease its energy efficiency and economic value. Thus, it is necessary to further increase the amount of oxygen vacancies and enhance the H₂ splitting ability to improve the intrinsic activity of these oxide catalysts.

Apart from further developing more efficient catalysts for milder reaction conditions, sufficient attention should be paid on reactor design and optimization.
Recent years have seen emerging experimental and computational technologies for more efficient search and design of catalysts and other materials. Experimental technologies such as high-throughput catalyst synthesis and performance evaluation, 3D printing, and in situ characterizations and monitoring are increasingly being employed for the rapid discovery of novel catalysts and materials.\textsuperscript{131–133} On the other hand, a similar array of computational technologies including high-throughput and automated computational simulations and reaction modeling coupled with machine learning algorithms also start to enable the theoretical understanding and prediction of new catalysts.\textsuperscript{134–136} The applicability of the above experimental and computational technologies in designing industrially relevant heterogeneous catalysts vary due to their greater complexity and stringent requirements. Nevertheless, these new technologies hold great potential in revolutionizing the way that industrial catalysts have been traditionally developed, and thus great progress can be expected in this research. Apart from further developing more efficient catalysts for milder reaction conditions, we should also pay sufficient attention to reactor design and optimization. For example, a membrane reactor can shift the equilibrium-limited CO\(_2\) hydrogenation to liquid fuels by selective and continuous in situ removal of the byproduct water, leading to a substantial increase in CO\(_2\) conversion as well as the yield of liquid fuels.\textsuperscript{137–139}

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\section*{Notes}

The authors declare no competing financial interest.

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1666

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