

Novel Heterogeneous Catalysts for CO₂ Hydrogenation to Liquid Fuels

Peng Gao,^{*,#} Lina Zhang,[#] Shenggang Li,[#] Zixuan Zhou, and Yuhan Sun



Cite This: *ACS Cent. Sci.* 2020, 6, 1657–1670



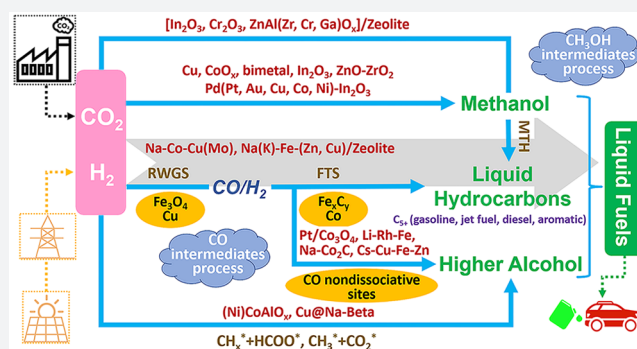
Read Online

ACCESS |

Metrics & More

Article Recommendations

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 (C_{5–11}), jet fuel (C_{8–16}), and diesel (C_{10–20}) 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 including liquid hydrocarbons. Moreover, the synthesis of C₂₊ alcohols is even more

Received: July 23, 2020

Published: September 18, 2020



challenging than C_{2+} hydrocarbons either in CO_2 or CO hydrogenation, which requires more precise control of the C–C coupling.^{20–22}

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 CO_2 hydrogenation to C_{2+} hydrocarbons including liquid hydrocarbons.

In this Outlook, we will discuss recent developments in designing heterogeneous catalysts for direct CO_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_{5+} 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_2 to CH_3OH , as there have been many excellent recent reviews on methanol synthesis via heterogeneous catalysis.^{12,23–27}

■ CO_2 HYDROGENATION TO METHANOL

During CO_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.²⁸ However, the low temperature and/or high space velocity usually result in low single pass CO_2 conversion. Thus, it remains a great challenge to simultaneously obtain high CO_2 conversion and high methanol selectivity. Very recently, significant progress has been made in developing more efficient catalysts for CO_2 hydrogenation to CH_3OH , including metal-supported catalysts, bimetallic systems, and reducible metal oxides.

Industrial methanol production from CO_2 -containing syngas uses the well-known $Cu-ZnO-Al_2O_3$ catalysts. Currently, CH_3OH synthesis from catalytic CO_2 hydrogenation has been implemented at the pilot-plant level by Lurgi, Mitsui, CRI, among others.^{12,29} These processes mainly used modified $Cu-ZnO-Al_2O_3$ 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_2 hydrogenation to CH_3OH . The methanol synthesis reaction is known to show strong support effects. Using a suitable support material can enhance CH_3OH selectivity, attributed to structural, electronic, and chemical promotional effects. For example, CH_3OH selectivity is usually high (>70%) at 200–260 °C when ZrO_2 is used as the support.^{30–32} Recently, several works have clarified the origin of the promotional effect of the ZrO_2 support that is unknown before. Larmier et al. confirmed that the Cu/ZrO_2 interface can promote the conversion of the

formate intermediates to methanol by combined experimental and computational investigations.³⁰ Tada et al. found that the interfacial sites on $Cu/a-ZrO_2$ (a: amorphous) are favored for methanol production compared to those on tetragonal and monoclinic ZrO_2 supported Cu .³³ Additionally, the oxygen vacancies on tetragonal ZrO_2 were proposed to play a crucial role in enhancing the activity of methanol formation by stabilizing the Cu^+ active sites adjacent to them.³² Lam et al. suggested that the surface Lewis acid $Zr(IV)$ sites with Cu particles in the vicinity are responsible for improving CH_3OH activity and selectivity on the Cu/ZrO_2 -based catalysts.³¹ Apart from conventional metal oxides, researchers recently also explored other supports such as TiO_2 nanotubes³⁴ and $Mg-Al$ layered double hydroxide (LDH)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.^{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).³⁷ The CH_3OH space time yield (STY) is $0.59 \text{ g}_{MeOH} \text{ g}_{cat}^{-1} \text{ h}^{-1}$ with selectivity of ~49% at CO_2 conversion of ~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_2 hydrogenation.^{40–44} For example, Liu et al. synthesized three-dimensional porous $Cu@ZrO_2$ framework catalysts using the $Cu@UiO-66$ precursor, which displays CH_3OH STY of $0.796 \text{ g}_{MeOH} \text{ g}_{cat}^{-1} \text{ h}^{-1}$ 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 $g^{-1} \text{ h}^{-1}$ and $H_2/CO_2 = 3$.⁴³

Recently, several groups have developed novel cobalt (Co)-based catalytic systems that display a promising performance for methanol synthesis from CO_2 hydrogenation.^{45–48} Co catalysts are widely used and extensively studied for FTS and can easily catalyze the CO_2 methanation reaction.^{2,17,46,49–52} The high performance for CH_3OH 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_x nanoparticles supported on a mesoporous Co_3O_4 for methanol production at low pressure (0.1–0.6 MPa).⁴⁵ They showed the importance of the CoO phase and revealed the strong interaction between MnO_x nanoparticles and $Co@CoO$ core–shell grains, which enhances the performance of CO_2 hydrogenation to CH_3OH . Lian et al. ascribed the increased CH_3OH selectivity to the oxygen defects on the surface of $Co@Co_3O_4$ core–shell active species supported on the nitrogen-doped carbon material, which is derived from zeolitic imidazolate framework precursors.⁴⁷ Wang et al. also inferred that the cobalt oxide phase on silica supported Co catalyst with $Co-O-SiO_n$ linkages via Co phyllosilicates could suppress the CO and CH_4 formation and promote methanol production (Figure 1B).⁴⁸ This novel Co catalyst shows CH_3OH STY of $0.096 \text{ g}_{MeOH} \text{ g}_{cat}^{-1} \text{ h}^{-1}$ (3.0 mmol $g_{cat}^{-1} \text{ h}^{-1}$) with a selectivity of 70.5% at 8.6% conversion at 320 °C. Because the H_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

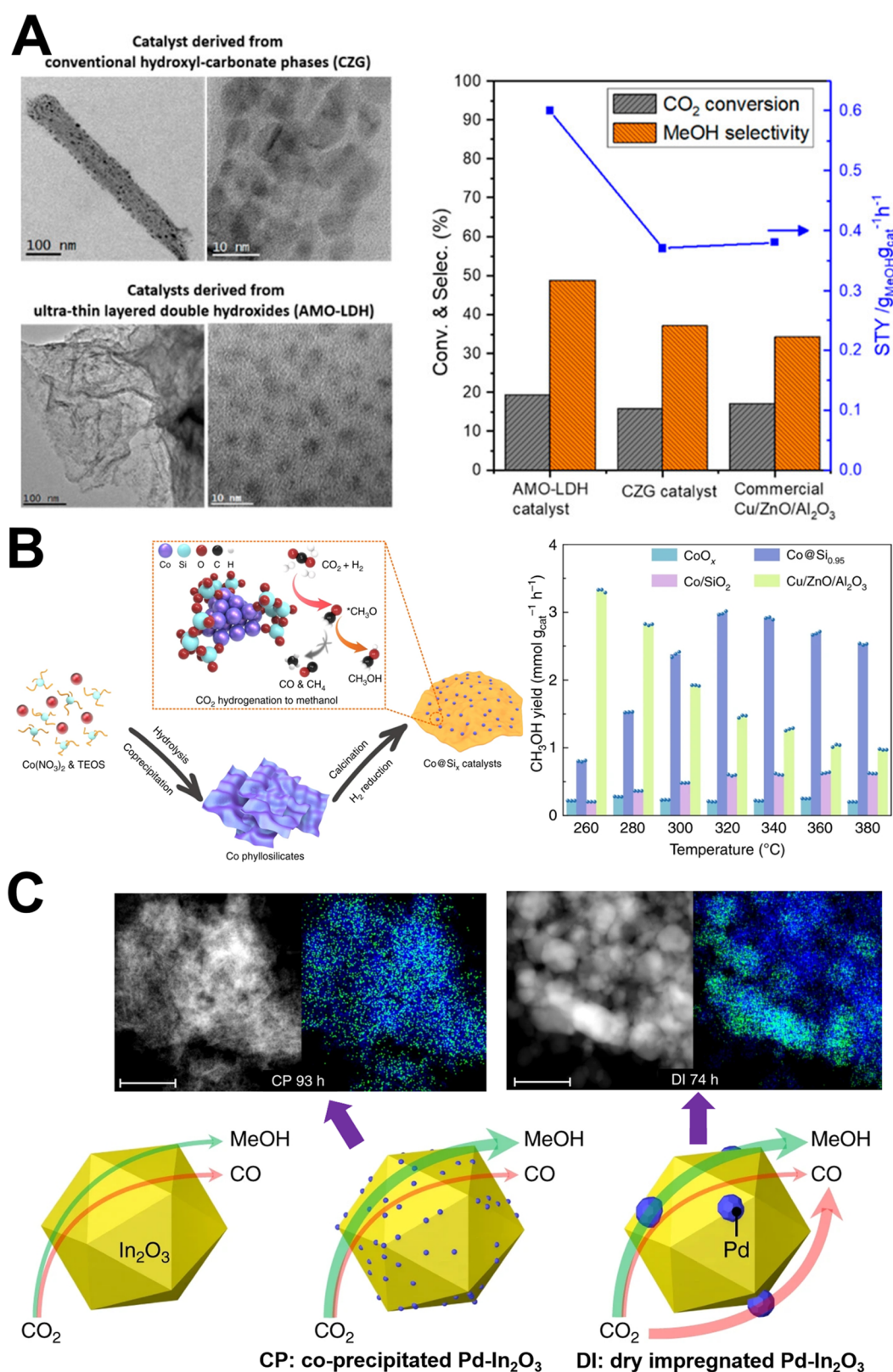


Figure 1. (A) TEM images of Cu–Zn–Ga catalysts derived from conventional hydroxyl-carbonate phases and ultrathin LDH (left) as well as their performance (right).³⁷ Reaction conditions: 270 °C, 4.5 MPa, 18 000 mL g⁻¹ h⁻¹, and H₂/CO₂ = 3. (B) Synthesis and catalysis strategies (left) as well as CO₂ hydrogenation 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,^{62–66} 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, Ni₅Ga₃ intermetallic compounds exhibited a higher CH₃OH 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 Ni₅Ga₃ during the catalysis after low temperature reduction promoted CO₂ activation.⁶³ The Ni_{3.5}In_{5.3}Al/SiO₂ catalyst with 15% metal loading via a phyllosilicate precursor also shows a higher conversion and a better stability, while yielding lower CH₃OH 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 CH₃OH selectivity than Cu–ZnO–Al₂O₃ have been observed at above 200 °C and atmospheric pressure.⁵⁷ 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 CH₃OH 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 CH₃OH.⁷⁸ 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. CH₃OH selectivity is as high as 92.4% with a CO₂ conversion of more than 17% under 300 °C, 5.0 MPa, 9000 mL g_{cat}⁻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.^{74,79} It was suggested that synergic effects between In₂O₃ and ZrO₂ carriers favorably tuned CH₃OH 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 nanocatalyst reached above 20% with CH₃OH selectivity of ~70% and STY up to 0.89 g_{MeOH} g_{cat}⁻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, CH₃OH STY dropped slightly from 1.01 to 0.96 g_{MeOH} g_{cat}⁻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.^{69,85–89} For the Au^{δ+}–In₂O_{3–x} catalyst, the strong Au–In₂O₃ interaction is responsible for the promising methanol synthesis performance.⁸⁹ Shi et al. found that the Cu₁₁In₉ phase is formed by controlled reduction of CuO–In₂O₃ mixed oxides, and the synergy between Cu₁₁In₉ and In₂O₃ gives a CH₃OH STY of 0.2 g_{MeOH} g_{cat}⁻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 In₂O_{3–x} films. The CH₃OH STY is as high as 0.86 g_{MeOH} g_{cat}⁻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 CH₃OH STY of 0.73 g_{MeOH} g_{cat}⁻¹ h⁻¹ at CH₃OH 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 = 3.⁹⁰ Under similar reaction conditions, a high selectivity of more than 80% is obtained over CdZrO_x and GaZrO_x 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.⁹⁰

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.

Compared with Cu-based catalysts, the biggest advantage of the reducible metal oxides (In_2O_3 -based oxides or ZnO-ZrO_2 solid solution catalysts) is that the undesired RWGS reaction can be effectively inhibited even if the reaction temperature is as high as 320 °C.

■ CO₂ HYDROGENATION TO LIQUID HYDROCARBONS

As CO₂ can be easily converted to CO via RWGS, modified CO-FTS catalysts were widely used for direct CO₂ 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 H₂ is usually needed in CO₂-based FTS, and the concentration of the CO intermediates is also lower during CO₂ hydrogenation, which results in a higher H/C ratio on the catalyst surface. As CO₂ can be directly hydrogenated to CH₄, the high H/C ratio favors methane formation and leads to a decrease in the chain growth probability. Therefore, CO₂-FTS catalysts to be

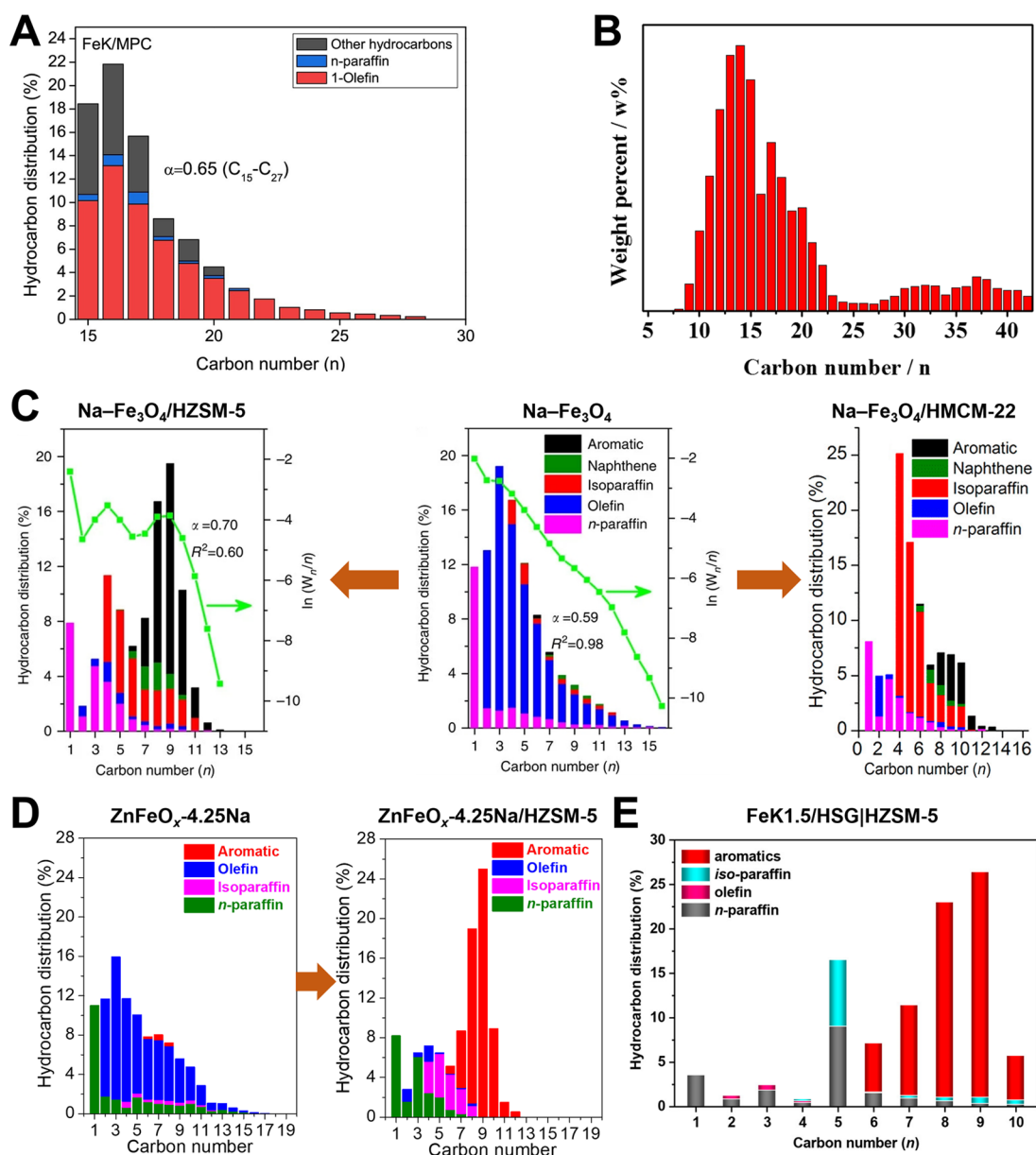


Figure 2. Detail hydrocarbon product distribution obtained over (A) well-defined mesoporous carbon (MPC) supported Fe–K in the range of C_{15-27} ,⁹⁵ (B) Fe–Cu,⁹⁸ (C) Na–Fe₃O₄ (middle),¹⁰⁵ Na–Fe₃O₄/HZSM-5 (left),¹⁰⁵ and Na–Fe₃O₄/HMCM-22 (right),¹⁰⁹ (D) ZnFeO_x-4.25Na (left) and ZnFeO_x-4.25Na/HZSM-5 (right) under the reaction conditions of 320 °C, 3.0 MPa, H₂/CO₂ = 3, and 4000 mL g⁻¹ h⁻¹,¹⁰⁷ as well as (E) FeK1.5/HSG/HZSM-5 (SiO₂/Al₂O₃ molar ratio of HZSM-5 = 50) catalysts during the CO₂ hydrogenation reaction.¹¹⁰ 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.^{92,93} For example, the optimized Na-Co-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 Nevertheless, Fe catalysts seem to be more suitable for direct CO₂ conversion because it has high RWGS reactivity but relatively lower CO₂ methanation activity. Albrecht et al. prepared a bare Fe₂O₃ catalyst using the cellulose-templated synthesis method, which achieves C₅₊ hydrocarbons selectivity of 36% at CO₂ conversion of 40% at 350 °C and 1.5 MPa.⁹⁴ Additionally, the selectivities of C₂₋₄ hydrocarbons (olefin/paraffin (o/p) ratio = 2.7) and CH₄ are 36% and 12%, respectively.

To decrease CH₄ selectivity and enhance chain growth ability of Fe catalysts, promoters such as K, Na, Cu, Zn, Mn, and/or Ce are introduced. Simultaneously, some uniquely structured Fe catalysts were fabricated with improved activity and stability. Hwang et al. synthesized a well-defined mesoporous carbon (MPC) supported Fe-K catalyst, and the weak metal-support interaction favored the formation of iron carbide (Fe₃C₂), which is the active site for CO-FTS.⁹⁵ The C₅₊ hydrocarbon selectivity over Fe-K/MPC reaches 44.5% with a CH₄ selectivity of 15.4% and chain growth probability (C₁₅₋₂₇) of 0.65 at 300 °C and 2.5 MPa (Figure 2A). Liu et al. chose modified ZIF-8 as the precursor to synthesize the Fe-Zn-K catalyst with a hollow sphere structure, which gives the Fe catalyst a high stability under harsh reaction conditions (320 °C and 3.0 MPa).⁹⁶ The introduction of Cu as a promoter facilitates the reduction of ferric oxide and enhances CO₂ adsorption, which can increase conversion and C₅₊ selectivity as well as decrease CH₄ selectivity.⁹⁷ Delafossite (CuFeO₂) derived Fe-Cu catalysts give C₅₊ hydrocarbon selectivity as high as 66.3% among all hydrocarbons with 31% of C₂₋₄ (o/p = 7.3) and only 2.7% of methane under 300 °C, 1.0 MPa, 1800 mL g⁻¹ h⁻¹, and H₂/CO₂ = 3.⁹⁸ The presence of Cu⁺ species in CuFeO₂ promotes the reduction of the Fe catalyst and thus promotes the formation of the FTS active phase (γ-Fe₅C₂). As shown in Figure 2B, apart from gasoline and diesel range hydrocarbons, the liquid products also contain about 15 wt % of waxes. To the best of our knowledge, there have been no reports on wax (C₂₁₊) production directly from CO₂. Therefore, CuFeO₂ shows an unprecedented chain growth ability in the CO₂-FTS reaction, which can be suitable for CO₂ hydrogenation to wax. For spinel ZnFe₂O₄ derived Zn- and Na-modulated Fe catalysts, Zn serves as the structural promoter to improve the dispersion of Fe species.^{99,100} Gasoline and diesel range hydrocarbons can also be obtained over the reduced ZnFe₂O₄.¹⁰⁰ Under the same reaction condition, C₅₊ selectivity over the Fe-Zn catalyst is lower than the Fe-Cu catalyst (58.5% vs 66.3%) with much higher CO₂ conversion (34.0% vs 17.3%) and lower CO selectivity (11.7% vs 31.7%).^{98,100} K-promoted Fe-Co/Al₂O₃ with Co/(Co+Fe) = 0.17 also enables CO₂ hydrogenation to liquid hydrocarbons with jet fuel-range α-olefins as the main products.¹⁰¹

The excellent performance for the synthesis of heavier hydrocarbons using these Co or Fe catalysts is usually related to the presence of alkaline metals (K or Na) because these promoters can enhance the RWGS reaction while suppressing the methanation reaction.^{100,102-104} Additionally, the high temperature applied for traditional Fe-based FTS favors the endothermic RWGS reaction, and the traditional Co-based catalyst usually operates at a lower temperature of 180–240 °C. Therefore, compared to catalysts with metallic Co as the active site, it is easier to obtain heavier hydrocarbons from CO₂, and the product distribution is closer to that derived from CO-FTS over the Fe catalyst with iron carbides as active sites at a higher reaction temperature (300 °C).

However, the CO₂ hydrogenation product distribution over the modified Fe-based FTS catalysts still follows the well-known Anderson-Schulz-Flory (ASF) distribution because CO₂- and CO-FTS have similar reaction mechanisms. In addition, the hydrocarbons are mainly olefins and normal-paraffins (*n*-paraffins) for Fe-based FTS (Figure 2).¹⁰⁵⁻¹⁰⁷ Recently, Wei et al. combine Fe catalysts with HZSM-5 zeolites to significantly increase the fraction of high-octane gasoline-range isoparaffins and aromatics in the CO₂ hydrogenation product (Figure 2C).¹⁰⁵ The generated olefins on Na-Fe₃O₄ diffuse to the acid sites of zeolites and are then converted to C₅₋₁₁ isoparaffins and aromatics via oligomerization, isomerization, and aromatization reactions. As a result, the selectivity of C₅₋₁₁ hydrocarbons among all hydrocarbons is up to 73% with 7.9% methane at CO₂ conversion of 33.6% and CO selectivity of 14.2% under 320 °C, 3.0 MPa, 4000 mL g⁻¹ h⁻¹, and H₂/CO₂ = 3. Moreover, the isoparaffin/aromatic ratio in C₅₋₁₁ hydrocarbons over this bifunctional catalyst system containing Fe-based oxides and zeolites can be tuned by regulating the types, structures, and properties of zeolites.^{105,108} HMC-22 zeolite with a unique pore network and appropriate Brønsted acid density and strength enables the formation of branched hydrocarbons with superior selectivity (Figure 2C, ~35% in all hydrocarbons).¹⁰⁹ Recent studies also demonstrate that Na-ZnFeO_x/HZSM-5 comprised of Na modified ZnFeO_x and hierarchical nanocrystalline HZSM-5 aggregated with an appropriate density of Brønsted acid sites can realize the highly efficient synthesis of aromatics from CO₂ hydrogenation (Figure 2D).¹⁰⁷ The selectivity of gasoline-range hydrocarbons over this composite catalyst reaches as high as 83.7%, and aromatics selectivity is up to 75.6%. Of course, the enhanced performance of Fe catalysts for CO₂ hydrogenation to light olefin intermediates is also favorable for the synthesis of liquid hydrocarbons. For example, Wang et al. synthesized potassium-promoted iron using honeycomb-structured graphene (HSG) as the support and achieved an exceptionally high activity in hydrogenating CO₂ to lower olefins, which results in a high liquid hydrocarbons selectivity of 92% and aromatics STY of 11.8 μmol_{CO}, g_{cat}⁻¹ s⁻¹ at 340 °C, 2.0 MPa, and 26 000 mL g⁻¹ h⁻¹ when coupled with the HZSM-5 zeolite (Figure 2E).¹¹⁰

Although the selectivity of hydrocarbons among CO₂ hydrogenation products can be increased by coupling olefination with aromatization, the ratio of isoparaffins to *n*-paraffins (iso/*n*) is no more than 3, leading to a low octane number.¹⁰⁹ It was found that the reducible indium oxides in combination with HZSM-5 zeolites enable direct CO₂ conversion into gasoline-range hydrocarbons with a very high iso/*n* ratio of 16.8 through the formation of methanol as the

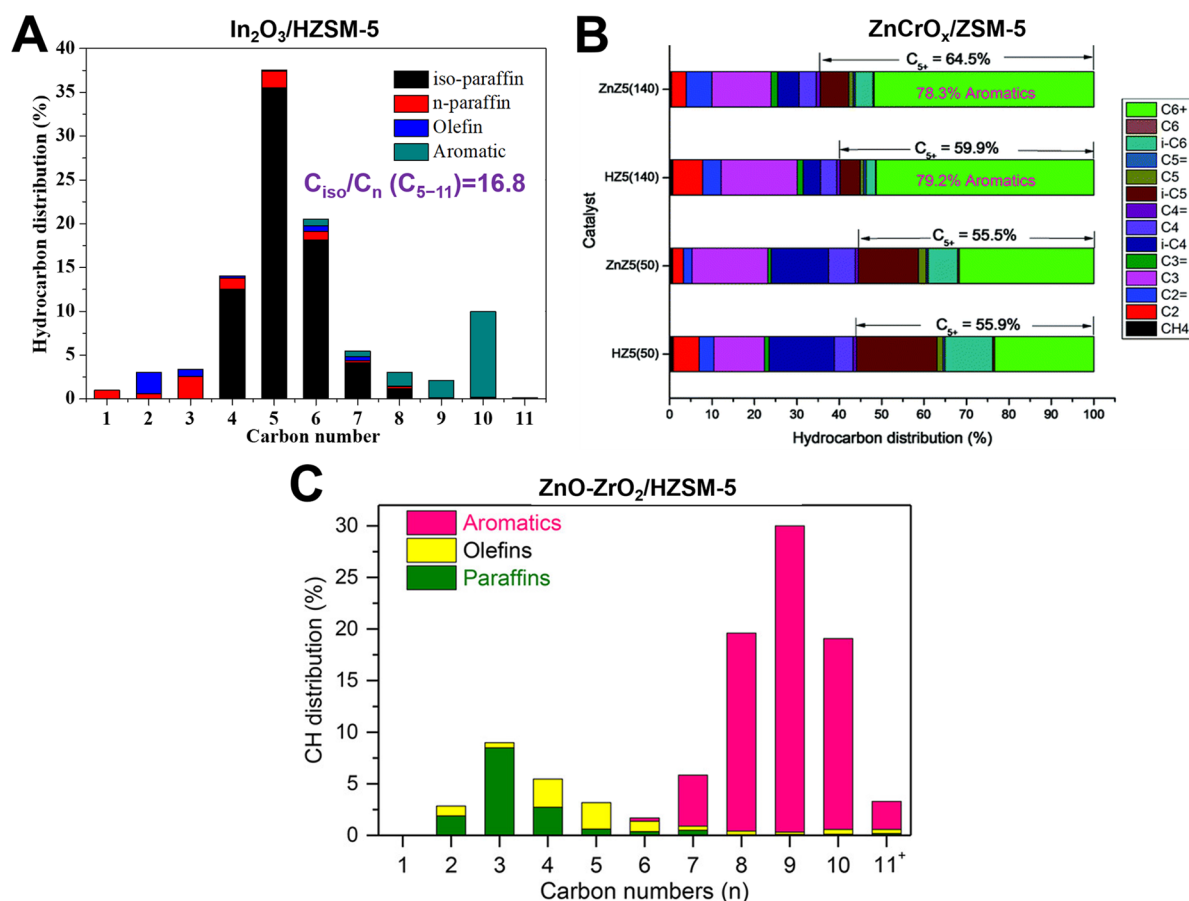


Figure 3. CO₂ hydrogenation hydrocarbon product distribution over (A) In₂O₃/HZSM-5 under reaction conditions of 340 °C, 3.0 MPa, H₂/CO₂ = 3, and 9000 mL g⁻¹ h⁻¹,¹¹¹ (B) composite catalyst containing ZnCrO_x and various HZSM-5 zeolites (with and without Zn-exchange) at 330 °C, 5.0 MPa, H₂/CO₂ = 3, and 2000 mL g⁻¹ h⁻¹,¹¹⁴ and (C) ZnO-ZrO₂/HZSM-5 (reaction conditions: 340 °C, 4.0 MPa, H₂/CO₂ = 3, and 7200 mL g⁻¹ h⁻¹).¹¹⁵ Reprinted with permission from refs 111, 114, and 115. Copyright 2017 Springer-Nature, Copyright 2019 Royal Society of Chemistry, and Copyright 2020 American Chemical Society.

reaction intermediate (Figure 3A).¹¹¹ 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 ZnAlO_x, ZnZrO_x, ZnCrO_x, ZnGaO_x, or Cr₂O₃ oxides (Figure 3B,C).^{112–117} 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.^{113,115} 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.^{111,116} 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.¹¹⁶ 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 CH_x hydrogenation.²¹ Noble metal (Au, Pd)-based catalysts were developed for direct synthesis of ethanol from CO₂ hydrogenation with high selectivity in a batch reactor.^{118–120} Han's group reported water promoted CO₂ hydrogenation to C_{2–4} 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.¹²⁰ Recently, non-noble metal-based catalysts were found to also enable highly efficient liquid-phase ethanol

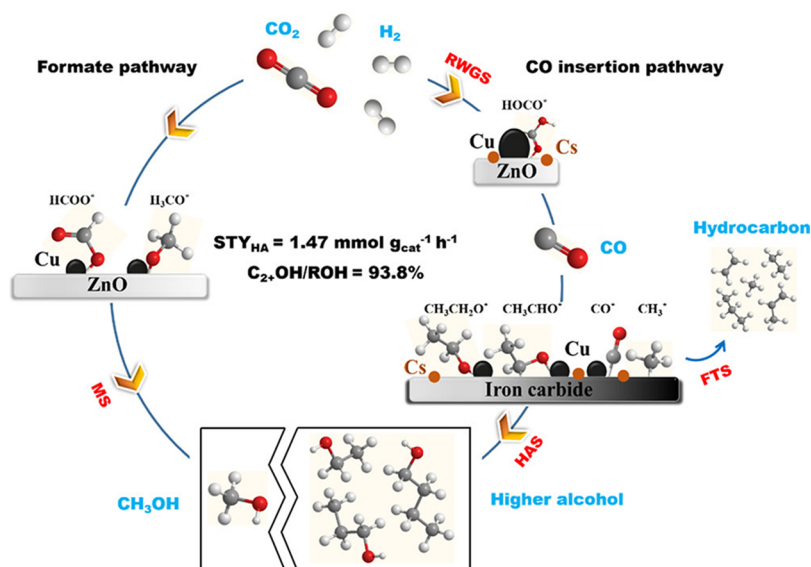


Figure 4. Reaction pathways of CO₂ hydrogenation over the Cs–Cu–Fe–Zn catalyst. Reprinted with permission from ref 22. Copyright 2020 American Chemical Society.

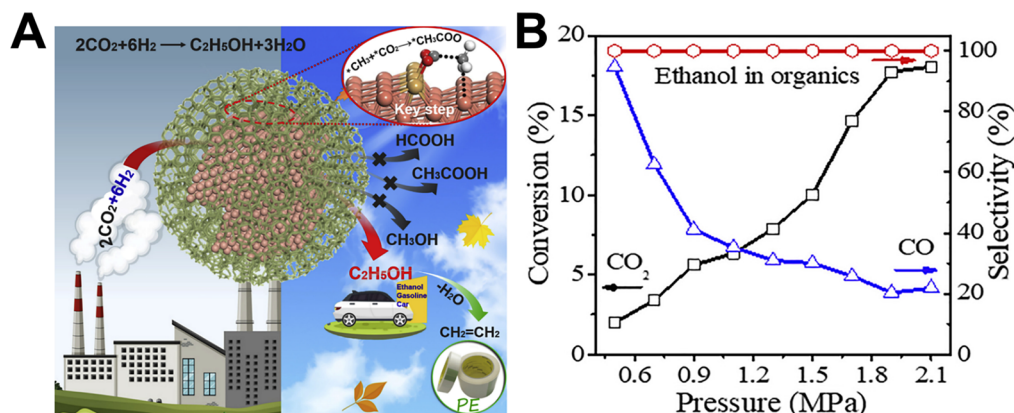


Figure 5. (A) The CO₂ hydrogenation to ethanol reaction process over Cu@Na-Beta catalyst. (B) The influence of reaction pressure on CO₂ hydrogenation performance of Cu@Na-Beta. Reaction condition: 300 °C, 12 000 mL g⁻¹ h⁻¹, and H₂/CO₂ = 3.¹²⁵ Reprinted with permission from ref 125. Copyright 2020 Elsevier.

synthesis from direct CO₂ hydrogenation. The Co–Al LDH derived CoAlO_x catalyst gives an ethanol selectivity of 92.1% and an ethanol time yield of 0.444 mmol g⁻¹ h⁻¹ at 140 °C.¹⁰ In addition, the introduction of nickel species into the CoAlO_x catalyst accelerates the formation of the relatively stable CH_x intermediates, which enables Co_{0.52}Ni_{0.48}AlO_x to achieve excellent performance for the selective conversion of CO₂ to ethanol.¹²¹

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).^{22,122–124} 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.¹²⁴ 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.¹²³ They suggested that CO can form via RWGS at Co₂C sites and then insert into the CH_x intermediates to produce ethanol. Xu et al. reported Cs-modified Cu–Fe–Zn catalysts for HAS from CO₂ hydrogenation, which exhibits 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_{cat}⁻¹ h⁻¹ at 330 °C and 5.0 MPa.²² It was suggested that Fe₇C₃ and Cu are responsible for CO dissociation to form CH_x species and CO nondissociative adsorption, respectively, and a good balance between them enables Cs_{3 wt %}-Cu_{0.8}-Fe_{1.0}-Zn_{1.0} 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).¹²⁵ 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 CH₃* 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 C₂₊OH fraction of 92.0 wt %.²¹ The Cu–Zn–Al–Zr oxides could provide more CH_xO* species and selectively promote the CO* (or CH_xO*) 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.¹²⁶ The alcohol selectivity was enhanced to 60.4% with >72.7% C₂₊OH selectivity in alcohols. Wang's group proposed relay catalysis strategy using a three-component catalytic system that enables syngas-to-methanol/dimethyl ether (DME), methanol/DME carbonylation, and acetic acid hydrogenation reactions in one reactor.^{20,127} 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.³ 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 very 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 C₂₊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.

Together with the development of multifunctional catalysts, 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, SO_x, and/or NO_x.^{128,129} Cost associated with cleaning the flue gas especially via deep desulfurization will decrease the economic viability of CO₂ conversion.¹³⁰ 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.^{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.^{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 CO₂ hydrogenation to liquid fuels by selective and continuous *in situ* removal of the byproduct water, leading to a substantial increase in CO₂ conversion as well as the yield of liquid fuels.^{137–139}

AUTHOR INFORMATION

Corresponding Author

Peng Gao – CAS Key Laboratory of Low-Carbon Conversion Science and Engineering, Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201210, PR China; University of Chinese Academy of Sciences, Beijing 100049, PR China; Dalian National Laboratory for Clean Energy, Dalian 116023, PR China; orcid.org/0000-0003-4859-4488; Phone: +86-021-20350994; Email: gaopeng@sari.ac.cn

Authors

Lina Zhang – CAS Key Laboratory of Low-Carbon Conversion Science and Engineering, Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201210, PR China

Shenggang Li – CAS Key Laboratory of Low-Carbon Conversion Science and Engineering, Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201210, PR China; University of Chinese Academy of Sciences, Beijing 100049, PR China; School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, P.R. China; Dalian National Laboratory for Clean Energy, Dalian 116023, PR China; orcid.org/0000-0002-5173-0025

Zixuan Zhou – CAS Key Laboratory of Low-Carbon Conversion Science and Engineering, Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201210, PR China; University of Chinese Academy of Sciences, Beijing 100049, PR China

Yuhan Sun – CAS Key Laboratory of Low-Carbon Conversion Science and Engineering, Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201210, PR China; School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, P.R. China; Shanghai Institute of Clean Technology, Shanghai 201620, P.R. China

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acscentsci.0c00976>

Author Contributions

[#]These authors contributed equally: P.G., L.Z., and S.L.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank Dr. Alexander van der Made, Dr. Alexander Petrus van Bavel, and Dr. Joost Smits from Shell Global Solutions International B.V. for helpful discussions. P.G. acknowledges funding support from Strategic Priority Research Program of the Chinese Academy of Sciences (XDA21090204), the National Natural Science Foundation of China (21773286, U1832162), Youth Innovation Promotion Association CAS (2018330), the “Frontier Science” program of Shell Global Solutions International B.V. (PT65197, CW373032), and Shanghai Rising-Star Program, China (19QA1409900).

REFERENCES

- (1) Sakakura, T.; Choi, J. C.; Yasuda, H. Transformation of carbon dioxide. *Chem. Rev.* **2007**, *107* (6), 2365–2387.
- (2) Zhou, W.; Cheng, K.; Kang, J. C.; Zhou, C.; Subramanian, V.; Zhang, Q. H.; Wang, Y. New horizon in C1 chemistry: breaking the selectivity limitation in transformation of syngas and hydrogenation of CO₂ into hydrocarbon chemicals and fuels. *Chem. Soc. Rev.* **2019**, *48* (12), 3193–3228.
- (3) Leonzio, G. State of art and perspectives about the production of methanol, dimethyl ether and syngas by carbon dioxide hydrogenation. *J. CO₂ Util.* **2018**, *27*, 326–354.
- (4) Shih, C. F.; Zhang, T.; Li, J.; Bai, C. Powering the Future with Liquid Sunshine. *Joule* **2018**, *2* (10), 1925–1949.
- (5) Buttler, A.; Spliethoff, H. Current status of water electrolysis for energy storage, grid balancing and sector coupling via power-to-gas and power-to-liquids: A review. *Renewable Sustainable Energy Rev.* **2018**, *82*, 2440–2454.
- (6) Varone, A.; Ferrari, M. Power to liquid and power to gas: An option for the German Energiewende. *Renewable Sustainable Energy Rev.* **2015**, *45*, 207–218.
- (7) Deutz, S.; Bongartz, D.; Heuser, B.; Kätelhön, A.; Schulze Langenhorst, L.; Omari, A.; Walters, M.; Klankermayer, J.; Leitner, W.; Mitsos, A.; Pischinger, S.; Bardow, A. Cleaner production of cleaner fuels: wind-to-wheel – environmental assessment of CO₂-based oxymethylene ether as a drop-in fuel. *Energy Environ. Sci.* **2018**, *11* (2), 331–343.
- (8) Bos, M. J.; Kersten, S. R. A.; Brillman, D. W. F. Wind power to methanol: Renewable methanol production using electricity, electrolysis of water and CO₂ air capture. *Appl. Energy* **2020**, *264*, 114672.
- (9) Zhang, C. D.; Gao, R. X.; Jun, K. W.; Kim, S. K.; Hwang, S. M.; Park, H. G.; Guan, G. F. Direct conversion of carbon dioxide to liquid fuels and synthetic natural gas using renewable power: Techno-economic analysis. *J. CO₂ Util.* **2019**, *34*, 293–302.
- (10) Wang, L.; Wang, L.; Zhang, J.; Liu, X.; Wang, H.; Zhang, W.; Yang, Q.; Ma, J.; Dong, X.; Yoo, S. J.; Kim, J.-G.; Meng, X.; Xiao, F.-S. Selective Hydrogenation of CO₂ to Ethanol over Cobalt Catalysts. *Angew. Chem., Int. Ed.* **2018**, *57* (21), 6104–6108.
- (11) Stangeland, K.; Li, H. L.; Yu, Z. X. Thermodynamic Analysis of Chemical and Phase Equilibria in CO₂ Hydrogenation to Methanol, Dimethyl Ether, and Higher Alcohols. *Ind. Eng. Chem. Res.* **2018**, *57* (11), 4081–4094.
- (12) Zhong, J.; Yang, X.; Wu, Z.; Liang, B.; Huang, Y.; Zhang, T. State of the art and perspectives in heterogeneous catalysis of CO₂ hydrogenation to methanol. *Chem. Soc. Rev.* **2020**, *49* (5), 1385–1413.
- (13) Guo, L. S.; Sun, J.; Ge, Q. J.; Tsubaki, N. Recent advances in direct catalytic hydrogenation of carbon dioxide to valuable C₂+ hydrocarbons. *J. Mater. Chem. A* **2018**, *6* (46), 23244–23262.
- (14) Yang, H. Y.; Zhang, C.; Gao, P.; Wang, H.; Li, X. P.; Zhong, L. S.; Wei, W.; Sun, Y. H. A review of the catalytic hydrogenation of

carbon dioxide into value-added hydrocarbons. *Catal. Sci. Technol.* **2017**, *7* (20), 4580–4598.

(15) Li, J. C.; Wang, L. G.; Cao, Y.; Zhang, C. J.; He, P.; Li, H. Q. Recent advances on the reduction of CO₂ to important C₂+ oxygenated chemicals and fuels. *Chin. J. Chem. Eng.* **2018**, *26* (11), 2266–2279.

(16) Bao, J.; Yang, G. H.; Yoneyama, Y.; Tsubaki, N. Significant Advances in C₁ Catalysis: Highly Efficient Catalysts and Catalytic Reactions. *ACS Catal.* **2019**, *9* (4), 3026–3053.

(17) Khodakov, A. Y.; Chu, W.; Fongarland, P. Advances in the development of novel cobalt Fischer–Tropsch catalysts for synthesis of long-chain hydrocarbons and clean fuels. *Chem. Rev.* **2007**, *107* (5), 1692–1744.

(18) Ilias, S.; Bhan, A. Mechanism of the Catalytic Conversion of Methanol to Hydrocarbons. *ACS Catal.* **2013**, *3* (1), 18–31.

(19) Olsbye, U.; Svelle, S.; Bjorgen, M.; Beato, P.; Janssens, T. V. W.; Joensen, F.; Bordiga, S.; Lillerud, K. P. Conversion of Methanol to Hydrocarbons: How Zeolite Cavity and Pore Size Controls Product Selectivity. *Angew. Chem., Int. Ed.* **2012**, *51* (24), 5810–5831.

(20) Kang, J.; He, S.; Zhou, W.; Shen, Z.; Li, Y.; Chen, M.; Zhang, Q.; Wang, Y. Single-pass transformation of syngas into ethanol with high selectivity by triple tandem catalysis. *Nat. Commun.* **2020**, *11* (1), 827.

(21) Lin, T. J.; Qi, X. Z.; Wang, X. X.; Xia, L.; Wang, C. Q.; Yu, F.; Wang, H.; Li, S. G.; Zhong, L. S.; Sun, Y. H. Direct Production of Higher Oxygenates by Syngas Conversion over a Multifunctional Catalyst. *Angew. Chem., Int. Ed.* **2019**, *58* (14), 4627–4631.

(22) Xu, D.; Ding, M.; Hong, X.; Liu, G.; Tsang, S. C. E. Selective C₂+ Alcohol Synthesis from Direct CO₂ Hydrogenation over a Cs-Promoted Cu-Fe-Zn Catalyst. *ACS Catal.* **2020**, *10*, 5250–5260.

(23) Jiang, X.; Nie, X.; Guo, X.; Song, C.; Chen, J. G. Recent Advances in Carbon Dioxide Hydrogenation to Methanol via Heterogeneous Catalysis. *Chem. Rev.* **2020**, *120*, 7984.

(24) Ye, R. P.; Ding, J.; Gong, W.; Argyle, M. D.; Zhong, Q.; Wang, Y.; Russell, C. K.; Xu, Z.; Russell, A. G.; Li, Q.; Fan, M.; Yao, Y. G. CO₂ hydrogenation to high-value products via heterogeneous catalysis. *Nat. Commun.* **2019**, *10* (1), 5698.

(25) Guil-Lopez, R.; Mota, N.; Llorente, J.; Millan, E.; Pawelec, B.; Fierro, J. L. G.; Navarro, R. M. Methanol Synthesis from CO₂: A Review of the Latest Developments in Heterogeneous Catalysis. *Materials* **2019**, *12* (23), 3902.

(26) Din, I. U.; Shaharun, M. S.; Alotaibi, M. A.; Alharthi, A. I.; Naem, A. Recent developments on heterogeneous catalytic CO₂ reduction to methanol. *J. CO₂ Util.* **2019**, *34*, 20–33.

(27) Dang, S. S.; Yang, H. Y.; Gao, P.; Wang, H.; Li, X. P.; Wei, W.; Sun, Y. H. A review of research progress on heterogeneous catalysts for methanol synthesis from carbon dioxide hydrogenation. *Catal. Today* **2019**, *330*, 61–75.

(28) Martin, O.; Mondelli, C.; Curulla-Ferre, D.; Drouilly, C.; Hauert, R.; Perez-Ramirez, J. Zinc-Rich Copper Catalysts Promoted by Gold for Methanol Synthesis. *ACS Catal.* **2015**, *5* (9), 5607–5616.

(29) Olah, G. A.; Mathew, T.; Goepfert, A.; Prakash, G. K. S. Difference and Significance of Regenerative Versus Renewable Carbon Fuels and Products. *Top. Catal.* **2018**, *61* (7–8), 522–529.

(30) Larmier, K.; Liao, W. C.; Tada, S.; Lam, E.; Verel, R.; Bansode, A.; Urakawa, A.; Comas-Vives, A.; Coperet, C. CO₂-to-Methanol Hydrogenation on Zirconia-Supported Copper Nanoparticles: Reaction Intermediates and the Role of the Metal-Support Interface. *Angew. Chem., Int. Ed.* **2017**, *56* (9), 2318–2323.

(31) Lam, E.; Larmier, K.; Wolf, P.; Tada, S.; Safonova, O. V.; Coperet, C. Isolated Zr Surface Sites on Silica Promote Hydrogenation of CO₂ to CH₃OH in Supported Cu Catalysts. *J. Am. Chem. Soc.* **2018**, *140* (33), 10530–10535.

(32) Samson, K.; Sliwa, M.; Socha, R. P.; Gora-Marek, K.; Mucha, D.; Rutkowska-Zbik, D.; Paul, J. F.; Ruggiero-Mikolajczyk, M.; Grabowski, R.; Sloczynski, J. Influence of ZrO₂ Structure and Copper Electronic State on Activity of Cu/ZrO₂ Catalysts in Methanol Synthesis from CO₂. *ACS Catal.* **2014**, *4* (10), 3730–3741.

(33) Tada, S.; Kayamori, S.; Honma, T.; Kamei, H.; Nariyuki, A.; Kon, K.; Toyao, T.; Shimizu, K.; Satokawa, S. Design of Interfacial Sites between Cu and Amorphous ZrO₂ Dedicated to CO₂-to-Methanol Hydrogenation. *ACS Catal.* **2018**, *8* (9), 7809–7819.

(34) Shi, Z. S.; Tan, Q. Q.; Wu, D. F. Enhanced CO₂ hydrogenation to methanol over TiO₂ nanotubes-supported CuO-ZnO-CeO₂ catalyst. *Appl. Catal., A* **2019**, *581*, 58–66.

(35) Fang, X.; Men, Y. H.; Wu, F.; Zhao, Q. H.; Singh, R.; Xiao, P.; Du, T.; Webley, P. A. Improved methanol yield and selectivity from CO₂ hydrogenation using a novel Cu-ZnO-ZrO₂ catalyst supported on Mg-Al layered double hydroxide (LDH). *J. CO₂ Util.* **2019**, *29*, 57–64.

(36) Kuhl, S.; Tarasov, A.; Zander, S.; Kasatkin, I.; Behrens, M. Cu-Based Catalyst Resulting from a Cu, Zn, Al Hydrotalcite-Like Compound: A Microstructural, Thermoanalytical, and In Situ XAS Study. *Chem. - Eur. J.* **2014**, *20* (13), 3782–3792.

(37) Li, M. M. J.; Chen, C. P.; Ayvali, T.; Suo, H. R.; Zheng, J. W.; Teixeira, I. F.; Ye, L.; Zou, H. B.; O'Hare, D.; Tsang, S. C. E. CO₂ Hydrogenation to Methanol over Catalysts Derived from Single Cationic Layer CuZnGa LDH Precursors. *ACS Catal.* **2018**, *8* (5), 4390–4401.

(38) Kuhl, S.; Schumann, J.; Kasatkin, I.; Havecker, M.; Schlögl, R.; Behrens, M. Ternary and quaternary Cr or Ga-containing ex-LDH catalysts-Influence of the additional oxides onto the microstructure and activity of Cu/ZnAl₂O₄ catalysts. *Catal. Today* **2015**, *246*, 92–100.

(39) Gao, P.; Zhong, L.; Zhang, L.; Wang, H.; Zhao, N.; Wei, W.; Sun, Y. Yttrium oxide modified Cu/ZnO/Al₂O₃ catalysts via hydrotalcite-like precursors for CO₂ hydrogenation to methanol. *Catal. Sci. Technol.* **2015**, *5*, 4365–4377.

(40) Yang, H.; Gao, P.; Zhang, C.; Zhong, L.; Li, X.; Wang, S.; Wang, H.; Wei, W.; Sun, Y. Core-shell structured Cu@m-SiO₂ and Cu/ZnO@m-SiO₂ catalysts for methanol synthesis from CO₂ hydrogenation. *Catal. Commun.* **2016**, *84*, 56–60.

(41) Mureddu, M.; Ferrara, F.; Pettinau, A. Highly efficient CuO/ZnO/ZrO₂@SBA-15 nanocatalysts for methanol synthesis from the catalytic hydrogenation of CO₂. *Appl. Catal., B* **2019**, *258*, 117941.

(42) An, B.; Zhang, J.; Cheng, K.; Ji, P.; Wang, C.; Lin, W. Confinement of Ultrasmall Cu/ZnOx Nanoparticles in Metal-Organic Frameworks for Selective Methanol Synthesis from Catalytic Hydrogenation of CO₂. *J. Am. Chem. Soc.* **2017**, *139* (10), 3834–3840.

(43) Liu, T. K.; Hong, X. L.; Liu, G. L. In Situ Generation of the Cu@3D-ZrOx Framework Catalyst for Selective Methanol Synthesis from CO₂/H₂. *ACS Catal.* **2020**, *10* (1), 93–102.

(44) Hu, B.; Yin, Y. Z.; Zhong, Z. X.; Wu, D. D.; Liu, G. L.; Hong, X. L. Cu@ZIF-8 derived inverse ZnO/Cu catalyst with sub-5 nm ZnO for efficient CO₂ hydrogenation to methanol. *Catal. Sci. Technol.* **2019**, *9* (10), 2673–2681.

(45) Li, C. S.; Melaet, G.; Ralston, W. T.; An, K.; Brooks, C.; Ye, Y. F.; Liu, Y. S.; Zhu, J. F.; Guo, J. H.; Alayoglu, S.; Somorjai, G. A. High-performance hybrid oxide catalyst of manganese and cobalt for low-pressure methanol synthesis. *Nat. Commun.* **2015**, *6*, 6538.

(46) Stangeland, K.; Kalai, D. Y.; Ding, Y.; Yu, Z. X. Mesoporous manganese-cobalt oxide spinel catalysts for CO₂ hydrogenation to methanol. *J. CO₂ Util.* **2019**, *32*, 146–154.

(47) Lian, Y.; Fang, T. F.; Zhang, Y. H.; Liu, B.; Li, J. L. Hydrogenation of CO₂ to alcohol species over Co@Co₃O₄/C-N catalysts. *J. Catal.* **2019**, *379*, 46–51.

(48) Wang, L.; Guan, E.; Wang, Y.; Wang, L.; Gong, Z.; Cui, Y.; Meng, X.; Gates, B. C.; Xiao, F. S. Silica accelerates the selective hydrogenation of CO₂ to methanol on cobalt catalysts. *Nat. Commun.* **2020**, *11* (1), 1033.

(49) Schubert, M.; Pokhrel, S.; Thome, A.; Zielasek, V.; Gesing, T. M.; Roessner, F.; Madler, L.; Baumer, M. Highly active Co-Al₂O₃-based catalysts for CO₂ methanation with very low platinum promotion prepared by double flame spray pyrolysis. *Catal. Sci. Technol.* **2016**, *6* (20), 7449–7460.

- (50) Melaet, G.; Ralston, W. T.; Li, C. S.; Alayoglu, S.; An, K.; Musselwhite, N.; Kalkan, B.; Somorjai, G. A. Evidence of Highly Active Cobalt Oxide Catalyst for the Fischer–Tropsch Synthesis and CO₂ Hydrogenation. *J. Am. Chem. Soc.* **2014**, *136* (6), 2260–2263.
- (51) Wang, W.; Wang, S. P.; Ma, X. B.; Gong, J. L. Recent advances in catalytic hydrogenation of carbon dioxide. *Chem. Soc. Rev.* **2011**, *40* (7), 3703–3727.
- (52) Iglesia, E. Design, synthesis, and use of cobalt-based Fischer–Tropsch synthesis catalysts. *Appl. Catal., A* **1997**, *161* (1–2), 59–78.
- (53) Nie, X. W.; Jiang, X.; Wang, H. Z.; Luo, W. J.; Janik, M. J.; Chen, Y. G.; Guo, X. W.; Song, C. S. Mechanistic Understanding of Alloy Effect and Water Promotion for Pd–Cu Bimetallic Catalysts in CO₂ Hydrogenation to Methanol. *ACS Catal.* **2018**, *8* (6), 4873–4892.
- (54) Liu, L. N.; Fan, F.; Jiang, Z.; Gao, X. F.; Wei, J. J.; Fang, T. Mechanistic Study of Pd–Cu Bimetallic Catalysts for Methanol Synthesis from CO₂ Hydrogenation. *J. Phys. Chem. C* **2017**, *121* (47), 26287–26299.
- (55) Alvarez-Garcia, A.; Florez, E.; Moreno, A.; Jimenez-Orozco, C. CO₂ activation on small Cu–Ni and Cu–Pd bimetallic clusters. *Mol. Catal.* **2020**, *484*, 110733.
- (56) Garcia-Trenco, A.; White, E. R.; Regoutz, A.; Payne, D. J.; Shaffer, M. S. P.; Williams, C. K. Pd₂Ga-Based Colloids as Highly Active Catalysts for the Hydrogenation of CO₂ to Methanol. *ACS Catal.* **2017**, *7* (2), 1186–1196.
- (57) Fiordaliso, E. M.; Sharafutdinov, I.; Carvalho, H. W. P.; Grunwaldt, J. D.; Hansen, T. W.; Chorkendorff, I.; Wagner, J. B.; Damsgaard, C. D. Intermetallic GaPd₂ Nanoparticles on SiO₂ for Low-Pressure CO₂ Hydrogenation to Methanol: Catalytic Performance and In Situ Characterization. *ACS Catal.* **2015**, *5* (10), 5827–5836.
- (58) Garcia-Trenco, A.; Regoutz, A.; White, E. R.; Payne, D. J.; Shaffer, M. S. P.; Williams, C. K. PdIn intermetallic nanoparticles for the Hydrogenation of CO₂ to Methanol. *Appl. Catal., B* **2018**, *220*, 9–18.
- (59) Snider, J. L.; Streibel, V.; Hubert, M. A.; Choksi, T. S.; Valle, E.; Upham, D. C.; Schumann, J.; Duyar, M. S.; Gallo, A.; Abild-Pedersen, F.; Jaramillo, T. F. Revealing the Synergy between Oxide and Alloy Phases on the Performance of Bimetallic In–Pd Catalysts for CO₂ Hydrogenation to Methanol. *ACS Catal.* **2019**, *9* (4), 3399–3412.
- (60) Wu, P. P.; Yang, B. Intermetallic PdIn catalyst for CO₂ hydrogenation to methanol: mechanistic studies with a combined DFT and microkinetic modeling method. *Catal. Sci. Technol.* **2019**, *9* (21), 6102–6113.
- (61) Li, X. L.; Liu, G. L.; Xu, D.; Hong, X. L.; Tsang, S. C. E. Confinement of subnanometric PdZn at a defect enriched ZnO/ZIF-8 interface for efficient and selective CO₂ hydrogenation to methanol. *J. Mater. Chem. A* **2019**, *7* (41), 23878–23885.
- (62) Studt, F.; Sharafutdinov, I.; Abild-Pedersen, F.; Elkjaer, C. F.; Hummelshøj, J. S.; Dahl, S.; Chorkendorff, I.; Norskov, J. K. Discovery of a Ni–Ga catalyst for carbon dioxide reduction to methanol. *Nat. Chem.* **2014**, *6* (4), 320–324.
- (63) Gallo, A.; Snider, J. L.; Sokaras, D.; Nordlund, D.; Kroll, T.; Ogasawara, H.; Kovarik, L.; Duyar, M. S.; Jaramillo, T. F. Ni₅Ga₃ catalysts for CO₂ reduction to methanol: Exploring the role of Ga surface oxidation/reduction on catalytic activity. *Appl. Catal., B* **2020**, *267*, 118369.
- (64) Tang, Q. L.; Ji, W. C.; Russell, C. K.; Cheng, Z. W.; Zhang, Y. L.; Fan, M. H.; Shen, Z. M. Understanding the catalytic mechanisms of CO₂ hydrogenation to methanol on unsupported and supported Ga–Ni clusters. *Appl. Energy* **2019**, *253*, 113623.
- (65) Tang, Q. L.; Shen, Z. M.; Russell, C. K.; Fan, M. H. Thermodynamic and Kinetic Study on Carbon Dioxide Hydrogenation to Methanol over a Ga₃Ni₅(111) Surface: The Effects of Step Edge. *J. Phys. Chem. C* **2018**, *122* (1), 315–330.
- (66) Sharafutdinov, I.; Elkjaer, C. F.; de Carvalho, H. W. P.; Gardini, D.; Chiarello, G. L.; Damsgaard, C. D.; Wagner, J. B.; Grunwaldt, J. D.; Dahl, S.; Chorkendorff, I. Intermetallic compounds of Ni and Ga as catalysts for the synthesis of methanol. *J. Catal.* **2014**, *320*, 77–88.
- (67) Li, M. M.; Zou, H.; Zheng, J.; Wu, T. S.; Chan, T. S.; Soo, Y. L.; Wu, X. P.; Gong, X. Q.; Chen, T.; Roy, K.; Held, G.; Tsang, S. C. E. Methanol Synthesis at a Wide Range of H₂/CO₂ Ratios over a Rh–In Bimetallic Catalyst. *Angew. Chem., Int. Ed.* **2020**, DOI: 10.1002/anie.202000841.
- (68) Shi, Z. S.; Tan, Q. Q.; Wu, D. F. A novel Core–Shell structured CuIn@SiO₂ catalyst for CO₂ hydrogenation to methanol. *AIChe J.* **2019**, *65* (3), 1047–1058.
- (69) Shi, Z. S.; Tan, Q. Q.; Tian, C.; Pan, Y.; Sun, X. W.; Zhang, J. X.; Wu, D. F. CO₂ hydrogenation to methanol over Cu–In intermetallic catalysts: Effect of reduction temperature. *J. Catal.* **2019**, *379*, 78–89.
- (70) Pustovarenko, A.; Dikhtiarenko, A.; Bavykina, A.; Gevers, L.; Ramirez, A.; Russkikh, A.; Telalovic, S.; Aguilar, A.; Hazemann, J.-L.; Ould-Chikh, S.; Gascon, J. Metal–Organic Framework-Derived Synthesis of Cobalt Indium Catalysts for the Hydrogenation of CO₂ to Methanol. *ACS Catal.* **2020**, *10* (9), 5064–5076.
- (71) Richard, A. R.; Fan, M. The effect of lanthanide promoters on NiInAl/SiO₂ catalyst for methanol synthesis. *Fuel* **2018**, *222*, 513–522.
- (72) Richard, A. R.; Fan, M. H. Low-Pressure Hydrogenation of CO₂ to CH₃OH Using Ni–In–Al/SiO₂ Catalyst Synthesized via a Phyllosilicate Precursor. *ACS Catal.* **2017**, *7* (9), 5679–5692.
- (73) Zhao, F. Z.; Gong, M.; Cao, K.; Zhang, Y. H.; Li, J. L.; Chen, R. Atomic Layer Deposition of Ni on Cu Nanoparticles for Methanol Synthesis from CO₂ Hydrogenation. *ChemCatChem* **2017**, *9* (19), 3772–3778.
- (74) Martin, O.; Martin, A. J.; Mondelli, C.; Mitchell, S.; Segawa, T. F.; Hauert, R.; Drouilly, C.; Curulla-Ferre, D.; Perez-Ramirez, J. Indium Oxide as a Superior Catalyst for Methanol Synthesis by CO₂ Hydrogenation. *Angew. Chem., Int. Ed.* **2016**, *55* (21), 6261–6265.
- (75) Ye, J. Y.; Liu, C. J.; Mei, D. H.; Ge, Q. F. Active Oxygen Vacancy Site for Methanol Synthesis from CO₂ Hydrogenation on In₂O₃(110): A DFT Study. *ACS Catal.* **2013**, *3* (6), 1296–1306.
- (76) Frei, M. S.; Capdevila-Cortada, M.; Garcia-Muelas, R.; Mondelli, C.; Lopez, N.; Stewart, J. A.; Ferre, D. C.; Perez-Ramirez, J. Mechanism and microkinetics of methanol synthesis via CO₂ hydrogenation on indium oxide. *J. Catal.* **2018**, *361*, 313–321.
- (77) Wang, J. Y.; Liu, C. Y.; Senftle, T. P.; Zhu, J.; Zhang, G. H.; Guo, X. W.; Song, C. S. Variation in the In₂O₃ Crystal Phase Alters Catalytic Performance toward the Reverse Water Gas Shift Reaction. *ACS Catal.* **2020**, *10* (5), 3264–3273.
- (78) Dang, S.; Qin, B.; Yang, Y.; Wang, H.; Cai, J.; Han, Y.; Li, S.; Gao, P.; Sun, Y. Rationally designed indium oxide catalysts for CO₂ hydrogenation to methanol with high activity and selectivity. *Sci. Adv.* **2020**, *6* (25), eaaz2060.
- (79) Dang, S. S.; Gao, P.; Liu, Z. Y.; Chen, X. Q.; Yang, C. G.; Wang, H.; Zhong, L. S.; Li, S. G.; Sun, Y. H. Role of zirconium in direct CO₂ hydrogenation to lower olefins on oxide/zeolite bifunctional catalysts. *J. Catal.* **2018**, *364*, 382–393.
- (80) Chen, T. Y.; Cao, C. X.; Chen, T. B.; Ding, X. X.; Huang, H.; Shen, L.; Cao, X. Y.; Zhu, M. H.; Xu, J.; Gao, J.; Han, Y. F. Unraveling Highly Tunable Selectivity in CO₂ Hydrogenation over Bimetallic In–Zr Oxide Catalysts. *ACS Catal.* **2019**, *9* (9), 8785–8797.
- (81) Frei, M. S.; Mondelli, C.; Cesarini, A.; Krumeich, F.; Hauert, R.; Stewart, J. A.; Ferre, D. C.; Perez-Ramirez, J. Role of Zirconia in Indium Oxide-Catalyzed CO₂ Hydrogenation to Methanol. *ACS Catal.* **2020**, *10* (2), 1133–1145.
- (82) Jiang, H. X.; Lin, J.; Wu, X. H.; Wang, W. Y.; Chen, Y. F.; Zhang, M. H. Efficient hydrogenation of CO₂ to methanol over Pd/In₂O₃/SBA-15 catalysts. *J. CO₂ Util.* **2020**, *36*, 33–39.
- (83) Rui, N.; Wang, Z. Y.; Sun, K. H.; Ye, J. Y.; Ge, Q. F.; Liu, C. J. CO₂ hydrogenation to methanol over Pd/In₂O₃: effects of Pd and oxygen vacancy. *Appl. Catal., B* **2017**, *218*, 488–497.
- (84) Frei, M. S.; Mondelli, C.; Garcia-Muelas, R.; Kley, K. S.; Puertolas, B.; Lopez, N.; Safonova, O. V.; Stewart, J. A.; Curulla-Ferre, D.; Perez-Ramirez, J. Atomic-scale engineering of indium oxide promotion by palladium for methanol production via CO₂ hydrogenation. *Nat. Commun.* **2019**, *10* (1), 3377.

- (85) Yao, L. B.; Shen, X. C.; Pan, Y. B.; Peng, Z. M. Synergy between active sites of Cu-In-Zr-O catalyst in CO₂ hydrogenation to methanol. *J. Catal.* **2019**, *372*, 74–85.
- (86) Bavykina, A.; Yarulina, I.; Al Abdulghani, A. J.; Gevers, L.; Hedhili, M. N.; Miao, X. H.; Galilea, A. R.; Pustovarenko, A.; Dikhtiarenko, A.; Cadiau, A.; Aguilar-Tapia, A.; Hazemann, J. L.; Kozlov, S. M.; Oud-Chikh, S.; Cavallo, L.; Gascon, J. Turning a Methanation Co Catalyst into an In-Co Methanol Producer. *ACS Catal.* **2019**, *9* (8), 6910–6918.
- (87) Jia, X.; Sun, K.; Wang, J.; Shen, C.; Liu, C.-j. Selective hydrogenation of CO₂ to methanol over Ni/In₂O₃ catalyst. *J. Energy Chem.* **2020**, *50*, 409–415.
- (88) Han, Z.; Tang, C.; Wang, J.; Li, L.; Li, C. Atomically dispersed Ptn+ species as highly active sites in Pt/In₂O₃ catalysts for methanol synthesis from CO₂ hydrogenation. *J. Catal.* **2020**, DOI: 10.1016/j.jcat.2020.06.018.
- (89) Rui, N.; Zhang, F.; Sun, K.; Liu, Z.; Xu, W.; Stavitski, E.; Senanayake, S. D.; Rodriguez, J. A.; Liu, C.-J. Hydrogenation of CO₂ to Methanol on a Auδ+–In₂O_{3-x} Catalyst. *ACS Catal.* **2020**, DOI: 10.1021/acscatal.0c02120.
- (90) Wang, J.; Li, G.; Li, Z.; Tang, C.; Feng, Z.; An, H.; Liu, H.; Liu, T.; Li, C. A highly selective and stable ZnO-ZrO₂ solid solution catalyst for CO₂ hydrogenation to methanol. *Sci. Adv.* **2017**, *3* (10), e1701290.
- (91) Wang, J.; Tang, C.; Li, G.; Han, Z.; Li, Z.; Liu, H.; Cheng, F.; Li, C. High-Performance MaZrOx (Ma = Cd, Ga) Solid-Solution Catalysts for CO₂ Hydrogenation to Methanol. *ACS Catal.* **2019**, *9* (11), 10253–10259.
- (92) Owen, R. E.; Plucinski, P.; Mattia, D.; Torrente-Murciano, L.; Ting, V. P.; Jones, M. D. Effect of support of Co-Na-Mo catalysts on the direct conversion of CO₂ to hydrocarbons. *J. CO₂ Util.* **2016**, *16*, 97–103.
- (93) Shi, Z. B.; Yang, H. Y.; Gao, P.; Chen, X. Q.; Liu, H. J.; Zhong, L. S.; Wang, H.; Wei, W.; Sun, Y. H. Effect of alkali metals on the performance of CoCu/TiO₂ catalysts for CO₂ hydrogenation to long-chain hydrocarbons. *Chin. J. Catal.* **2018**, *39* (8), 1294–1302.
- (94) Albrecht, M.; Rodemerck, U.; Schneider, M.; Bröring, M.; Baabe, D.; Kondratenko, E. V. Unexpectedly efficient CO₂ hydrogenation to higher hydrocarbons over non-doped Fe₂O₃. *Appl. Catal., B* **2017**, *204*, 119–126.
- (95) Hwang, S. M.; Zhang, C. D.; Han, S. J.; Park, H. G.; Kim, Y. T.; Yang, S.; Jun, K. W.; Kim, S. K. Mesoporous carbon as an effective support for Fe catalyst for CO₂ hydrogenation to liquid hydrocarbons. *J. CO₂ Util.* **2020**, *37*, 65–73.
- (96) Liu, J. H.; Sun, Y. W.; Jiang, X.; Zhang, A. F.; Song, C. S.; Guo, X. W. Pyrolyzing ZIF-8 to N-doped porous carbon facilitated by iron and potassium for CO₂ hydrogenation to value-added hydrocarbons. *J. CO₂ Util.* **2018**, *25*, 120–127.
- (97) Liu, J. H.; Zhang, A. F.; Jiang, X.; Liu, M.; Sun, Y. W.; Song, C. S.; Guo, X. W. Selective CO₂ Hydrogenation to Hydrocarbons on Cu-Promoted Fe-Based Catalysts: Dependence on Cu-Fe Interaction. *ACS Sustainable Chem. Eng.* **2018**, *6* (8), 10182–10190.
- (98) Choi, Y. H.; Jang, Y. J.; Park, H.; Kim, W. Y.; Lee, Y. H.; Choi, S. H.; Lee, J. S. Carbon dioxide Fischer–Tropsch synthesis: A new path to carbon-neutral fuels. *Appl. Catal., B* **2017**, *202*, 605–610.
- (99) Zhai, P.; Xu, C.; Gao, R.; Liu, X.; Li, M. Z.; Li, W. Z.; Fu, X. P.; Jia, C. J.; Xie, J. L.; Zhao, M.; Wang, X. P.; Li, Y. W.; Zhang, Q. W.; Wen, X. D.; Ma, D. Highly Tunable Selectivity for Syngas-Derived Alkenes over Zinc and Sodium-Modulated Fe₃C₂ Catalyst. *Angew. Chem., Int. Ed.* **2016**, *55* (34), 9902–9907.
- (100) Choi, Y. H.; Ra, E. C.; Kim, E. H.; Kim, K. Y.; Jang, Y. J.; Kang, K. N.; Choi, S. H.; Jang, J. H.; Lee, J. S. Sodium-Containing Spinell Zinc Ferrite as a Catalyst Precursor for the Selective Synthesis of Liquid Hydrocarbon Fuels. *ChemSusChem* **2017**, *10* (23), 4764–4770.
- (101) Satthawong, R.; Koizumi, N.; Song, C. S.; Prasassarakich, P. Bimetallic Fe-Co catalysts for CO₂ hydrogenation to higher hydrocarbons. *J. CO₂ Util.* **2013**, *3–4*, 102–106.
- (102) Amoyal, M.; Vidruk-Nehemya, R.; Landau, M. V.; Herskowitz, M. Effect of potassium on the active phases of Fe catalysts for carbon dioxide conversion to liquid fuels through hydrogenation. *J. Catal.* **2017**, *348*, 29–39.
- (103) Liu, J. H.; Zhang, A. F.; Jiang, X.; Liu, M.; Zhu, J.; Song, C. S.; Guo, X. W. Direct Transformation of Carbon Dioxide to Value-Added Hydrocarbons by Physical Mixtures of Fe₃C₂ and K-Modified Al₂O₃. *Ind. Eng. Chem. Res.* **2018**, *57* (28), 9120–9126.
- (104) Wei, J.; Sun, J.; Wen, Z. Y.; Fang, C. Y.; Ge, Q. J.; Xu, H. Y. New insights into the effect of sodium on Fe₃O₄-based nanocatalysts for CO₂ hydrogenation to light olefins. *Catal. Sci. Technol.* **2016**, *6* (13), 4786–4793.
- (105) Wei, J.; Ge, Q.; Yao, R.; Wen, Z.; Fang, C.; Guo, L.; Xu, H.; Sun, J. Directly converting CO₂ into a gasoline fuel. *Nat. Commun.* **2017**, *8*, 15174.
- (106) Wang, S.; Wu, T.; Lin, J.; Ji, Y.; Yan, S.; Pei, Y.; Xie, S.; Zong, B.; Qiao, M. Iron–Potassium on Single-Walled Carbon Nanotubes as Efficient Catalyst for CO₂ Hydrogenation to Heavy Olefins. *ACS Catal.* **2020**, *10*, 6389–6401.
- (107) Cui, X.; Gao, P.; Li, S. G.; Yang, C. G.; Liu, Z. Y.; Wang, H.; Zhong, L. S.; Sun, Y. H. Selective Production of Aromatics Directly from Carbon Dioxide Hydrogenation. *ACS Catal.* **2019**, *9* (5), 3866–3876.
- (108) Xu, Y. B.; Shi, C. M.; Liu, B.; Wang, T.; Zheng, J.; Li, W. P.; Liu, D. P.; Liu, X. H. Selective production of aromatics from CO₂. *Catal. Sci. Technol.* **2019**, *9* (3), 593–610.
- (109) Wei, J.; Yao, R. W.; Ge, Q. J.; Wen, Z. Y.; Ji, X. W.; Fang, C. Y.; Zhang, J. X.; Xu, H. Y.; Sun, J. Catalytic Hydrogenation of CO₂ to Isoparaffins over Fe-Based Multifunctional Catalysts. *ACS Catal.* **2018**, *8* (11), 9958–9967.
- (110) Wang, S. W.; Wu, T. J.; Lin, J.; Tian, J.; Ji, Y. S.; Pei, Y.; Yan, S. R.; Qiao, M. H.; Xu, H. L.; Zong, B. N. FeK on 3D Graphene-Zeolite Tandem Catalyst with High Efficiency and Versatility in Direct CO₂ Conversion to Aromatics. *ACS Sustainable Chem. Eng.* **2019**, *7* (21), 17825–17833.
- (111) Gao, P.; Li, S.; Bu, X.; Dang, S.; Liu, Z.; Wang, H.; Zhong, L.; Qiu, M.; Yang, C.; Cai, J.; Wei, W.; Sun, Y. Direct conversion of CO₂ into liquid fuels with high selectivity over a bifunctional catalyst. *Nat. Chem.* **2017**, *9* (10), 1019–1024.
- (112) Ni, Y.; Chen, Z.; Fu, Y.; Liu, Y.; Zhu, W.; Liu, Z. Selective conversion of CO₂ and H₂ into aromatics. *Nat. Commun.* **2018**, *9* (1), 3457.
- (113) Li, Z. L.; Qu, Y. Z.; Wang, J. J.; Liu, H. L.; Li, M. R.; Miao, S.; Li, C. Highly Selective Conversion of Carbon Dioxide to Aromatics over Tandem Catalysts. *Joule* **2019**, *3* (2), 570–583.
- (114) Zhang, J.; Zhang, M.; Chen, S.; Wang, X.; Zhou, Z.; Wu, Y.; Zhang, T.; Yang, G.; Han, Y.; Tan, Y. Hydrogenation of CO₂ into aromatics over a ZnCrOx-zeolite composite catalyst. *Chem. Commun.* **2019**, *55* (7), 973–976.
- (115) Zhou, C.; Shi, J. Q.; Zhou, W.; Cheng, K.; Zhang, Q. H.; Kang, J. C.; Wang, Y. Highly Active ZnO-ZrO₂ Aerogels Integrated with H-ZSM-5 for Aromatics Synthesis from Carbon Dioxide. *ACS Catal.* **2020**, *10* (1), 302–310.
- (116) Wang, Y.; Tan, L.; Tan, M.; Zhang, P.; Fang, Y.; Yoneyama, Y.; Yang, G.; Tsubaki, N. Rationally Designing Bifunctional Catalysts as an Efficient Strategy To Boost CO₂ Hydrogenation Producing Value-Added Aromatics. *ACS Catal.* **2019**, *9*, 895–901.
- (117) Zhang, X. B.; Zhang, A. F.; Jiang, X.; Zhu, J.; Liu, J. H.; Li, J. J.; Zhang, G. H.; Song, C. S.; Guo, X. W. Utilization of CO₂ for aromatics production over ZnO/ZrO₂-ZSM-5 tandem catalyst. *J. CO₂ Util.* **2019**, *29*, 140–145.
- (118) Wang, D.; Bi, Q. Y.; Yin, G. H.; Zhao, W. L.; Huang, F. Q.; Xie, X. M.; Jiang, M. H. Direct synthesis of ethanol via CO₂ hydrogenation using supported gold catalysts. *Chem. Commun.* **2016**, *52* (99), 14226–14229.
- (119) Bai, S.; Shao, Q.; Wang, P.; Dai, Q.; Wang, X.; Huang, X. Highly Active and Selective Hydrogenation of CO₂ to Ethanol by Ordered Pd-Cu Nanoparticles. *J. Am. Chem. Soc.* **2017**, *139* (20), 6827–6830.

- (120) He, Z.; Qian, Q.; Ma, J.; Meng, Q.; Zhou, H.; Song, J.; Liu, Z.; Han, B. Water-Enhanced Synthesis of Higher Alcohols from CO₂ Hydrogenation over a Pt/Co₃O₄ Catalyst under Milder Conditions. *Angew. Chem., Int. Ed.* **2016**, *55*, 737–741.
- (121) Wang, L. X.; He, S. X.; Wang, L.; Lei, Y.; Meng, X. J.; Xiao, F. S. Cobalt-Nickel Catalysts for Selective Hydrogenation of Carbon Dioxide into Ethanol. *ACS Catal.* **2019**, *9* (12), 11335–11340.
- (122) Liu, B.; Ouyang, B.; Zhang, Y. H.; Lv, K. L.; Li, Q.; Ding, Y. B.; Li, J. L. Effects of mesoporous structure and Pt promoter on the activity of Co-based catalysts in low-temperature CO₂ hydrogenation for higher alcohol synthesis. *J. Catal.* **2018**, *366*, 91–97.
- (123) Zhang, S. N.; Liu, X. F.; Shao, Z. L.; Wang, H.; Sun, Y. H. Direct CO₂ hydrogenation to ethanol over supported Co₂C catalysts: Studies on support effects and mechanism. *J. Catal.* **2020**, *382*, 86–96.
- (124) Yang, C. S.; Mu, R. T.; Wang, G. S.; Song, J. M.; Tian, H.; Zhao, Z. J.; Gong, J. L. Hydroxyl-mediated ethanol selectivity of CO₂ hydrogenation. *Chem. Sci.* **2019**, *10* (11), 3161–3167.
- (125) Ding, L.; Shi, T.; Gu, J.; Cui, Y.; Zhang, Z.; Yang, C.; Chen, T.; Lin, M.; Wang, P.; Xue, N.; Peng, L.; Guo, X.; Zhu, Y.; Chen, Z.; Ding, W. CO₂ Hydrogenation to Ethanol over Cu@Na-Beta. *Chem.* **2020**, DOI: 10.1016/j.chempr.2020.07.001.
- (126) Luan, X.; Ren, Z.; Dai, X.; Zhang, X.; Yong, J.; Yang, Y.; Zhao, H.; Cui, M.; Nie, F.; Huang, X. Selective Conversion of Syngas into Higher Alcohols via a Reaction-Coupling Strategy on Multifunctional Relay Catalysts. *ACS Catal.* **2020**, *10* (4), 2419–2430.
- (127) Zhou, W.; Kang, J. C.; Cheng, K.; He, S.; Shi, J. Q.; Zhou, C.; Zhang, Q. H.; Chen, J. C.; Peng, L. M.; Chen, M. S.; Wang, Y. Direct Conversion of Syngas into Methyl Acetate, Ethanol, and Ethylene by Relay Catalysis via the Intermediate Dimethyl Ether. *Angew. Chem., Int. Ed.* **2018**, *57* (37), 12012–12016.
- (128) MacDowell, N.; Florin, N.; Buchard, A.; Hallett, J.; Galindo, A.; Jackson, G.; Adjiman, C. S.; Williams, C. K.; Shah, N.; Fennell, P. An overview of CO₂ capture technologies. *Energy Environ. Sci.* **2010**, *3* (11), 1645–1669.
- (129) Goepfert, A.; Czaun, M.; Jones, J. P.; Prakash, G. K. S.; Olah, G. A. Recycling of carbon dioxide to methanol and derived products - closing the loop. *Chem. Soc. Rev.* **2014**, *43* (23), 7995–8048.
- (130) Alvarez, A.; Bansode, A.; Urakawa, A.; Bavykina, A. V.; Wezendonk, T. A.; Makkee, M.; Gascon, J.; Kapteijn, F. Challenges in the Greener Production of Formates/Formic Acid, Methanol, and DME by Heterogeneously Catalyzed CO₂ Hydrogenation Processes. *Chem. Rev.* **2017**, *117* (14), 9804–9838.
- (131) Tabor, D. P.; Roch, L. M.; Saikin, S. K.; Kreisbeck, C.; Sheberla, D.; Montoya, J. H.; Dwaraknath, S.; Aykol, M.; Ortiz, C.; Tribukait, H.; Amador-Bedolla, C.; Brabec, C. J.; Maruyama, B.; Persson, K. A.; Aspuru-Guzik, A. Accelerating the discovery of materials for clean energy in the era of smart automation. *Nat. Rev. Mater.* **2018**, *3* (5), 5–20.
- (132) Raccuglia, P.; Elbert, K. C.; Adler, P. D. F.; Falk, C.; Wenny, M. B.; Mollo, A.; Zeller, M.; Friedler, S. A.; Schrier, J.; Norquist, A. J. Machine-learning-assisted materials discovery using failed experiments. *Nature* **2016**, *533* (7601), 73–76.
- (133) Corma, A.; Diaz-Cabanas, M. J.; Jorda, J. L.; Martinez, C.; Moliner, M. High-throughput synthesis and catalytic properties of a molecular sieve with 18- and 10-member rings. *Nature* **2006**, *443* (7113), 842–845.
- (134) Tran, K.; Ulissi, Z. W. Active learning across intermetallics to guide discovery of electrocatalysts for CO₂ reduction and H₂ evolution. *Nat. Catal.* **2018**, *1* (9), 696–703.
- (135) Boyd, P. G.; Chidambaram, A.; Garcia-Diez, E.; Ireland, C. P.; Daff, T. D.; Bounds, R.; Gladysiak, A.; Schouwink, P.; Moosavi, S. M.; Maroto-Valer, M. M.; Reimer, J. A.; Navarro, J. A. R.; Woo, T. K.; Garcia, S.; Stylianou, K. C.; Smit, B. Data-driven design of metal-organic frameworks for wet flue gas CO₂ capture. *Nature* **2019**, *576* (7786), 253–256.
- (136) Zhong, M.; Tran, K.; Min, Y. M.; Wang, C. H.; Wang, Z. Y.; Dinh, C. T.; De Luna, P.; Yu, Z. Q.; Rasouli, A. S.; Brodersen, P.; Sun, S.; Voznyy, O.; Tan, C. S.; Askerka, M.; Che, F. L.; Liu, M.; Seifitokaldani, A.; Pang, Y. J.; Lo, S. C.; Ip, A.; Ulissi, Z.; Sargent, E. H. Accelerated discovery of CO₂ electrocatalysts using active machine learning. *Nature* **2020**, *581* (7807), 178–183.
- (137) Li, H.; Qiu, C.; Ren, S.; Dong, Q.; Zhang, S.; Zhou, F.; Liang, X.; Wang, J.; Li, S.; Yu, M. Na(+)-gated water-conducting nanochannels for boosting CO₂ conversion to liquid fuels. *Science* **2020**, *367* (6478), 667–671.
- (138) Saeidi, S.; Amin, N. A. S.; Rahimpour, M. R. Hydrogenation of CO₂ to value-added products-A review and potential future developments. *J. CO₂ Util.* **2014**, *5*, 66–81.
- (139) Tran, T. V.; Nguyen, L. P.; Nguyen, T. H.; Dang, T. T.; Ngo, P. T.; Nguyen, D. A. Application of NaA Membrane Reactor for Methanol Synthesis in CO₂ Hydrogenation at Low Pressure. *Int. Int. J. Chem. React. Eng.* **2018**, *16* (4), 20170046.