Hydrogenation of CO2 for sustainable fuel and chemical production

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REVIEW SUMMARY

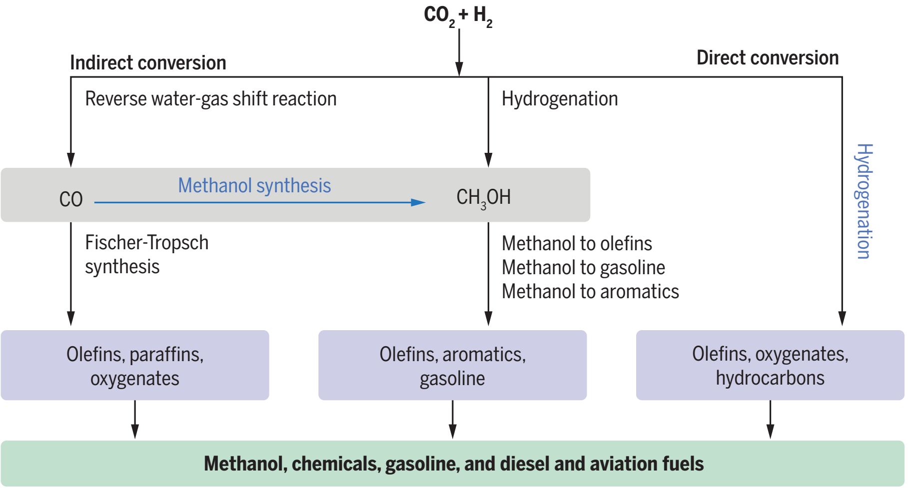
CATALYSIS

Hydrogenation of CO_2 for sustainable fuel and chemical production

Jingyun Ye, Nikolaos Dimitratos, Liane M. Rossi, Nils Thonemann, Andrew M. Beale, Robert Wojcieszak*

BACKGROUND: Carbon dioxide (CO_2) has become synonymous with climate change. Acting like a blanket in the atmosphere, it traps heat, causing a rise in global temperatures. This warming disrupts weather patterns, melts glaciers, and raises sea levels, posing a substantial threat to the planet. The primary culprit? The burning of fossil fuels such as coal, oil, and natural gas, which releases massive quantities of CO_2 into the air. But what if CO_2 was not just waste? Innovative technologies are emerging that aim to transform CO_2 into a valuable resource. These technologies focus on utilizing captured CO_2 as a feedstock for producing cleaner fuels and chemicals. One promising approach involves creating "green methanol." By combining captured CO_2 with hydrogen, methanol, a versatile fuel and chemical building block, can be synthesized. Methanol's story stretches back thousands of years, when the ancient Egyptians used it for embalming. A breakthrough in methanol synthesis arrived in the 1920s with the development of a zinc chromite catalyst. This paved the way for the introduction of $Cu/Zn/Al_2O3$ (CZA), a game-changing catalyst, in the 1940s, which became the industry standard. However, CZA catalysts have a drawback—they favor the reverse water-gas shift (RWGS) reaction over direct CO_2 conversion to methanol. This reduces the efficiency of CO_2 utilization in the process. In addition, a large contributor to catalyst deactivation is sintering, where the catalyst particles clump together, reducing their active surface area and hindering performance. Interestingly, a link between high activity and faster deactivation exist—catalysts with the highest initial activity (often containing the most copper) also deactivate most rapidly. The CZA life span ranges from 2 to 8 years, with a gradual decline in activity.

ADVANCES: Scientists are hunting for the most effective catalysts to convert CO_2 into useful fuels (methanol, or CH_3OH). Recently, indium oxide–based catalysts (In_2O_3) have garnered considerable interest. In research articles published between 2020 and 2024, most of the studied catalysts (85 out of 96) achieved selectivity to methanol above 50%. Most methanol catalysts work best at lower temperatures (below 300°C) and higher pressures (above 3 MPa), whereas most hydrocarbon catalysts perform better at higher temperatures (above 300°C) and lower pressures (below 3 MPa). A positive development is that reported methanol yields are still increasing. The present champion is a Cu/ZnO/MnO/KIT-6 catalyst, which operates at a moderate temperature (180°C) and efficiently converts CO_2 while producing a high yield of methanol. However, the fight against climate change goes beyond optimizing methanol production—it is about creating a sustainable future for all. CO_2 hydrogenation seems promising for reducing greenhouse gas emissions compared with traditional production methods, especially when powered by renewable energy sources such as wind power. However, it is not a simple picture. Trade-offs exist between different environmental impacts. For example, the source of the CO_2 and the specific conversion technology used can markedly affect the overall environmental footprint. CO_2 hydrogenation offers a clean-fuel solution (e-fuels) for hard-to-electrify sectors such as aviation and shipping. However, sustainability requires efficient water management and heat integration. Moreover, when considering the environmental impacts of the hydrogenation technologies, the major benefit in the "independence" of crude-oil carbon sources is its potential to substantially reduce greenhouse gas emissions.



Reaction pathways in CO_2 thermal conversion. Several routes for CO_2 hydrogenation are possible depending on the nature of the catalyst. Methanol can be produced directly from CO_2 using, for example, CZA and indirectly, by passing through the RWGS reaction favored by the presence of non-noble metals such as Ni and Fe or metal carbides.

OUTLOOK: Present catalysts such as CZA have limitations, including short life spans and reliance on critical elements. Research efforts should focus on designing new catalysts that promote direct CO_2 conversion to methanol while minimizing the RWGS reaction. Strategies to mitigate sintering and extend catalyst life span are crucial. This might involve exploring different catalyst supports or incorporating stabilizing elements into the catalyst structure. Understanding the relationship between activity, copper content, and deactivation is essential for developing catalysts that offer a balance between high initial performance and long-term stability. Alternatives such as Pd-In catalysts are presently being researched, but costs are a concern. Despite remaining challenges, advancements in catalyst design and characterization techniques are paving the way for a cleaner future fueled by CO_2 hydrogenation. Although CO_2 hydrogenation is attractive as a means of utilizing a readily available carbon source, its climate mitigation potential is less clear-cut. Net negativity can only be achieved when CO_2 comes from direct air capture, and considering all background emissions, net negativity might be difficult to achieve. However, for sectors that are hard to make sustainable, such as aviation, use of CO_2 might be an optimal option. ■

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Ye *et al.*, *Science* **387**, 943 (2025) 28 February 2025 **1 of 1**

REVIEW

CATALYSIS

Hydrogenation of CO_2 for sustainable fuel and chemical production

Jingyun Ye[1], Nikolaos Dimitratos[2], Liane M. Rossi[3], Nils Thonemann[4], Andrew M. Beale[5,6], Robert Wojcieszak[7,8]*

Catalytic carbon dioxide (CO_2) hydrogenation is a potential route for producing sustainable fuels and chemicals, but existing catalysts need improvement. In particular, identifying active sites and understanding the interaction between components and the dynamic behavior of the participant species remain unclear. This fundamental knowledge is essential for the design of more efficient and stable catalysts. Because the nature of the active site (metal, oxide, carbide) is the main factor that determines the catalytic activity of the catalysts, this Review focuses on various types of heterogeneous catalysts that have been recently reported in the literature as efficient for CO_2 conversion to C1 [carbon monoxide (CO), methanol (CH_3OH), methane (CH_4)], and higher hydrocarbons. We focus on establishing key connections between active-site structures and selectivity, regardless of catalyst composition.

An important path toward carbon neutrality in the transport sector is the development of carbon capture and utilization (*1*), in which CO_2 emissions are captured and then converted into fuels and chemical feedstocks. This captured carbon becomes a feedstock for the production of fuels and chemicals as a replacement for carbon derived directly from fossil sources. Given substantial fuel consumption and the presence of hard-to-electrify sectors, such as aviation and maritime transport, the use of CO_2 as a feedstock for fuels would allow renewable electricity to, in effect, be stored in CO_2 reduction products. For example, methanol can be synthesized directly from CO_2, and green hydrogen is often referred to as the "fuel of the future" because it is a liquid at room temperature with high energy density (*2*). Despite notable advancements in CO_2 utilization for products such as urea, salicylic acid, and sodium carbonate, the total annual utilization remains a fraction of anthropogenic emissions (less than 0.6%) (*3*). However, the growing interest in renewable energy and the need to reduce greenhouse gas emissions have driven a surge in CO_2 hydrogenation projects. The demand for renewable methanol is rapidly increasing, driven by sectors such as transportation and energy storage. Ninety-eight million metric tons of methanol are consumed per annum, with industry estimates suggesting that the total market for renewable methanol could reach 500 million metric tons by 2050. However, today, <0.2% of manufactured methanol originates from renewable sources (*4*).

Liquid fossil fuels are known to pose health risks, with methanol being particularly toxic. Despite these risks, methanol's potential as a sustainable fuel for the shipping sector is undeniable. Compared with traditional oil-based fuels, methanol offers several advantages, including its rapid biodegradability, with a half-life of approximately 6 days in marine environments (*5*). At low concentrations, it is readily biodegradable in the presence of oxygen. Although methanol exhibits a relatively high lethal concentration 50 (or LC50, the concentration of a substance that kills 50% of a test population within a specified period of time) of 15,400 mg liter^{-1}, it can still pose risks to aquatic ecosystems, particularly at higher concentrations. This is in contrast to substances like ammonia, which exhibit substantially higher toxicity, with a LC50 of 0.068 mg liter^{-1} (*5*).

For decades, researchers have explored the possibility of synthesizing methanol directly from CO_2 to replace the industrial synthesis that uses CO augmented by added CO_2. Practical realization of this vision has been hindered by the lack of efficient and cost-effective processes that can facilitate large-scale green methanol production (*6*). The sheer complexity of catalytic systems, with countless potential compositions and configurations, has posed a scientific challenge to traditional research approaches. The need for clean and affordable energy sources for hydrogen production has also limited the commercialization of the existing technologies. The conversion of CO_2 to CO through the reverse water-gas shift (RWGS) reaction is important because CO serves as a precursor to numerous valuable chemicals, including methanol and various hydrocarbons, through the Fischer-Tropsch synthesis (FTS) process, which can lead to "drop-in" synthetic fuels in the gasoline and kerosene range. The conversion of CO_2 to CH_4 (methanation) also presents opportunities for energy storage and grid balancing (*3*).

The hydrogenation of CO_2 to methanol offers several advantages over producing CO or CH_4. First, methanol has a higher energy density than both molecules. This means that a smaller volume of methanol can store the same amount of energy, making it more efficient for transportation and storage. Second, methanol is a liquid at room temperature, which makes it easier to handle and store compared with compressing gases such as CO or CH_4. This reduces the need for expensive infrastructure and storage facilities. Finally, methanol is a versatile chemical that can be used for wide range of applications. It is an essential building block for a more sustainable chemicals market, according to European Union roadmaps, the Green Deal, and United Nations Sustainable Development Goals. In addition, the 26th United Nations Climate Change Conference (COP26) recommended reducing stranded CH_4 (flaring, offshore) into storable liquid intermediates, for example, CH_3OH, which would considerably reduce transport costs and enable it to be used as a tool to contribute to energy security in decentralized areas. Although we focus here on thermal routes to CO_2 reduction, we note that the electrochemical reduction of CO_2 is also an important potential route to similar products. Converting CO_2 to value-added chemicals via electrocatalysis [electrochemical reduction of carbon dioxide (e-CO_2RR)] has been regarded as one of the most promising routes for balancing the carbon cycle. In principle, the direct e-CO_2RR can have several advantages compared with thermochemical hydrogenation of CO_2 using hydrogen produced electrochemically from water splitting. e-CO_2RR in an aqueous medium can generate a source of protons and facilitate hydrogenation of CO_2 in a single process that can make products such as methanol and C2+. However, several challenges regarding the efficient design and eventual commercialization of e-CO_2RR processes remain. A major challenge in e-CO_2RR with water is its inefficient energy performance, requiring high potentials to produce the desired products. Multiple electron reduction pathways demand high overpotentials, which causes increased energy input and promotes parasitic hydrogen evolution, reducing faradaic efficiency (FE) (*7*). Additional challenges include the low solubility of CO_2 in water, high salinity, and optimal electrolyser composition and design. Improving

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the efficiency of electrocatalysts for CO_2 reduction remains a substantial challenge. Researchers have focused on understanding the underlying thermodynamic and kinetic processes to develop more efficient and robust catalysts (*8*). Recent advancements in catalyst design, reactor engineering, theoretical modeling, and in situ characterization techniques have led to notable improvements in product conversion and selectivity. Finally, considering economic and potential commercialization perspectives, fuels and fuel additives that include methanol, ethanol, petrochemicals such as ethylene, and chemicals such as formic acid and propanol are desirable e-CO_2RR products, whereas some products such as CH_4 do not offset the costs for the electricity consumed. In the case of CO as the prime product from e-CO_2RR, a current density of 1010 mA cm^{-2} with a FE of 80% at an overpotential of 489 mV is required to achieve a target of 60% energy efficiency, whereas in the case of methanol, a current density of 1180 mA cm^{-2} with a FE of 80% at an overpotential of 418 mV is required to achieve the same target of energy efficiency (60%), taking into account that thermocatalytic methanol production using hydrogen from water electrolysis can achieve around 50% energy efficiency (*9*, *10*). The production of CO and HCOOH is presently the only e-CO_2RR process with a current density close to industrial application, even though it is still far from the required values (*10*).

Copper-zinc/alumina catalysts for methanol synthesis

Early methanol production research that was centered on copper as a key catalyst originated in 1905, proposed by Paul Sabatier and Jean-Baptiste Senderens (*11*). In the 1920s, the process was industrialized when BASF developed a zinc chromite (Cr_2O_3-ZnO) catalyst that operated at extreme conditions, with a pressure in excess of 300 atm and temperatures between 300° and 400°C (*12*). The first $Cu/Zn/Al_2O_3$ (CZA) catalyst for methanol synthesis was patented in 1947 (*13*). However, copper catalysts were susceptible to sulfur poisoning. A new process was developed by Imperial Chemical Industries (ICI) using CZA that operates at much lower pressure and temperature (10 to 150 atm and 200° to 300°C) in combination with a desulfurization unit (*14*). The carbon source for methanol production has typically been syngas (CO and H_2) derived from fossil fuels. After the introduction of automated testing equipment in the mid-1970s, catalyst development accelerated.

A shift from syngas toward pure CO_2 and "green" hydrogen has great potential to achieve net-zero carbon emissions. In the 1990s, Lurgi announced the first-in-the-world demonstration of direct CO_2 hydrogenation to methanol over commercial CZA (*15*). In the meantime, the Research Institute of Innovative Technology for the Earth (RITE) and the National Institute for Rural Engineering (NIRE) in Japan developed the Mitsui process over a series of Cu/ZnO-based catalysts for methanol synthesis from CO_2 and H_2 (*16*). In 2012, the first commercial CO_2–to–renewable methanol plant was completed in Iceland by Carbon Recycling International (CRI), where CO_2 is captured from flue gases from the nearby HS Orka geothermal power plant and hydrogen is produced from water electrolysis (*17*). Great progress was achieved recently, such as the "Liquid solar fuel: Development of methanol synthesis technology from CO_2 hydrogenation" project led by Chinese enterprises and the mefCO_2 project led by the European Union (*18*). Major players such as Maersk have announced plans to use renewable methanol as a fuel for their shipping fleet, leading to demand in the range of several million metric tons per year. Methanol production from CO_2 has been a focal point, with several pilot and commercial plants already in operation. However, methanol produced in these plants ranges from 4000 to 150,000 metric tons per year, which is far from the millions of metric tons required by the industry, illustrating the challenge of scale-up of CO_2 hydrogenation processes.

The industrial CZA catalyst is typically prepared by coprecipitation using metal nitrates and a precipitating base under highly controlled conditions because of the so-called "chemical memory" effect. To ensure reproducibility of the catalyst's final physicochemical properties, the chemical parameters (such as temperature ~70°C and neutral pH) and physical parameters (such as the rate of addition, solid concentration, stirring speed, and aging time at ~120°C) of the coprecipitation process are carefully controlled. Standard catalysts typically contain an excess of the active Cu component, with a typical 70:30 Cu:Zn composition (with ~10 wt % Al_2O_3). Precipitates can contain a mixture of amorphous precursors in addition to poorly crystalline malachite $[Cu/Zn_2CO_3(OH)_2]$ and hydrotalcite $[(Cu,Zn)_6Al_2CO_3(OH)_{16}]$. Subsequent calcination at ~350°C forms predominantly CuO/ZnO powder; any remaining malachite or hydrotalcite is often exploited for binding, lubrication, and strength, although graphite is also added before pressing to form cylindrical pellets with cross sections and lengths of ~5 mm at a rate of thousands per hour.

Activation of the catalyst in H_2 typically forms ~10-nm-sized Cu and ZnO nanoparticles with a Cu surface area ranging from 40 to 80 m^2 g^{-1} (*19*, *20*). The reactants are an equimolar mixture of CO:CO_2 and at least a three- to fourfold excess of H_2, and the operational lifetime of the CZA catalyst is between 2 and 8 years. Deactivation is heralded by a build-up of reactor (back)pressure, with recovered catalysts showing loss of active Cu surface area (*21*). Methanol synthesis is exothermic and runs near equilibrium, so it is typically performed at low temperatures. However, the reaction rate is greater at higher temperatures, and a compromise is reached at ~230°C, with methanol yields of ~30% diminishing above this temperature.

Most research has suggested that CZA mainly converts CO_2 and that CO serves to mitigate the low-temperature water-gas shift (WGS) activity that CZA catalysts are also used for commercially (*22*). However, the active sites and the reaction mechanism are still under debate. Persistent questions concern the effect of Cu nanoparticle size (*23*, *24*) and the role of the support (*25*, *26*), the nature and location of the active site at the Cu-ZnO interface or a CuZn alloy (*27*, *28*), and whether the reaction mechanism follows the formate (*29*) or RWGS routes (*30*, *31*). Advanced characterization techniques and computational simulation tools have enhanced understanding of the structure and behavior of CZA catalysts. In 2016, it was shown (*27*) that the activity of Cu/ZnO catalyst for methanol synthesis from syngas critically depends on the coverage of metallic Zn atoms on the copper surface (CuZn alloy) formed through the reduction and migration of Zn species from the ZnO support. The smaller the ZnO nanoparticle, the easier it is to reduce, resulting in higher Zn coverage and a higher turnover frequency for methanol. In 2017, Kattel *et al.* (*28*) compared ZnO and ZnO/Cu model catalysts for methanol synthesis. Under reaction conditions, the surface metallic Zn transforms into ZnO, enabling ZnCu to achieve the activity of ZnO/Cu with the same Zn coverage. This finding underscores the pivotal role of the Cu-ZnO interface as the active site for methanol synthesis.

Next-generation catalysts for CO_2 conversion

High Cu content in CZA catalysts and the comparatively short operation time has led to the community spending more time on considering alternative formulations based on various oxide supports, synthesis methods, and metal doping, as well as noble metal and non–noble metal supported catalysts. Of note are In_2O_3-based catalysts (*32*–*36*). We conducted a comprehensive survey of catalysts reported between 2020 and 2024 for converting CO_2 to methanol or hydrocarbons. For methanol synthesis catalysts, 85 out of 96 exhibited methanol selectivity >50%, with 96% of these catalysts exhibiting CO_2 conversion rates <20% (Fig. 1A). The reported methanol yield has shown an increasing trend in the past 5 years (Fig. 1B). The catalyst with the highest yield was Cu/ZnO/MnO/KIT-6 (KIT-6 is a porous silica) synthesized by the citric acid impregnation method, operating at 180°C, with a weight hourly space velocity of 60,000 ml $hour^{-1}$ $g_{cat}{}^{-1}$ and a CO_2:H_2 mole ratio of 1:3 at a pressure of 4 MPa (*37*).

Recently, direct CO_2 hydrogenation to hydrocarbons has become increasingly appealing, albeit more challenging compared with the production of C1 products. For hydrocarbon production, out of 50, 35 are Fe-based catalysts, 2 are Co-based catalysts, and 9 are FeCo catalysts. Fe and Co catalysts show high CO_2 conversion, low CO selectivity, and high hydrocarbon distribution, as shown at the upper right corner of Fig. 1C. In Fig. 1D, 80% of methanol synthesis catalysts operated at temperatures <300°C and pressures >3 MPa, consistent with the observation that methanol production is optimal at lower temperatures and higher pressures. Conversely, 90% of catalysts used for CO_2-to-hydrocarbon conversion operated at temperatures ≥300°C and pressures <3 MPa because higher temperatures favor the RWGS process and increased FTS activity.

Alloying and support effects

Metal-metal and metal-oxide interactions are crucial in facilitating the adsorption and activation of CO_2 molecules (and hydrogen) on the catalyst surface and initiating the hydrogenation process by breaking the strong carbon-oxygen bonds. Moreover, strong metal-oxide interactions contribute to the stability of catalysts by preventing metal sintering and facilitating regeneration. Additionally, these interactions modulate surface chemistry and reaction pathways, promoting specific reactions such as methanol formation. As discussed above, a CZA-based catalyst shows the best performance for methanol synthesis. Although the role of Cu and ZnO species has been widely studied, the role of Al_2O_3 is somewhat less understood. The formation of spinel structures between Zn and Al_2O_3 can efficiently increase the adsorption of CO_2 during the process. In situ spectroscopic characterization demonstrated that the coordinatively unsaturated metal sites, arising from oxygen vacancies in $ZnAl_2O_x$, are crucial for the dissociative adsorption and activation of CO_2 (*38*).

Although Cu-based catalysts have shown promise for CO_2 hydrogenation, their performance can be limited by factors such as the difficulty of reoxidizing the metal surface and the less efficient dissociation of H_2 compared with that of other metals. By contrast, Pd-based catalysts exhibit superior hydrogenation capabilities owing to their ability to readily dissociate H_2. Alloying palladium with other transition metals can further enhance catalytic activity by modifying the electronic structure and creating new active sites. The synergistic interaction between different metal components in bimetallic catalysts, such as Pd-Cu or Pd-Ag, can lead to improved catalytic performance.

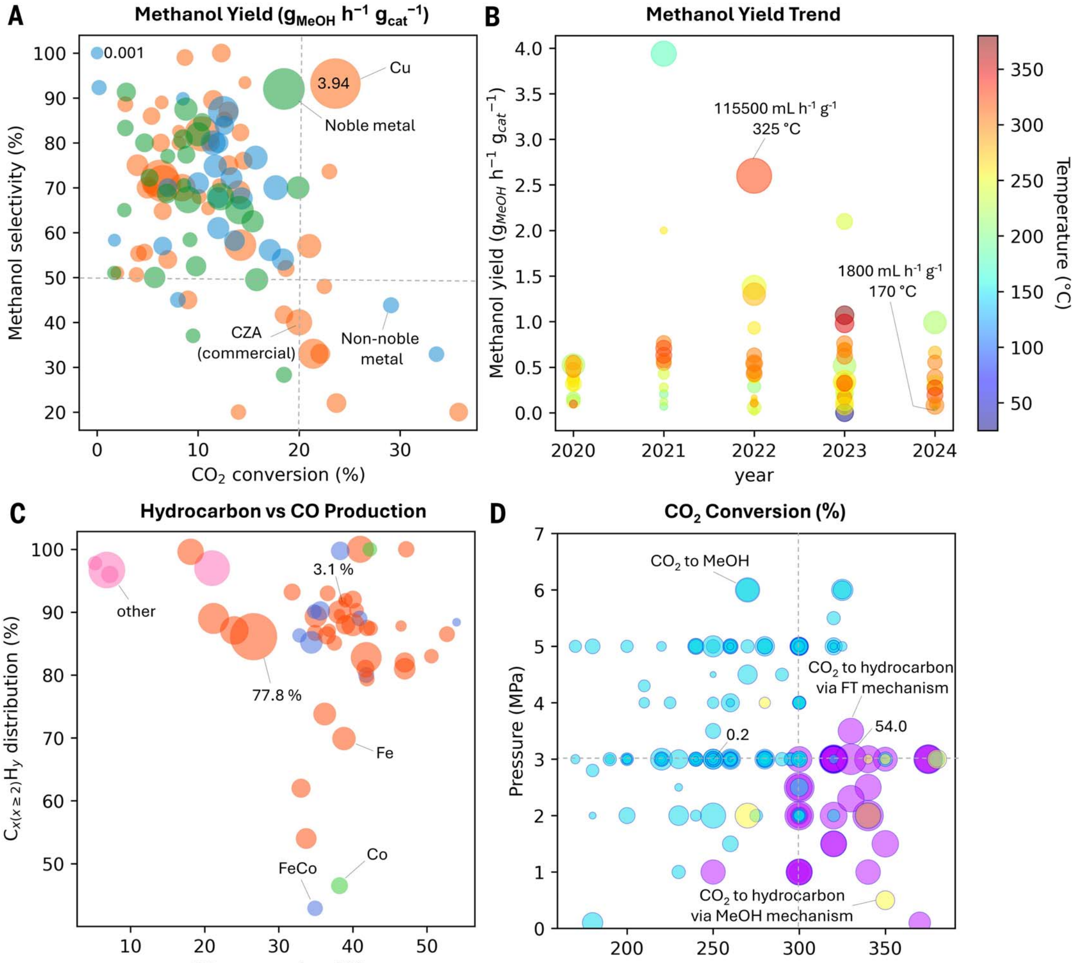

Fig. 1. CO_2 hydrogenation. (**A**) The methanol yield from CO_2 hydrogenation plotted as a function of CO_2 conversion and methanol selectivity for catalysts reported in 2020–2024 [163 articles were analyzed, with 96 of them providing data on CO_2 conversion, methanol selectivity and methanol yield in g_{MeOH} $hour^{-1}$ g_{cat}^{-1}]. Each circle represents the best performance catalyst reported in each article. The circle size corresponds to the yield of methanol in the range of 0.001 to 3.94 g_{MeOH} $hour^{-1}$ g_{cat}^{-1}. The catalysts are grouped into three categories: Cu-based catalysts (orange), noble metal (Pd, Pt, Au, Ir, Ru, Rh, Re) supported catalysts (blue), and non-noble metal (Fe, Co, Ni, Mo, Mn, Ga, In, Zr, C, N) supported, mixed oxide, or carbide and nitride catalysts (green). The commercialized CZA catalyst is from Clariant Produkte (Deutschland) GmbH. (**B**) The trend of methanol yield in the past 5 years. The circle size represents a weight hourly space velocity in the range of 1800 to 115,500 ml $hour^{-1}$ g^{-1}). Note that the space velocities are not averaged. (**C**) The hydrocarbon (C_xH_y, $x \geq 2$) in the range of 42.9 to 100% distribution (CH_4 % + C_xH_y % = 100%) plot as a function of CO_2 conversion to hydrocarbon catalysts. Each circle represents the best performance catalyst reported in each article. The circle size corresponds to the CO selectivity. The catalysts are grouped into three categories: Fe-based catalysts (orange), Co-based catalysts (green), FeCo catalysts (blue), and other catalysts (pink). (**D**) The CO_2 conversion plot as a function of temperature and pressure for CO_2 conversion catalysts. The circle size represents CO_2 conversion (%) in the range of 0.2 to 54%. The catalysts are grouped into three categories: CO_2 to methanol (MeOH, cyan), CO_2 to hydrocarbon via the FTS mechanism (purple, 43 catalysts), and tandem catalysis where CO_2 is converted to hydrocarbons via methanol (yellow, seven catalysts). A list of the articles from which data was obtained to produce the graphs in (A) to (D) is provided via Github (*71*).

This is due to the induced changes in the electronic structure around the Fermi level through charge transfer between both metals. These bimetallic catalysts can combine the strengths of both metals, resulting in higher activity, selectivity, and stability for CO_2 hydrogenation. All these aspects suggest a real benefit in using Pd for CO_2 hydrogenation. For example, Pd/ZnO catalysts prepared by different synthesis methods (*39*) showed high CO selectivity (99%) with 12% CO_2 conversion, whereas sol-immobilized catalysts had high methanol selectivity (70%) at 10.7% conversion. Higher Pd loading increased conversion but decreased methanol selectivity, and high-temperature calcination reduced activity and increased CO production. The presence of Cl^- impurities after the synthesis in the impregnated samples enhanced sintering and the formation of large Pd-Zn alloy nanoparticles (from 6 to 28 nm), which was detrimental to methanol selectivity (*39*). This was not observed for sol-immobilized catalysts where no Cl^- impurities were present and the main particle size remained stable even after high temperature reduction (7 nm at 700°C) (*39*). Pd-Zn alloy catalysts are reported to be good methanol synthesis catalysts but only when the specific β-Pd-Zn alloy is formed. Pd deposited onto ZnO exhibited a CO_2 conversion of approximately 14% at 230°C with a methanol selectivity of 35% for a 15% Pd loading. By contrast, a 1% Pd loading resulted in a lower conversion of 2.5% but a higher selectivity of 72%, demonstrating a clear correlation between Pd loading and catalytic performance (*40*). Theoretical calculations suggest that the β-phase PdZn alloy is thermodynamically favored, because it exhibits the highest exothermic heat of formation and the presence of the β-Pd-Zn alloy was shown to be crucial to obtain high activity and methanol selectivity (*40*). In addition, a linear relation between selectivity and conversion for the β-Pd-Zn alloy catalysts was observed, indicating consistent catalytic performance among different preparation methods and metal loadings (*40*). Pd, a transition metal with a nearly filled d-band, exhibits distinctive catalytic properties. However, when alloyed with s-band metals, such as copper, electronic interactions can substantially alter its behavior. This charge transfer phenomenon can lead to a shift in the d-band center, potentially modifying the adsorption and desorption properties of key intermediates such as CO and H. This electronic tuning can enhance catalytic activity and selectivity toward methanol synthesis. Although copper-based catalysts are well established in methanol synthesis, they typically require high metal loadings. By incorporating palladium into the Cu-based catalyst, it may be possible to achieve comparable or even superior performance with lower metal loadings, thus reducing costs and environmental impact (*41*). In the case of Pd-Cu supported on SiO_2 catalysts, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) studies showed that CO_2 was adsorbed as carbonate and bicarbonate species on the surface, the adsorption of which was significantly improved with bimetallic catalysts in comparison to the monometallic counterpart (*42*). In addition, the lowest barrier for formate formation was observed at a Pd/(Pd + Cu) atomic ratio of 0.33 and was accompanied by a moderate level of CO_2 conversion and high methanol selectivity (34 mol % selectivity to methanol at 7% CO_2 conversion) (*42*).

Alloying Pd with other metals and oxides can lead to similar electronic effects, as discussed earlier in the text. Pd-promoted In_2O_3 catalysts are efficient for methanol synthesis, but their activity depends on the preparation method used, specifically when comparing coprecipitated (CP) and dry impregnated (DI) catalysts (*43*). The catalysts showed good initial performance stemming from the formation of Pd clusters in the CP and DI catalysts. The CP catalyst showed a stable activity enhancement compared with bulk In_2O_3 for methanol production, whereas the improvement with the DI catalyst declined for both methanol and CO production. The authors concluded that Pd embedded into indium oxide with the CP catalysts prevented clustering and facilitated water desorption, minimizing sintering (*43*). This anchoring of Pd clusters enhanced activity, selectivity, and long-term stability. Additionally, the catalyst could efficiently operate at reduced temperatures, with hydrogen-lean feeds, and in the presence of more water.

Enhanced methanol production with bimetallic catalysts such as In-Pd and In-Ni with a specific metal molar ratio of In:Pd of 2:1 supported on SiO_2 was also reported (*44*). It was found that the interaction between indium oxide and the In-Pd or In-Ni bimetallic structure is crucial to obtain enhanced methanol synthesis. Surface enrichment in In_3Pd_2 species promoted the interaction with the In_2O_3 phase that enhanced methanol activity and selectivity. Additionally, the interaction between the metal and support and the presence of surface oxide species was shown to play a crucial role in improving catalytic performance. For Pd-In catalysts, the ideal structure for CO_2 hydrogenation (Pd-In alloy, close proximity, or separate sites) remained unclear. However, recent works suggest that the synergy between Pd and In in these catalysts does not involve appreciable alloy formation. Instead, each element likely occupies distinct sites, with Pd activating hydrogen and In_2O_3 activating CO_2 (Fig. 2). Although there might be subtle interactions between Pd and In_2O_3 under reaction conditions (such as suppressing the RWGS reaction), extensive alloying did not improve methanol yield (*45*).

Figure 2 highlights the importance of carefully balancing individual CO_2 and H_2 activation processes, as well as optimizing the location and interactions between Pd and In_2O_3 for future catalyst design. Alloying seems beneficial for some catalyst formulations but not for all. However, for the best-performing catalysts, the interface and proximity between sites that activate H_2 and those that activate CO_2 is crucial. The design of efficient catalysts must also take into account the important role of oxygen vacancies, which are also considered as active sites (*46*, *47*). In_2O_3 supported (9 wt % In) on various carriers (TiO_2, SnO_2, Al_2O_3, and ZrO_2) was studied in order to achieve higher dispersion, enhanced resistance against sintering, and potentially beneficial interactions with the support material. Analysis based on methanol space-time yield and the reaction

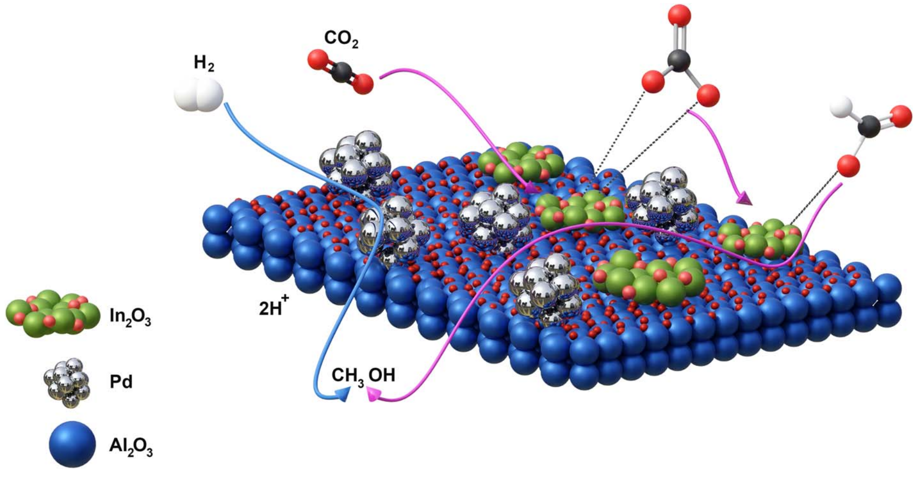

Fig. 2. Bifunctional catalytic process. CO_2 hydrogenation to methanol reaction mechanism on Pd/In_2O_3 supported on Al_2O_3. Two distinct active sites are present: The H_2 is activated on Pd, and the CO_2 is activated on In_2O_3. [Figure adapted from (45), which is available under a CC BY 4.0 license]

rate of In-based CO_2 hydrogenation experiments revealed the superiority of ZrO_2 over other carriers such as TiO_2 and CeO_2, resulting in a material that surpassed bulk In_2O_3 performance at all reaction temperatures. Evaluation of ZrO_2-supported catalysts with varying In loadings demonstrated that 9 wt % In was optimal for space-time yield, whereas the reaction rate per gram of In increased with decreased loading (46). X-ray photoelectron spectroscopy revealed an increase in the O-defect signal after the catalytic test, which was beneficial for methanol production. In addition, electron paramagnetic resonance spectroscopy detected at least one type of vacancy in the fresh support, indicative of electrons near Zr cations transitioning from Zr^{+4} to Zr^{+3}. After In_2O_3 deposition, these electrons were depleted, suggesting that reduced Zr centers abstracted O atoms from the active phase and generated additional vacancies (46).

Mechanistic considerations

The reaction mechanisms of CO_2 hydrogenation on CZA catalyst are still hotly debated. The evolution with time of the active site (48) and the interaction between the components that make up the catalysts should be clarified to facilitate the design of new catalytic formulations with improved performance metrics (i.e., methanol yield and catalyst lifetime). The nature of the active site (metal, oxide, carbide) determines the catalytic activity of the catalysts and the product distribution. Knowledge of the active site–CO_2 interactions is crucial to increasing the possibility of applying these catalysts for CO_2 hydrogenation and their potential for industrial-level applications. For CZA catalysts, most experimental and theoretical data highlight a critical role of (zinc) formates formed from CO_2 adsorption at the Cu/ZnO interface, which can be readily hydrogenated through methoxy species to form methanol. Further rationalization of the likely reaction mechanism is given below.

Mechanistic understanding is derived from a combination of catalytic kinetic studies, in situ characterization, and theoretical investigations examining CO_2 conversion pathways via the formate HCOO* pathway versus the carboxyl COOH* pathway. Theoretically, an alternative pathway for methanol synthesis involves the sequential production of CO* from CO_2* followed by its successive hydrogenation. However, the stability of COOH* is much less than that of HCOO* (49). Additionally, the conversion of CO_2* to COOH* faces a substantial energy barrier of 0.69 eV, making this process less favorable than the barrier-free formation of HCOO* from CO_2* + H*. Despite the potential presence of COOH* during the reaction, weakly bonded CO* resulting from CO_2 tends to desorb from the surface rather than undergo hydrogenation. Thus, CO_2 hydrogenation to methanol on the ZnO-ZrO_2 surface primarily proceeds via the formate pathway. Moreover, density functional theory (DFT) calculations indicate that ZnO-ZrO_2 exhibits higher methanol selectivity than pure ZnO, with the energy barrier for the conversion of H_2COO^* to H_2CO^* + H_2O^* being lower on ZnO-ZrO_2 (1.27 eV) than on ZnO (1.37 eV). This difference suggests that ZnO-ZrO_2 would have relatively higher methanol selectivity and lower CO selectivity. These findings align with experimental results, with the enhanced methanol selectivity of ZnO-ZrO_2 attributed to the synergistic effect in H_2 activation between Zn and Zr sites and the simultaneous activation of H_2 and CO_2 on neighboring Zn and Zr sites, respectively (49).

Several studies have explored catalysts that feature an inverted CeO_x/Cu configuration, proposing that the interface between these species acts as the active site for methanol synthesis via carboxylate species after a RWGS reaction plus CO hydrogenation reaction mechanism (50, 51). These conclusions stem from observations of Ce acquiring a 3+ oxidation state when reduced near copper clusters, which facilitates H_2 adsorption and distribution to the support (52). However, conflicting findings from other studies suggest that CeO_2 does not influence methanol synthesis because spectator carbonates block the Cu-Ce interface (53). Inconsistencies persist regarding whether bidentate carbonate species formed at the interface are active toward methanol. There remains uncertainty about the nature of the active site and the effects of CeO_2 content and TiO_2 support on catalyst morphology and kinetics. The presence of carboxylate species was notably observed only when cerium oxide was dispersed on the copper substrate, but these species were not stable under ultrahigh vacuum conditions.

Compared with the higher stability of formate species, the lower stability of the $CO_2^{\delta-}$ species suggests that they serve as more favorable intermediates for methanol synthesis. Formate species, known for their high stability, may not efficiently facilitate the transient conversion of CO_2 to CH_3OH. Thus, incorporating CeO_x nanoparticles onto Cu(111) establishes a metal-oxide interface capable of adsorbing and activating CO_2, thereby initiating a new reaction pathway for methanol synthesis.

Some studies demonstrated that for $CuCeO_x$/TiO_2 catalysts, the mechanism unequivocally excludes a RWGS reaction and CO hydrogenation pathway for methanol synthesis. Instead, this species is formed through the stepwise hydrogenation of formates over Cu-Ce interfacial sites. Additionally, it was concluded that the formation of CO is assisted by hydrogen on a site distinct from that involved in methanol synthesis. Furthermore, the kinetic relevance of surface-detected carbonate species was dismissed (54). However, in both works (53, 54), the oxidation state of CeO_x seems different (Ce^{3+}/Ce^{4+} and mostly Ce^{3+}, respectively), and the reaction conditions differ (batch and flow reactors, respectively). These studies underscore the distinct roles of interfacial active sites in shaping product selectivity through different CO_2 hydrogenation mechanisms. They highlight the importance of integrating kinetic and spectroscopic analyses with isotopic labeling to unravel reaction mechanisms over catalysts where the interface between a metal and metal oxide is pivotal (54).

Iron and cobalt catalysts for direct hydrocarbon synthesis from CO_2

Early hydrocarbons production research centered on the FTS process developed in the mid-1920s to produce liquid hydrocarbons using syngas (CO/H_2). There has been an increasing interest in the direct utilization of CO_2 in the FTS process for the production of olefins and hydrocarbons, ranging from light hydrocarbons to liquids and waxes. Since the 1990s, the FTS process using syngas has been part of the modern gas-to-liquid industry. All the previous research developed over the past century on iron and cobalt FTS catalysts, which focused on explaining CO activation, monomer species formation, and chain growth, is now helping the development of CO_2-to-hydrocarbon processes (CO_2-FTS). Surface science and computational chemistry studies have revealed site requirements for reactant adsorption and dissociation in FTS, highlighting the dynamic nature of catalyst surfaces. Promoters like alkali metals (Na, K, Cs), transition metal oxides (Mn, V, Ti), and lanthanide and actinide oxides influence Co and Fe catalyst activity and selectivity. Phase transformation and surface reconstruction of catalysts are likely to occur during the FTS process, and depending on the metal, this may be related to carburization, that is, the formation of metal carbides, which are often thought to be the most active phases. The direct hydrogenation of CO_2 usually requires an additional step, the reduction of CO_2 to CO by the RWGS reaction and the subsequent hydrogenation of CO into hydrocarbons by the FTS reaction. Fe-based catalysts are known to perform both reactions: The RWGS reaction is catalyzed by Fe_3O_4 (high-temperature shift catalyst), whereas the iron carbide phase (particularly the χ-Fe_5C_2 polymorph) catalyzes CO hydrogenation and carbon-chain growth (55).

Distinguishing the diverse species (M^0/MO_x/MC_x, where M is Fe or Co) and characterizing the surface structure is challenging, but the resultant structure-activity relationships can inform rational design of new catalysts. The structural evolution of iron and iron oxides into iron carbides has been investigated more widely in CO hydrogenation, but it is also extremely important in CO_2 hydrogenation. Converting

CO_2 into CO and CH_4 creates an atmosphere with reactive gases for carburization, with Fe_3O_4 and Fe_5C_2 the main phases observed on spent iron catalysts (*56*). This detailed study revealed that the carburization of Fe^0 mainly occurs during the first hour to form amorphous or crystalline iron carbide. Then, a large amount of iron oxides is formed, accompanied by the further crystallization of iron carbide. After 40 hours on stream, a balanced composition of 20% Fe_5C_2 (surface) and 80% Fe_3O_4 (core) is reached. Under identical conditions, the normalized CO_2 conversion rate is determined to be $Fe_5C_2 > Fe_3C \gg Fe_3O_4$. The surface properties of iron carbide enable the efficient adsorption and activation of CO_2 molecules, facilitating subsequent hydrogenation reactions. Its capability to break the strong carbon-oxygen bonds in CO_2 is pivotal for initiating hydrogenation reactions and olefin production. DFT investigations support the finding that CO_2 activation and hydrogenation are more favorable on carbides than on metallic iron and magnetite (*57*). Under reaction conditions, the unavoidable presence of H_2O, a side product of RWGS, may cause catalyst deactivation, notably by oxidizing the activated catalyst Fe_5C_2 to Fe_3O_4. Finally, the C2+ hydrocarbon formation rate also correlates with the content of Fe_5C_2, suggesting that Fe_5C_2 is the main active species for C2+ production (*56*). By increasing the H_2/CO_2 feed ratio, iron carbides are protected from oxidation, effectively slowing down catalyst deactivation. However, one downside of this is that too much hydrogen also causes the termination of chain growth. Interestingly, potassium, a well-known promotor for FTS, has a promotion effect on the adsorption and activation of CO_2 on metallic Fe and Fe_5C_2 but not on Fe_3O_4 (*58*).

Cobalt carbide (Co_2C) is also a promising catalyst for CO_2 hydrogenation. In FTS, cobalt oxide (CoO) is first reduced to metallic cobalt (Co^0) and then carburized to Co_2C under syngas (CO/H_2) or CO. The reaction is run below 260°C because cobalt carbide is thermally unstable and decomposes into Co^0 and graphite. CO_2 hydrogenation often requires a high temperature, and the Co_2C catalyst tends to partially decompose to Co^0, which leads to a loss of selectivity toward deep hydrogenation of CO_2 into CH_4. Unlike iron carbide, H_2O and K-promoter on Co_2C catalyst accelerate carburization (*59*). The Co_3O_4 catalysts are reduced to CoO and then directly to Co^0, whereas the K-promoted Co_3O_4 catalysts are reduced to CoO and then directly to Co_2C at 260°C. CO_2 adsorption and activation are enhanced on Co_2C compared with metallic Co, but Co_2C is also sensitive to air, so approaches for stabilizing this phase are needed. A delicate balance of the reaction atmosphere and the K-promoter plays a vital role in stabilizing Co_2C. Cofeeding a small amount of water also helps to stabilize Co_2C. However, excessive H_2O addition can be detrimental. The low intrinsic activity of cobalt for RWGS, can be overcome by combination with other metals, such as iron. The dual active sites composed of iron carbides and metallic cobalt are suitable for C-C coupling and olefin secondary hydrogenation reactions to achieve high selectivity for propane and butane (liquid petroleum gas) with the highest space-time yield reported so far (151.0 g of product per kg of catalyst per hour) (*60*).

Nickel catalysts were not included in Fig. 1, C and D, because they generally produce CH_4 during CO_2 hydrogenation. However, in situ analysis to track the surface reconstruction of Ni catalysts revealed the presence of nickel carbide (Ni_3C) after treating the Ni catalysts under reaction conditions (H_2/CO_2 atmosphere with a heating ramp from 100°C up to 800°C). The main change observed after the build-up of a Ni_3C like phase was a pronounced change in selectivity toward CO (RWGS) and suppression of CH_4 formation (*61*).

Environmental sustainability

Several life-cycle assessments (LCAs) that were conducted to gauge the environmental impacts of CO_2 conversion processes have focused on various metrics, mainly climate change (*62*). CO_2-based hydrogenation shows promise in reducing global warming impacts (GWIs) compared with traditional fossil-based production routes, mainly when powered by renewable energy sources (*63*). However, trade-offs between different environmental impacts exist, and the overall environmental sustainability of carbon capture and utilization processes hinges on factors such as the source of CO_2, the origin of the electricity needed for producing H_2, and the specific conversion technology used (*6*). LCAs have been conducted to evaluate the environmental impacts of CO_2-based methane (*64*), carbon monoxide (*64*), and methanol production (*65*) among others, and consider different CO_2 and H_2 sources (*62*). The most favorable outcomes regarding GWIs are observed when wind electricity supplies hydrogen through water electrolysis. Incorporating the impact of CO_2 hydrogenation catalyst production is under development but is usually not part of any LCA, which limits the assessments.

The cradle-to-gate GWIs of CO_2-based methane, carbon monoxide, and methanol production (*62*) are shown for grid- or wind-based electricity in Fig. 3 (indicated by blue circles and purple crosses, respectively). When powering with wind, the GWI is reduced, and on a cradle-to-gate basis, negative GWI occurs (however, these are, of course, not net-negative on a cradle-to-grave basis, including the CO_2 emission after the relatively short lifetime of the products).

Sustainable production of fuels with reactants derived from renewable electricity must also address water management and heat integration. The amount of water produced during the synthesis of fuels is less than the amount of water needed for hydrogen production with electrolyzers (*65*), so additional water inputs are needed. Synthesis of methanol and methane generates heat, but additional heat inputs are needed (methanol and methane synthesis can utilize 24 and 81% of the heat, respectively). For comparison, kerosene synthesis via FTS generates 124% of the heat required (*66*). The climate mitigation effectiveness of e-fuels, which are synthetic fuels made from renewable energy sources such as wind and solar power, depends on the carbon intensity of the electricity used for their production and the source of CO_2, with substantial reductions in greenhouse gas emissions achievable only when powered by nearly 100% renewable electricity, as for the chemicals above. Although e-fuels can be a partial solution for hard-to-abate sectors such as aviation, they are less effective for light- and heavy-duty vehicles compared with direct electrification or hydrogen and are incompatible with long-term climate goals if fossil-derived CO_2 is used, which also holds true for the other chemicals discussed above.

Conclusions

Fuels obtained from CO_2, including oxygenates and hydrocarbons, are a promising solution for decarbonizing the transportation sector, particularly in hard-to-electrify sectors such as aviation, shipping, and long-haul trucking. Although CZA and Fe- or Co-based catalysts have been the workhorses for this, their limitations are apparent. The increasing demand and availability of "critical" elements such as Co, Cu, and Zn [according to EuChemS, Zn is considered as at-risk as In and more at-risk than Pd, whereas Cu and Co are considered

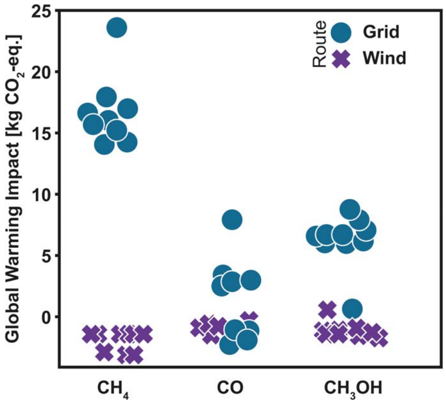

Fig. 3. Global warming impacts. Cradle-to-gate GWIs of the production of CH_4, CO, and CH_3OH depending on the energy supplier (blue circles indicate electricity provided by the grid mix, and purple crosses indicate electricity provided by wind turbines). Each circle and cross represent one LCA. [Figure adapted from (*62*)]

increasingly at risk (*67*)] raises a crucial question: Are we solely reliant on the well-studied catalysts or are alternatives needed? Research has particularly highlighted the drawbacks of CZA catalysts, including their short life span and difficulties in production. As shown earlier (Fig. 1A), reformulating existing catalysts will not yield substantial improvement in the desired product yield. Instead, research efforts in catalyst preparation should focus on extending their active life through strategies such as improving sinter resistance or, from a process perspective, regeneration in situ (*68*). Alternative catalysts such as those formulated around Pd (i.e., Pd-In) are promising in terms of performance (*69*) but are prohibitively expensive, and all novel formulations will struggle for acceptance until tested at scale or, at the very least, exhibit robust scaling relationships. High-throughput screening techniques to rapidly test and analyze large numbers of potential catalyst candidates are becoming routinely available and show much potential for accelerating the discovery of catalysts with improved performance (*70*).

De novo catalyst design, however, remains a challenge because identifying the key species involved in CO_2 hydrogenation and understanding the complete catalytic cycle at the molecular level pushes the boundaries of present experimental and computational capabilities. Second, the gap between theoretical models and real-world behavior makes it difficult to translate how tweaking catalyst design in silico will translate to improved performance in situ. Third, intrinsic deactivation mechanisms such as sintering as well as extrinsic ones, that is, poisoning and coking, are often poorly understood. Accurately incorporating all of the above variables to facilitate robust model generation has therefore yet to be done. Looking ahead, however, exciting possibilities could be unlocked using next-generation tools, including enhanced artificial intelligence (AI) and deep learning. By exploiting vast datasets from experiments and simulations coupled to an ability to exploit quantum computing, we could improve the size, breadth, and accuracy of simulations. This would permit us to obtain a more realistic understanding of the structure-activity relationship and saliency of catalyst properties. Alongside this, continuous advancements in operando characterization techniques, particularly realistic sample environment and improved detection (i.e., more photon-efficient data collection as well as more sophisticated data deconvolution techniques), also permit us to refine our observed knowledge on active-site and mechanism evolution. These advancements offer the potential to unlock a deeper level of understanding beyond the presently dominant focus on routinely observed formate, methoxy, and carbonyl species at the metal–metal oxide interfaces, whose importance is often unclear. Ultimately, we might soon be able to unravel a complete catalytic cycle for CO_2 hydrogenation, which could be considered the holy grail for the field of catalysis in this area, possibly paving the way for even more sustainable and often distributed CO_2 conversion processes (i.e., bio-derived, hybrid, photo- and electrochemical) that operate at lower temperatures and pressures.

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