Copper-based Catalysts for CO₂ Hydrogenation: A Perspective on the Active Site

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ABSTRACT: CO₂ hydrogenation is regarded as a revolutionized field in heterogeneous catalysis, not only mitigating environmental problems caused by greenhouse gas but also producing valuable chemicals. This Perspective, going over both theoretical and experimental advances, aims to bridge the Cu-based catalyst structures, the most important type of CO₂ hydrogenation catalysts, and their catalysis applications with varied activity and selectivity. We provide a systematic overview of the catalytic active site, the reaction mechanism, and their impact on the reaction selectivity, stability, and activity for CO₂ hydrogenation. There is a particular focus on the nature of the industrial Cu/ZnO/Al₂O₃ catalyst, where a large volume of literature is available exploring the reaction energetics on the possible reaction sites, including Cu metal, CuZn alloy, and ZnOₓ/Cu overlayers. The recent advances in designing better catalytic active sites, such as the Cu single-atom catalyst, supported Cu cluster catalyst, and bimetallic Cu-M are then followed to illustrate how the activity and selectivity vary upon the change of active sites. Our perspectives on the future research directions are finally provided, which should benefit the clarification of complex catalytic active sites and the design of better CO₂ hydrogenation catalysts.

Keywords: CO₂ hydrogenation, copper-based catalyst, catalytic active site.

1. Introduction

The conversion of carbon dioxide (CO₂) into value-added products via heterogeneous catalysis is a promising approach to reducing greenhouse gas emissions with great economic benefits. To date, the hydrogenation of CO₂ and CO mixed gas has already been realized in the industry through the low-pressure methanol synthesis process with a Cu-based catalyst, i.e. Cu/ZnO/Al₂O₃ (CZA) catalyst.¹,² The global CH₃OH production via this technology is massive, reaching 106.89 million metric tons in 2021.³ This industrial achievement demonstrates the great value of CO₂ conversion in making renewable fuel and chemical compounds. In recent years, significant efforts have been devoted to developing new types of catalysts for CO₂ hydrogenation (without CO presence), where the Cu element continues to play a pivotal role in these endeavors. This Perspective focuses on the recent theoretical and experimental advances in the structural characteristics of Cu-based catalysts and their linkages to the product selectivity in CO₂ hydrogenation from a fundamental point of view.

The industrial CZA catalyst serves as a textbook example for understanding how CO₂ is converted on Cu-based catalysts.⁴ Despite tremendous efforts, there is a huge debate regarding the active site of the CZA catalyst, not least because of the disparity between experimental characterization setups and industrial conditions. It was once accepted that metallic Cu serves as the active site while ZnO acts as a support,⁵ although, apparently, the synergy between Cu and Zn components is critical to this technology. Several hypotheses have been further proposed to rationalize the synergy effects, including Cu⁺ in ZnO lattice,⁶ lattice strain,⁷ Schottky Junction,⁸ et al. However, most of these hypotheses lack clear support from the latest experimental and theoretical results.

In 2012, Behrens et al.⁹ reported the experimental evidence for the enrichment of Zn on the Cu surface using X-ray photoelectron spectroscopy (XPS) and high-resolution transmission electron microscopy (HRTEM) methods. Since then, researchers focused on two models of the active sites: the CuZn surface alloy model,¹⁰ in which Zn is reduced to form the CuZn alloy phase, and the ZnOₓ/Cu interface model,¹¹ which grows in situ due to the Strong Metal-Support Interaction (SMSI) effect.

In addition to the fundamental efforts to clarify the reaction mechanism on CZA catalysis, the exploration of the possibility to apply Cu single-atom catalysts (SACs) for a low-temperature CO₂ hydrogenation catalyst is mainstream in heterogeneous catalysis.¹²,¹³ The Cu SACs refer to catalysts with Cu cations stabilized by the support material, where the valence state of Cu can be tuned by the coordination environment and thus depends on the synthetic routes. Recent literature shows that these Cu SACs can exhibit distinctive product selectivity due to the delicately designed Cu coordination environment.

Another active research direction relates to the alloying between Cu and the second metal element, for example, the bimetallic Cu-M system (M = Pd,¹⁴ Ni,¹⁵ Fe,¹⁶⁻¹⁸ etc.). Introducing a second metal to Cu-catalyst can result in the formation of non-methanol products, such as methane,¹⁵ long-chain hydrocarbons,¹⁸ or ethanol.¹⁶ For example, Cu-Ni catalyst can lead to high selectivity on CH₄,¹⁵ while Cu-Fe catalyst tends to produce long-chain hydrocarbons.¹⁷ However, the active site and reaction mechanism of these new catalytic systems are much less studied --- whether the alloy metal is indeed the active site remains skeptical. As pointed out by Hwang et al.¹⁶ in the Cu-Fe catalyst, although the CuFe alloy phase is regarded as the active site for Cu-Fe bimetallic catalyst,
FeOₓ and FeCₓ also exist in the catalyst and thus may still be the active centers.

With encouraging progress on Cu-based catalysts for CO₂ hydrogenation achieved in recent years, we here aim to overview the current understanding on the active site of different types of Cu-based catalysts, with particular emphasis on the atomic structure as revealed by joint theoretical calculations and experimental characterizations. This Perspective is organized as follows. The thermodynamics and reaction networks for CO₂ hydrogenation are first summarized. This follows sequentially the recent advancements in probing the catalytic active site using advanced theoretical and experimental techniques, including CZA catalyst, Cu SAC catalysts, and its closely-related supported Cu cluster catalysts, and bimetallic Cu-M catalysts. Finally, the outlook for future research directions is provided.

2. Thermodynamics and the kinetics of CO₂ hydrogenation on Cu surfaces

CO₂ hydrogenation can in principle yield a diverse range of products, including primary reduction products (such as CO, HCOOH, and HCHO), alcohols (CH₃OH and C₂H₅OH), and hydrocarbons (CH₄, C₂H₄, and even long-chain alkanes). It is noteworthy that while methanol is a commonly targeted product in industrial CO₂ hydrogenation, it is not the most thermodynamically favorable product at typical operating temperature of 500 K. Figure 1 illustrates the Gibbs free energy changes (ΔG) for these gas-phase reactions.¹⁹ It shows that CO and CH₃OH have similar ΔG at 500 K (0.21 and 0.39 eV, respectively), both slightly above zero. Compressing the feed gas to increase the input pressure the reaction can be driven forwardly, resulting in a more favorable equilibrium conversion of CH₃OH compared to the economically undesirable CO. However, the maximum one-pass conversion of CH₃OH is still limited to 15~35 %,²⁰ which can be increased by decreasing temperature and increasing pressure. Consequently, the methanol synthesis industry tends to favor lower reaction temperatures as long as the reaction rate remains acceptable.

Other products are less reported on Cu-based catalysts. HCOOH and HCHO are thermodynamically unfavorable than CH₃OH across the entire temperature range (ΔG is 0.26/0.34 eV higher than CH₃OH at 500 K, respectively). They exhibit low selectivity, likely due to their instability and susceptibility to further hydrogenation into CH₃OH. Products like CH₄, C₂H₄, and C₂H₅OH are consistently thermodynamically more favorable than CH₃OH (ΔG is 1.18/0.42/0.30 eV lower at 500 K), but they are rarely reported in the products using Cu-based catalysts. On Cu metal, a model system, CO₂ hydrogenation only produces CO and CH₃OH.²¹

The answer to the conflicts of product selectivity with thermodynamics preference lies in the reaction kinetics in catalysis. Figure 2 summarizes the generally-regarded CO₂ hydrogenation mechanism on Cu surfaces obtained from density functional theory (DFT) studies.²²⁻²⁷ Three general findings are outlined in the following.

(i) A most-mentioned CO₂ hydrogenation pathway to CH₃OH follows the sequence: CO₂* (superscript * indicates the adsorbed state) → HCOO* → HCOOH* → H₂COOH* → HCHO* → CH₃O*, termed as the formate pathway.²² The rate-determining step occurs in the first half of the reaction before the CH₂O formation, involving the hydrogenation of CHₓO₂ (x = 0~3) species, such as CO₂ to HCOO*, HCOOH* to H₂COOH*, or H₂COOH to HCHO*. If the overall barrier for the further hydrogenation of CH₂O across the entire temperature range (ΔG is 0.26/0.34 eV higher than CH₃OH at 500 K, respectively). They exhibit low selectivity, likely due to their instability and susceptibility to further hydrogenation into CH₃OH. Products like CH₄, C₂H₄, and C₂H₅OH are consistently thermodynamically more favorable than CH₃OH (ΔG is 1.18/0.42/0.30 eV lower at 500 K), but they are rarely reported in the products using Cu-based catalysts. On Cu metal, a model system, CO₂ hydrogenation only produces CO and CH₃OH.²¹
(ii) Another mechanism for CO₂ to CH₂OH is the reverse water-gas shift (r-WGS) coupling with CO hydrogenation. In the pathway, CO₂ is first hydrogenated to CO through CO₂* - COOH* - CO*, termed as the carboxyl pathway, and then CO* is further hydrogenated to CH₂OH* through CO* - CHO* - HCHO* - CH₂OH*, termed as the formyl pathway. This pathway on metal Cu surfaces appears to be kinetically unfavorable compared to the formate pathway due to the higher Gibbs energy barrier of CO₂* - COOH*, e.g. > 1.8 eV for Cu(111), Cu(100) and Cu(211). Additionally, COOH* is less stable than HCOO* on Cu surfaces, leading to a lower rate to subsequent reactions.

(iii) Hydrogenation toward hydrocarbons or multi-carbon products is challenging on pure Cu catalysts, but appears to be likely on Cu-based multi-metallic catalysts such as CuFe and CuNi catalysts. This is likely due to the high barrier associated with the C-O bond breaking to produce CH₄ (x = 0-4) species, which is essential for subsequent C-C coupling. The direct dissociation of CO* to form C* and O*, known to be feasible on Fe catalysts, encounters a high energy barrier (> 2 eV) on Cu surfaces, making it unlikely to occur. Another possible pathway of CH₄ generation is via the HCHO* - CH₂OH* - CH₃OH* route, but its overall barrier is higher than that of HCHO* - CH₂OH* - CH₃OH, leading to a low selectivity.

Quantitatively, the low coordinate number (CN) of Cu (the number of Cu atoms neighboring the centering Cu) is generally more active in CO₂ hydrogenation. Table 1 summarizes the overall energy barriers on different Cu surfaces. For the same reaction step, as listed in entries 1-3, and entries 4-8 in Table 1, generally the barrier is lower as long as the CN is reduced. When converting to the Gibbs free energy, the close-packed Cu (111) is found to be inert, as evidenced by the very high Gibbs free energy barrier of 1.98 eV for CO₂ hydrogenation, where the rate-determining step (RDS) is the HCHO* + H* step. To allow CO₂ hydrogenation, the introduction of step and point defects is thus a must. The Cu (211) surface exhibits a significantly lower Gibbs free barrier of 1.40 eV for methanol production. These findings indicate that the importance of manipulating the surface structure for enhancing the catalytic activity of Cu-based catalysts in CO₂ hydrogenation.

Table 1. The reaction and structure information of Cu cluster and surface. Eₐ note for overall barrier. RDS note for rate-determining steps.

<table>
<thead>
<tr>
<th>Cu surface</th>
<th>RDS</th>
<th>CN</th>
<th>Eₐ (eV)</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu (111)</td>
<td>HCOO* → H₂COOH*</td>
<td>9</td>
<td>1.27</td>
<td>22</td>
</tr>
<tr>
<td>Cu (100)</td>
<td>HCOO* → H₂COOH*</td>
<td>8</td>
<td>1.25</td>
<td>23</td>
</tr>
<tr>
<td>Cu (110)</td>
<td>HCOO* → H₂COOH*</td>
<td>7</td>
<td>1.19</td>
<td>23</td>
</tr>
<tr>
<td>Cu (111)</td>
<td>CO₂ → HCOO*</td>
<td>9</td>
<td>1.15</td>
<td>30</td>
</tr>
<tr>
<td>Cu (100)</td>
<td>CO₂ → HCOO*</td>
<td>8</td>
<td>1.03</td>
<td>30</td>
</tr>
<tr>
<td>Cu (111) point defect</td>
<td>CO₂ → HCOO*</td>
<td>7</td>
<td>0.92</td>
<td>30</td>
</tr>
<tr>
<td>Cu (100) point defect</td>
<td>CO₂ → HCOO*</td>
<td>7</td>
<td>0.92</td>
<td>30</td>
</tr>
<tr>
<td>Cu (211)</td>
<td>CO₂ → HCOO*</td>
<td>7</td>
<td>0.92</td>
<td>30</td>
</tr>
</tbody>
</table>

CO₂ and H₂ feed gas, instead of pure CO₂ or pure CO with H₂, is utilized in the fixed-bed catalysis, where the CO₂:CO ratio ranging in 0.5-4.134,35 Interestingly, the isotopic-labeling experiments revealed that CO₂ is the dominant carbon source for methanol production, accounting for more than 90% of the carbon in methanol. On the other hand, the CO-free CO₂/H₂ feed gas leads to a more oxidizing atmosphere.

There are two main vying views regarding the active sites of CZA catalysts, both of which have garnered experimental and theoretical evidence, fueling an ongoing debate. The first view posits that the ZnO oxide is partially reduced and the Zn migrates to the Cu surface, leading to intermixing with the Cu lattice and the formation of a surface alloy. According to DFT calculations, the reducing potential of the feed gas is sufficient to reduce ZnO to form a CuZn surface alloy with moderate Zn coverage (0.35 ML or 0.22 ML), but not enough to form CuZn bulk alloy or metallic Zn. Experiments also observe high content of CuZn surface alloy under strong reduction conditions, e.g., CO₂-free CO and H₂ atmosphere. Kuld et al.40 found an increasing Zn coverage with an increasing CO/CO₂ ratio in the feed gas, which led to a higher methanol reaction rate, indicating that stronger reducing potential in the feed gas resulted in higher Zn coverage. Nakamura et al.41 also found that the maximum TOF on a deposited Zn on Cu(111) model catalyst with 0.19 ML Zn coverage was 10 times faster compared to clean Cu (111) surface. While earlier DFT studies reported that the Zn-doped Cu (211) surface shows a lower energy barrier of CO₂ hydrogenation to methanol than that without Zn doping, following the same formate pathway, the later ab-initio microkinetics study reveals a negative effect of Zn alloying on CO₂ hydrogenation activity.

Recently, we developed a microkinetic-guided machine learning pathway search (MMLPS) method to explore the reaction network for CO₂ and CO hydrogenations on thermodynamically favorable Cu–Zn alloy surface structures. Taking Cu (211) as an example, Figure 3a plots 14,958 reaction pairs (IS, TS, FS) on Cu (211) surface through automated reaction sampling based on a global neural network potential (G-NN) calculations, from which the CO₂...
and CO hydrogenation reaction pathways are resolved and the reaction mechanism is identified to be the formate pathway rather than r-WGS pathway for CO2 hydrogenation on Cu (111) and Zn-alloyed Cu (211) surface (Figure 3b). The key intermediate along the pathways on 0.11 ML and 0.22 ML Zn-Cu (211) surface are shown in Figures 3c and 3d. Interestingly, we found that the Zn decorates at the step-edge at Cu (211) surface with coverage up to 0.22 ML under reaction conditions, and the Zn−Zn dimeric site is thermodynamically unfavorable. CO2 and CO hydrogenations occur exclusively at the step-edge of the (211) surface with Zn coverage up to 0.11 ML, where the low coverage of Zn (0.11 ML) does not much affect the reaction kinetics (Figure 3b), demonstrating no activity improvement on CuZn surface alloy. The microkinetics simulations based on DFT calculation reproduced nicely the experimental finding that CO2 hydrogenation dominates methanol synthesis, instead of CO hydrogenation.

Another popular view proposes that Zn species form a ZnOx(Hy)-Cu interface, where Zn atoms are primarily present as ZnOx(Hy) clusters of layers on the Cu surface. It is once suggested that the reduced Zn ions migrate to the Cu surface and undergo re-oxidation, forming a few layers of ZnOx on the Cu surface and leading to an SMSI effect. This phenomenon is indeed observed in HRTEM photos under ex-situ conditions, revealing the formation of a graphite-like ZnO overlayer on the surface of Cu nanoparticles after H2 activation (Figure 4). This phenomenon is also observed by other research groups. The presence of cationic Zn as the active site is also suggested by Laudenschleger et al., who conducted a high-pressure pulse experiment in which NH3 is injected into a high-pressure methanol synthesis. They observed a temporary decrease in methanol yield due to NH3 poisoning, but the co-fed C2H4 hydrogenates to C2H6 on the Cu surface at a normal rate. Based on these observations, they proposed that a positively charged Zn on Cu is responsible for the active sites in CO2 hydrogenation, which is poisoned by NH3. They also reported that the higher CO2 content, a more oxidizing condition, may lead to more positively charged Zn on the Cu surface, resulting in more obvious NH3 poisoning.

As for the phase of Zn cations in catalysts, growing experimental and theoretical results support that the presence of H species may be critical in the SMSI process and also in the active site, suggesting the relevance of the ZnOxH3 phase rather than the ZnO2 phase. Beck et al. first showed that the formation of active sites is influenced by the H2 pressure. They observed significant changes in the Zn K-edge X-ray absorption near edge structure (XANES) signals during temperature-programmed reduction around operating temperature when the H2 pressure was kept beyond 1 bar. However, no significant changes were observed in the zinc (+2) oxidation state until 500 °C under 1 mbar H2. In addition, theoretical studies also found the strong adsorption of H on the...
ZnOx cluster supported on Cu(111), stabilizing the ZnOx cluster on Cu at the H2-rich reaction condition.\textsuperscript{46-48-50} The presence of H may further alter the reaction kinetics. Reichenbach et al.\textsuperscript{51} showed that the energy barrier of CO2 hydrogenation on Zn7O3/Cu(111) is 1.33 eV, which decreases to 1.30 eV when H adsorbs on the ZnO cluster. Kattel et al. proposed another Zn6O7H7/Cu(111) model whose CO2 hydrogenation overall energy barrier is only 1.05 eV (HCOO*->H2COOH*), much lower than ZnCu(211) (1.49 eV). It should be noted that due to the complexity of the potential energy surface (PES), the structures of ZnOxHy clusters on Cu surfaces are not explored systematically yet and thus the reported energetics on the manually constructed ZnOxHy clusters may not be representative.

To date, it is apparent that the catalytic active site of CZA catalyst, although still in debate, should involve low-coordinated Cu sites. The presence of Zn, as both CuZn alloy and ZnOH are likely forms, at least helps to stabilize the active site. The advent of advanced characterization and theoretical methods has brought the understanding of active sites much closer to the truth.

4. Cu SACs

Cu SACs are promising low-temperature catalysts for CO2 hydrogenation with high selectivity towards desirable products. Table 2 summarizes the recent advances in Cu SACs, highlighting the Cu coordination environment, valence state, reaction intermediates, and the computed reaction barriers, if available. As shown, three types of elements, namely O, N, and C, were explored as the anionic coordination, which can alter the valence state of Cu and also the product selectivity.

Entries 1-4 in Table 3 exhibit an interesting trend in Cu SAC, that is, methanol selectivity decreases with the increase of Cu-O coordination number. For example, Chai et al.\textsuperscript{13} reported the 89.5% selectivity towards methanol on a faujasite-encaged mononuclear Cu center catalyst that has a higher [CuO3.8] coordination environment with a Cu valence state of +2 (Table 2, entry 1). Wu et al.\textsuperscript{53} conducted a study on Cu1/ZnO catalysts and found that CO2 hydrogenation to methanol had a selectivity of 99.1% with Cu coordination of [CuO3.5] and valence state of Cu\textsuperscript{+δ} (1<δ<2) (Table 2, entry 2). Interestingly, the study revealed that the presence of water at the optimal levels acts as an active chemical reagent, opening the reaction pathways of CO2 -> COOH -> HCOOH.

Table 2. The reaction and structure information of Cu SACs.

<table>
<thead>
<tr>
<th>Cu SAC</th>
<th>Temp. (K)</th>
<th>Product (Selectivity)</th>
<th>CN_{Cu}</th>
<th>Cu\textsuperscript{+δ}</th>
<th>Reaction intermediates</th>
<th>E\textsubscript{a} (eV)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu1@FAU zeolite</td>
<td>513</td>
<td>MeOH (89.5 %)</td>
<td>[CuO3.8]</td>
<td>+2</td>
<td>HCOO, HCOOH, CH3O</td>
<td>~2.30</td>
<td>13</td>
</tr>
<tr>
<td>Cu1/ZnO</td>
<td>443</td>
<td>MeOH (99.1 %)</td>
<td>[CuO3.8]</td>
<td>1&lt;δ&lt;2</td>
<td>COOH, CH3O</td>
<td>1.94</td>
<td>53</td>
</tr>
<tr>
<td>Cu1/amorphous-ZrO2</td>
<td>453</td>
<td>MeOH (100 %)</td>
<td>[CuO4]</td>
<td>+1.4</td>
<td>HCOO, CH3O</td>
<td>1.46</td>
<td>12</td>
</tr>
<tr>
<td>Cu1/Zr12-MOF</td>
<td>358</td>
<td>EtOH (&gt;99 %)</td>
<td>[CuO3]</td>
<td>+1</td>
<td>CHO, CH3O, CH3O</td>
<td>1.05</td>
<td>57</td>
</tr>
<tr>
<td>Cu1/C3N</td>
<td></td>
<td>HCOOH</td>
<td>[CuN3]</td>
<td></td>
<td></td>
<td>0.57</td>
<td>55</td>
</tr>
<tr>
<td>Cu1/C3N4</td>
<td></td>
<td>HCOOH</td>
<td>[CuN3]</td>
<td></td>
<td></td>
<td>0.86</td>
<td>56</td>
</tr>
<tr>
<td>Cu1/C3N4</td>
<td>423</td>
<td>CO (94.3 %)</td>
<td>[CuN3]</td>
<td>+1.64</td>
<td>COOH</td>
<td>0.86</td>
<td>57</td>
</tr>
<tr>
<td>Cu1/C3N4</td>
<td>423</td>
<td>MeOH (95.5 %)</td>
<td>[CuN3]</td>
<td>+1.05</td>
<td>HCOO, CH3O</td>
<td>1.47, 1.18</td>
<td>58, 59</td>
</tr>
</tbody>
</table>

Figure 5. The structure and catalytic performance of CO2 hydrogenation to methanol on Cu SAC supported on amorphous ZrO2 surface (CAZ-1). (a) The catalytic performance of CO2 conversion and selectivity. (b) The mean chemical valence of Cu\textsuperscript{+δ} species under in-situ test conditions detected by XANES spectra. (c) Fitting of k\textsuperscript{2}-weighted in-situ extended x-ray absorption fine structure (EXAFS) data. (d) The identified [CuO4] configuration from SSW-NN simulation. (e) Gibbs free energy profile of CO2 hydrogenation to CH3OH/CO. Reprinted with permission from ref. 12. Copyright 2022 Springer Nature.
Recently, CO\textsubscript{2} hydrogenation to methanol with 100% selectivity is achieved on an amorphous ZrO\textsubscript{2} surface (Cu\textsubscript{1}/ZrO\textsubscript{2}) Cu SAC, as shown by Zhao and colleagues\textsuperscript{12} (Table 2, entry 3). Not only the high selectivity, the catalyst also exhibits exceptional stability over 100 hours at 453 K reaction conditions (Figure 5a). The authors employed in-situ XANES and SSW-NN global PES exploration to identify the Cu coordination environment and found that the Cu single atom in the catalyst adopts a quasi-planar three-oxygen coordination and a valence state of +1.4, as depicted in Figure 5b-d. Furthermore, DFT calculations prove that the amorphous ZrO\textsubscript{2} plays a key role in stabilizing the Cu single atom. The formation of Cu SAC is exothermic on amorphous ZrO\textsubscript{2} but endothermic on ZrO\textsubscript{2} flat (111) and terrace (112) surfaces, indicating that the amorphous ZrO\textsubscript{2} support is instrumental in maintaining the high stability of the Cu atom. The CO\textsubscript{2} hydrogenation on the isolated Cu\textsuperscript{6+} cation site follows the CO\textsubscript{2} -> HCOO -> H\textsubscript{2}COO -> H\textsubscript{2}COOH -> H\textsubscript{2}CO pathway with the rate-determining step being the HCOO* species hydrogenation (Figure 5e). The calculated TOF for CO\textsubscript{2} hydrogenation to CH\textsubscript{3}OH on the isolated Cu\textsuperscript{6+} cation is approximately 2.89 h\textsuperscript{-1}, consistent with the experimental TOF of 1.37 h\textsuperscript{-1} and being about two orders of magnitude larger than the CO\textsubscript{2} hydrogenation to CO product (0.03 h\textsuperscript{-1}).

By coupling neighboring [CuO\textsubscript{2}]\textsuperscript{−}, CO\textsubscript{2} hydrogenation can also produce ethanol with high selectivity, as shown by An et al.\textsuperscript{54} (Table 2, entry 4). They synthesized Cu single atoms at a [CuO\textsubscript{2}] coordination supported on a Zr\textsubscript{12} cluster in a metal-organic framework (MOF). With the assistance of a Cs\textsuperscript{+} alkali cation, the catalyst exhibited >99% selectivity towards EtOH in tetrahydrofuran solution at 358 K. The proposed mechanism involved the coupling of CHO/CH\textsubscript{3}O on two cooperative Cu\textsuperscript{+1} sites for ethanol synthesis.

Compared to the common [CuO\textsubscript{2}], the [CuN\textsubscript{3}] and the [CuC\textsubscript{6}] patterns in Cu SACs are much less reported in the literature. The DFT calculations first reveal the low reaction barriers (< 0.9 eV) for CO\textsubscript{2} hydrogenation to HCOOH on the [CuN\textsubscript{3}] pattern (Table 2, entries 5-8).\textsuperscript{55-59} The energy barrier on the [CuC\textsubscript{6}] pattern is higher than that on the [CuN\textsubscript{3}] pattern, but still lower than that on the [CuO\textsubscript{2}] pattern (Table 2, entry 9).\textsuperscript{58,59} This suggests that the [CuN\textsubscript{3}] and [CuC\textsubscript{6}] sites may exhibit even higher CO\textsubscript{2} hydrogenation activity than the [CuO\textsubscript{2}] sites. Indeed, Yang et al.\textsuperscript{57} demonstrated the high selectivity and activity of a C\textsubscript{3}N\textsubscript{4}-supported Cu SAC with [CuN\textsubscript{3}] and [CuN\textsubscript{3}] coordinations for CO\textsubscript{2} hydrogenation at low temperatures (< 150 °C). The [CuN\textsubscript{3}] site with the valence state of Cu\textsuperscript{+1.05} favors producing methanol via the formate pathway. This catalyst achieves a methanol selectivity of 95.5% at a CH\textsubscript{3}OH productivity of 4.2 mmol g\textsuperscript{-1} h\textsuperscript{-1} (Table 2, entries 7 and 8), which surpasses that of the state-of-the-art CZA catalyst by 3.2 times (1 mmol g\textsuperscript{-1} h\textsuperscript{-1}). Overall, the Cu SAC exhibits excellent methanol selectivity in CO\textsubscript{2} hydrogenation, but the conversion rate is still too low due to the low concentration of active site. New synthetic approaches are pursued to precisely disperse Cu single sites and inhibit the subsequent catalyst sintering.

### 5. Supported/confined Cu nanocluster

Utilization of metal clusters is a common strategy to enhance catalytic performance, not only because of the large surface area of metal particles but also due to the availability of low-coordinating surface atoms. For CO\textsubscript{2} hydrogenation, theoretical calculations indeed show that Cu clusters possess a lower activation barrier of 1.18 eV for formate formation.\textsuperscript{60} In practice, it is a major concern on how to stabilize these Cu nanoclusters to achieve long-term catalyst stability.

Various supports, such as SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, ZrO\textsubscript{2}, and CeO\textsubscript{2}, have been tested and demonstrated to have good catalytic performances. The newly-formed Cu-O bonds were detected, which leads to the electron transfer between Cu and supports, giving rise to various ionic Cu species, including Cu\textsuperscript{2+}, Cu\textsuperscript{+}, and Cu\textsuperscript{0} that are coexisting with Cu\textsuperscript{6+} of nanoparticles. It was believed that Cu\textsuperscript{0} is responsible for dissociating H\textsubscript{2}, while Cu\textsuperscript{+} polarizes the C-O bond to promote intermediate conversion. The product selectivity can thus be tuned by adjusting the ratio of Cu\textsuperscript{6+}/Cu\textsuperscript{0}.\textsuperscript{61-63} For example, Yu et al.\textsuperscript{64} demonstrated that a Cu cluster catalyst supported on inert SiO\textsubscript{2} prepared using flame spray pyrolysis, results in five times more Cu\textsuperscript{+} species than the traditional catalyst made using ammonia evaporation, and increases the methanol selectivity by inhibiting CO desorption and promoting CO* hydrogenation to CH\textsubscript{3}OH. DFT calculations by Sun et al.\textsuperscript{65} also showed that CO adsorption on Cu\textsuperscript{+} sites is stronger than that on Cu\textsuperscript{0}, and CO can be further hydrogenated to CHO\textsuperscript{+} species.

![Figure 6](Image)

**Figure 6.** Adsorption energies (ΔE\textsubscript{ads} in kJ/mol) of CO\textsubscript{2} at different Cu/Uio-66-a interface sites. Reprinted with permission from ref. 72. Copyright 2020 Springer Nature.
The support may also participate in the reaction cycle by acting as the reaction site for key elementary steps. For the Cu/ZnO catalyst, Valant et al. investigated the effect of different Zn content on CO₂ hydrogenation and found that the catalyst with Zn:(Zn+Cu) = 0.62 shows the highest methanol activity of 4.6 mol h⁻¹ kg⁻¹ at 523 K. The adsorbed H amount on ZnO shows a volcano-like profile against the Zn:(Zn+Cu) content, consistent with the activity variation, pointing to the synergetic effect between Cu and ZnO. Song et al. unveiled the remarkable activity (11.3 %) and methanol STY (242 gCH₃OH kg⁻¹ cat⁻¹ h⁻¹) of 8 wt% Cu/ZnAl₂O₃ at 220 °C and 3 MPa, far surpassing that of conventional 8 wt% Cu/ZnO/Al₂O₃ composite oxides (6.8 % for CO₂ conversion and 144 gCH₃OH kg⁻¹ cat⁻¹ h⁻¹ for methanol yield). They believed that the ZnAl₂O₃ dispersed the Cu cluster with a small particle size of ~3.2 nm, quite smaller than that on ZnO/Al₂O₃ (~6.4 nm). And the higher H₂ dissociation ability on ZnAl₂O₃ strongly enhanced the CO₂ conversion and methanol yield. The Cu/ZrO₂ catalyst has been widely reported with high methanol yield, where ZrO₂ can facilitate the formation and transformation of formate, thereby enhancing methanol synthesis. Especially, the crystalline phase of ZrO₂ can significantly affect the catalytic performance. As reported by Tada et al., the active sites on Cu/a-ZrO₂ (a:- amorphous) with TOF of 29-39 h⁻¹ were more suitable for CO₂-to-methanol than those on Cu/t-ZrO₂ (t:- tetragonal) with TOF of 16-23 h⁻¹ and Cu/m-ZrO₂ (m:- monoclinic) with TOF of 6-8 h⁻¹.

Confining Cu nanocluster in small cages is another approach to stabilizing nanoparticles and achieving high catalytic performance. Zhu et al. have demonstrated that the Cu nanocluster encapsulated into MOF material with Zr₆ oxide nodes shows a high methanol activity. By subtly tuning the Zr-O-Cu interface, it is found that the Zr-O-Cu interface is at least part of the active site that strongly adsorbs CO₂. As illustrated in Figure 6, the binding of CO₂ is not energetically favored on the Cu metal particle with slightly positive adsorption energy. The adsorption of CO₂ to the O²⁻ or Zr⁺⁺⁻O⁻ sites of the Zr₆O₈ node to form a bidentate or tridentate carbonate is considerably stronger, resulting in adsorption energies of ~42.7 and ~51.0 kJ/mol, respectively. The adsorption of CO₂ at the Cu-Zr⁺⁺ interfacial sites is significantly stronger (~80.8 kJ/mol) than the adsorption on the Cu nanoparticles and ZrO₂ nodes. Cui et al. also reported a series of zeolite-fixed Cu/ZnO/Na-ZSM-5 catalysts. The ultrasmall Cu/ZnO nanoparticles (~2 nm) in Na-ZSM-5 zeolite exhibit the space-time yield of methanol of 44.88 gCH₃OH g⁻¹ Cu⁻¹ h⁻¹, much more efficient than the supported Cu/ZnO/Na-ZSM-5 catalyst (13.32 gCH₃OH g⁻¹ Cu⁻¹ h⁻¹) and industrial Cu/ZnO/Al₂O₃ catalyst (8.46 gCH₃OH g⁻¹ Cu⁻¹ h⁻¹) under identical conditions. The zeolite was suggested to prevent the separation of Cu-ZnO interfaces. Ding et al. prepared a high-performance Cu@Na-Beta catalyst which shows a high ethanol yield of ~14% at 300 °C (~12,000 mL g⁻¹ cat⁻¹ h⁻¹), and 2.1 MPa, corresponding to a space-time yield of ~398 mg g⁻¹ cat⁻¹ h⁻¹. They proposed the reaction key step as the CO₂⁺ reacting with the surface methyl species at step sites of Cu nanoparticles to form CH₃COO⁺, which finally leads to ethanol after the hydrogenation steps.

The supported/confined Cu nanocluster offers convenient ways to access rich chemical environments of Cu, leading to low-coordination Cu, positively charged Cu⁴⁺ and different interface-contacted Cu. While more adjustable variables in synthesis enable the fine tune of the catalytic performance for catalytic reactions such as CO₂ hydrogenation, it becomes increasingly difficult to resolve the catalytic active site and understand the catalytic mechanism. The higher yield and the desirable selectivity continue to be the main goals in this area of catalysis research.

6. Bimetallic Cu-based and high entropy alloy catalyst

Introducing other transition metal components into Cu can significantly modify the electronic and geometric structures of the catalyst and thus alter the catalytic performance. Table 3 summarizes the catalytic performance of representative Cu-based bimetallic catalysts and high entropy alloys (HEA) catalysts. At elevated temperatures (mostly 500~700 K) and pressure (mostly 1~5 MPa), the main products of these catalysts span a large range, including not only common CO and CH₃OH but also CH₄, long-chain hydrocarbon (HC) and even alcohols.

CO₂ hydrogenation on the Pd-Cu system produces methanol with CO byproduct. Song et al. investigated an amorphous silica-supported Pd-Cu catalyst with a Pd/(Pd+Cu) ratio of 0.25-0.34 and found that it exhibits twice the methanol selectivity compared to the sum of the two corresponding monometallic catalysts. Further screening of catalyst supports led to an improved methanol selectivity of 44.6 % on the Pd-Cu/TiO₂ZrO₂O₃ catalyst. Catalyst characterizations by using X-ray diffraction (XRD) and TEM confirm the formation of a Pd-Cu alloy nanoparticle comprising

![Figure 7](image_url)
Cu-Ni alloys can catalyze CO$_2$ hydrogenation to CO$_2$, CO, CH$_4$, and CO$_2$ dissociation has a lower energy barrier of 1.30 eV on Ni-annular dark-field scanning transmission electron microscopy derived catalyst for CO$_2$ hydrogenation to methane, achieving selectivity above 98% and CO$_2$ conversion up to 86%. XRD and XANES suggest the formation of Cu-Ni alloy during the reduction step. Furthermore, compared with Cu-free catalyst, promotion

### Table 3. Catalyst composition, reaction conditions and catalytic performance of various multi-metallic catalysts for CO$_2$ hydrogenation.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Active Site</th>
<th>Alloy Composition</th>
<th>Temp</th>
<th>Pressure</th>
<th>Conversion</th>
<th>Product (Selectivity)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuPd</td>
<td>Pd-Cu/SiO$_2$</td>
<td>Cu:Pd=0.34:0.66</td>
<td>523 K</td>
<td>4.1 Mpa</td>
<td>6.60 %</td>
<td>CO (66 %)</td>
<td>14</td>
</tr>
<tr>
<td>CuPd</td>
<td>Pd-Cu/TiO$_2$Zr$_2$O$_5$</td>
<td>Cu:Pd =3:1</td>
<td>523 K</td>
<td>4.1 MPA</td>
<td>10.10 %</td>
<td>CO (55.4 %)</td>
<td>78</td>
</tr>
<tr>
<td>CuPd</td>
<td>1Pd-10Cu/CeO$_2$</td>
<td>Cu:Pd = 1:0.06</td>
<td>543 K</td>
<td>3 MPA</td>
<td>17.8 %</td>
<td>CH$_4$ (23.7 %)</td>
<td>75</td>
</tr>
<tr>
<td>CuNi</td>
<td>Ni-in-Cu</td>
<td>Cu:Ni = 4.14:1</td>
<td>673 K</td>
<td>0.1 Mpa</td>
<td>26 %</td>
<td>CO (&gt;99.9 %)</td>
<td>81</td>
</tr>
<tr>
<td>CuNi-rGO</td>
<td>Cu:Ni = 2:1</td>
<td>498 K</td>
<td>4.0 Mpa</td>
<td>7.87 %</td>
<td>CH$_3$OH (98.7 %)</td>
<td>82</td>
<td></td>
</tr>
<tr>
<td>Cu-Ni/CeO$_2$-nanotubes</td>
<td>Cu:Ni = 2:1</td>
<td>533 K</td>
<td>4 MPA</td>
<td>17.8 %</td>
<td>CH$_3$OH (76 %)</td>
<td>84</td>
<td></td>
</tr>
<tr>
<td>Cu-Ni/MgAl$_2$O$_4$</td>
<td>Cu:Ni = 15.5:1</td>
<td>623 K</td>
<td>~</td>
<td>86 %</td>
<td>CH$_4$ (&gt;98 %)</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>CuFe</td>
<td>sp-CuFeZn</td>
<td>Cu:Fe = 15.9:5.7</td>
<td>613 K</td>
<td>3.0 MPA</td>
<td>33.40 %</td>
<td>CO (18 %)</td>
<td>18</td>
</tr>
<tr>
<td>CuFe</td>
<td>im-CuFeZn</td>
<td>Cu:Fe = 15.7:5.7</td>
<td>613 K</td>
<td>3.0 MPA</td>
<td>28.60 %</td>
<td>CO (26.5 %)</td>
<td>18</td>
</tr>
<tr>
<td>CuFe</td>
<td>Cs-Cu$_3$Fe$<em>2$Zn$</em>{1.0}$</td>
<td>Cu:Fe = 28.9:35.7</td>
<td>603 K</td>
<td>5.0 MPA</td>
<td>36.60 %</td>
<td>CO (~20 %)</td>
<td>88</td>
</tr>
<tr>
<td>CuFe</td>
<td>4.6K-Cu-Mg-Zn-Fe</td>
<td>Cu:Fe=1:0.98</td>
<td>593 K</td>
<td>5 MPA</td>
<td>30.40 %</td>
<td>C$_2$H$_4$ (15.7 %)</td>
<td>89</td>
</tr>
<tr>
<td>CuFe</td>
<td>Fe-Cu-K</td>
<td>Cu:Fe = 8.6:69.8</td>
<td>573 K</td>
<td>2.5 MPA</td>
<td>35 %</td>
<td>CO (30.6 %)</td>
<td>16</td>
</tr>
<tr>
<td>CuFeO$_2$-24</td>
<td>Cu:Fe = 1:1</td>
<td>573 K</td>
<td>1 MPA</td>
<td>16.70 %</td>
<td>CO (31.4 %)</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>HEA</td>
<td>CoNiCuRuPd/TiO$_2$</td>
<td>Co:Ni:Cu:Ru:Pd=1:1:1:1</td>
<td>673 K</td>
<td>0.1 MPA</td>
<td>~46 %</td>
<td>C$_3$H$_8$ (68.3 %)</td>
<td>92</td>
</tr>
<tr>
<td>HEA</td>
<td>Zr$<em>{0.3}$(NiFeCuMnCo)$</em>{0.7}$O$_x$</td>
<td>Zr:Ni:Fe:Cu:Mn:Co=5:1:1:1:1</td>
<td>673 K</td>
<td>0.1 MPA</td>
<td>~29 %</td>
<td>CO (90 %)</td>
<td>93</td>
</tr>
<tr>
<td>HEA</td>
<td>Co$_2$MnNiCuZnO$_x$</td>
<td>Cu:Co:Ni=1:3:1</td>
<td>773 K</td>
<td>0.1 MPA</td>
<td>48 %</td>
<td>CO (94 %)</td>
<td>94</td>
</tr>
</tbody>
</table>

bcc PdCu and fcc PdCu$_3$ phases. Nie et al. suggested that the catalytically active site is the bcc PdCu (111) surface with unsaturated Pd, as shown in Figure 7a. The reaction proceeds with water-assisted through a formate pathway at an overall Gibbs energy barrier of 1.23 eV, which is more active than the fcc PdCu$_3$ (111) surface. Microkinetics simulations show that CO formation from CO$_2$ through the r-WGS pathway is faster than CH$_3$OH synthesis, consistent with the experimental results of a high CO selectivity (>70%).
with Cu strongly increased the number of medium-strength basic sites revealed by CO2 temperature programmed desorption, which is crucial for methanation.

Catalysts with Cu and Fe can lead to a distribution of multi-carbon products in CO2 hydrogenation. Fe alone serves as a famous Fischer-Tropsch catalyst that converts CO to hydrocarbon, and its combination with Cu allows direct conversion of CO2 to multi-carbon product. Their product and selectivity are listed in Table 3. For example, Si et al.18 developed a FeCu nanoalloy catalyst supported on ZnO by a sputtering method (sp-CuFeZn), which demonstrated a high paraffin selectivity of 63.5% (containing ~14% of CH4). In-situ XRD reveals that in sp-CuFeZn the metal mainly exists as FeCu4 nanoalloy under the reaction conditions. Hwang et al.16 synthesized a Fe-Cu-K catalyst that exhibited superior selectivity towards liquid hydrocarbons (50.7% toward C5+, hydrocarbons, 72.7% toward olefin), with a 1.7-fold increase in CO2 conversion and higher chain growth probability compared to the Fe-K catalyst. The observed phases include Cu-Fe alloy, Fe3O4, and a small amount of iron carbide (Fe3C) after the reaction.

Theoretical calculations have been utilized to provide insights into the activity of Cu-Fe alloy. Nie et al.90,91 utilized Fe(100) and Cu-alloyed Fe(100) to investigate the reaction mechanism of CO2 hydrogenation towards C1 and C2 hydrocarbons. On the Cu-alloyed Fe(100) surface, the adsorption strength of CO2 decreases as the surface Cu coverage increases, increasing the CO2 dissociation barrier.91 At medium Cu coverage (θ = 0.4 ML), the CO2 hydrogenation to HCOO* occurs with a low hydrogenation barrier of 0.39 eV. The HCOO* species then undergoes a series of steps, including HCOO* - HCOOH* - HCO* - CH* - CHCH* - CH2CH* - CH2CH2*, to produce ethylene with a low energy barrier of 1.27 eV (Figure 7b). Since these theoretical studies generally utilize single-crystal surfaces, the active site of Cu-Fe catalysts requires further detailed characterization.

While HEA emerges as a new direction in catalysis, several Cu-based HEA catalysts have also been developed for CO2 hydrogenation. Mori et al.32 synthesized a TiO2 supported CoNiCuRuPd nanoparticle catalyst, which is found to be both active and extremely durable on CO2 hydrogenation. The main product lead to CH4 (selectivity 68.3 %) and CO (31.7 %) at 673K, 1 bar with a conversion of ~46 %, which retained 96% of its original activity after 72 h. Hou et al.90 report a high entropy cubic Zr0.5(NiFeCuMnCo)0.5Ox, where configuration entropy lead to observation of in situ reversible exsolution-dissolution of supported metallic species in multi redox cycles. In CO2 hydrogenation, the CO2 conversion is 29% and CO selectivity is over 90%, with no obvious activity loss during 500 h reaction, affording ultrahigh thermal stability. It is worth noting that although the HEA catalysts do not show the desirable selectivity to high-value products (other than CO and CH4), their ultrahigh thermal stability in long-term CO2 hydrogenation may provide useful hints to improve catalyst durability in general. As experimental reports of HEA’s applications in CO2 hydrogenation are limited, more research work are needed to identify how Cu cooperates with other metals during the HEA catalysis.

In general, Cu-based multi-metallic alloys feature the ability of making diverse products, but the activity and selectivity are still not satisfactory to meet the requirement of the industrial application. To optimize the catalyst performance, more fundamental researches are required in probing the active site structure and resolve the reaction intermediates during CO2 hydrogenation.

7. Perspectives

This perspective provides an overview of the current understanding of active sites in copper-based catalysts for CO2 hydrogenation, including commercial CZA, Cu SACs, supported/confined Cu clusters, and Cu-based alloy catalysts. Generally speaking, despite the variation of the valence state and the coordination environment of Cu, the CO2 hydrogenation main product of a monometallic Cu catalyst, e.g. CZA, Cu SACs, supported/confined Cu clusters, is either CO or methanol. Once the second metal is introduced to form the Cu-X alloy catalyst, the CO2 hydrogenation product can switch to long-chain hydrocarbons such as alkanes and olefins. Therefore, how to improve the catalysts’ selectivity and long-term stability is the general concern in research, which requires a deep understanding of the active sites and reaction mechanisms. There are still many challenges in the field and the representatives are highlighted as follow.

The SMSI effect observed during CZA catalyst activation is long believed to be the key reason for creating the active site and resulting in the high activity of the CZA catalyst. There is a growing interest in the in-situ atomic structure of ZnO/H2 on Cu surfaces. As mentioned in Section 3, the traditional techniques of structure characterization meet great difficulties due to the essentiality of reaction conditions (H2/CO pressure) and the great complexity of the potential energy surface.

The state-of-the-art machine-learning atomic simulations emerge as a promising approach to determining the overlayer structure. Recently, we utilized the G-NN potential based grand canonical global search method, namely automatic search of optimal phase (ASOP) to explore stable ZnO/H2/Cu(111) structures.

Figure 8a and b plot the PES of ZnO/H2/Cu(111) at typical reaction conditions (H2/CO pressure) and the great complexity of the potential energy surface.
conditions (500 K, $p_{\text{H}_2}=40 \text{ bar, } p_{\text{CO}}=p_{\text{CO}_2}=10 \text{ bar}$), where the $x$- and $y$-axes are the coverage of O and Zn/H and the contour is the free energy of the minimum from G-NN. The figure contains 1751 minimum structures at different periodic supercells of Cu(111) ($n_{\text{cell}}=4~12$) with varied ZnO$_x$H$_y$ composition (θ$_{\text{Zn}} = x/n_{\text{cell}} = 0~1$, the same for θ$_{\text{O}}$ and θ$_{\text{H}}$). It shows that besides clean Cu and CuZn surface alloy (where θ$_{\text{Zn}} \approx 0$), a stable region locates where the coverage is θ$_{\text{Zn}}$: θ$_{\text{O}}$: θ$_{\text{H}} \approx 1:1:1$. After further validation by DFT for low-lying minima, a number of energetically nearly-degenerate most stable structures are identified. The most stable one (GM) is Zn$_{6}$O$_{8}$H$_{8}$/Cu(111)-(2 × 3), whose free energy is $-0.043 \text{ eV per Cu(111) unit cell}$, being more stable than clean Cu(111) and bulk ZnO. Many other structures with similar energy are available, including Zn$_{6}$O$_{8}$H$_{8}$/Cu(111)-(2 × 3) (note as I, free energy $-0.038 \text{ eV / unit cell}$), Zn$_{6}$O$_{8}$H$_{8}$/Cu(111)-(2 × 3) (note as II, free energy $-0.029 \text{ eV / unit cell}$), as well as the Zn$_{2}$O$_{2}$H$_{2}$/Cu(111)-(√3 × √7) (note as III, free energy $-0.042 \text{ eV/unit cell}$). Apparently, these structures share the similar [-Zn-OH-Zn-] repeating unit and the multiple degenerate structures suggest the amorphous nature of the ZnO$_x$H$_y$ overlayer on the Cu(111) surface (Figure 8c). Further work is required to clarify the ZnO$_x$H$_y$ structures on the stepped Cu surfaces and determine the CO$_2$ hydrogenation mechanism over these overlayer structures.

In addition, the role of the Al$_2$O$_3$ component in the CZA catalyst needs to be revisited. While Al$_2$O$_3$ was traditionally viewed as a support material, it may still act as an active component in methanol synthesis. In particular, the presence of ZnAl$_2$O$_4$ spinel has been mentioned in recent literature as the factor promoting CO hydrogenation.96–97

For Cu SAC catalyst, the low conversion rate (for example, < 2%12,59) limits its practical applications, which calls for increasing the metal loading and the concentration of active Cu SAC sites. Moreover, as [Cu$_n$] active site has shown lower reaction barriers, it is fascinating to increase the concentration of [Cu$_n$] active sites by immobilizing Cu SACs on nitrides such as GaN or Ta$_2$N$_3$ which may achieve better catalysis performance for CO$_2$ hydrogenation than [CuO$_n$] and [Cu$_n$] active sites.

For the supported/confined Cu cluster catalyst, optimizing the Cu-oxide interface is an effective approach to improving the activity of CO$_2$ hydrogenation. Recent studies have shown that the inverse oxide/metal configuration can enhance interfacial reactivity in well-defined CeO$_x$/Cu(111), ZnO/Cu(111), and ZrO$_x$/Cu models used as catalysts for the water-gas shift and methanol synthesis reactions.98–100 In these models, the oxide species are grown as a thin layer on top of the copper surface, creating an interface that promotes catalytic activity by improving electron transfer and adsorption of CO$_2$ and H$_2$ molecules. The active site structures for these inverse catalysts are however unclear.

The solving of the above challenges in the future should be benefited greatly from the rapid progress of machine learning methodology and artificial intelligence (AI) applications to catalysis. First, machine learning atomic simulations that can speed up significantly the complex PES exploration are powerful new tools to identify unknown structures,72 and to search for unknown reactions.25,101 As practiced by our group using SSW-NN simulations in recent years. By combining these two features of SSW-NN, it is possible to resolve the active site center from first principles. Second, machine learning techniques hold great promise to guide the design of new materials/catalysts. A high-throughput screening scheme can be built via machine learning database of materials with essential catalytic properties and then utilized to predict the activity. Recent years have seen efforts to establish the database for key catalytic properties,102 such as the adsorption energy of key intermediates, the morphology and acidity of zeolites.103 These approaches should be possible to apply in the design of HEA (Cu, Co, Ni, Zn, and Sn) catalyst for CO$_2$ hydrogenation.104,105

We note that electrochemical CO$_2$ hydrogenation has attracted more and more attention in recent years, which is not the focus of the current perspective. There are many interesting progresses. For example, the electrochemical C-N coupling of CO$_2$ and nitrogenous small molecules (e.g. NO, NO$_2$) can simultaneously eliminate greenhouse gas emissions and environmental pollutants;106 the CO$_2$ electrochemical reduction on Cu-based catalyst can produce other high-value products (e.g. ethylene or ethanol) at ambient conditions.107,108 These new reaction routes together with the thermal approach of CO$_2$ hydrogenation are going to be the key catalysis hotspots towards greener and more sustainable future.

Notes
The authors declare no competing financial interests.

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