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## Copper-based catalysts for CO<sub>2</sub> hydrogenation: a perspective on active sites

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CO<sub>2</sub> hydrogenation is regarded as a revolutionized field in heterogeneous catalysis, not only mitigating environmental problems caused by greenhouse gases but also producing valuable chemicals. This Perspective, going over both theoretical and experimental advances, aims to bridge Cu-based catalyst structures, the most important type of CO<sub>2</sub> hydrogenation catalyst, and their catalysis applications with varied activity and selectivity. We provide a systematic overview of the catalytic active sites, the reaction mechanism, and their impact on the reaction selectivity, stability, and activity for CO<sub>2</sub> hydrogenation. There is a particular focus on the nature of the industrial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst, where a large volume of literature is available exploring the reaction energetics on the possible reaction sites, including Cu metal, CuZn alloy, and ZnO<sub>x</sub>H<sub>y</sub> 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 changing the active sites. Our perspectives on the future research directions are finally provided, which should benefit the understanding of complex catalytic active sites and the design of better CO<sub>2</sub> hydrogenation catalysts.

### Broader context

CO<sub>2</sub> 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 Cu-based catalyst structures, the most important type of CO<sub>2</sub> hydrogenation catalyst, and their catalysis applications with varied activity and selectivity. We believe that this Perspective can arouse the interest of researchers in related fields and provide some directions for the future research in energy and environmental catalysis.

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## 1. Introduction

The conversion of carbon dioxide ( $\text{CO}_2$ ) 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  $\text{CO}_2$  and CO mixed gas has already been realized in industry through the low-pressure methanol synthesis process with a Cu-based catalyst, *i.e.* a Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> (CZA) catalyst.<sup>1,2</sup> The global CH<sub>3</sub>OH production *via* this technology is massive, reaching 106.89 million metric tons in 2021.<sup>3</sup> This industrial achievement demonstrates the great value of  $\text{CO}_2$  conversion in making renewable fuels and chemical compounds. In recent years, significant efforts have been devoted to developing new types of catalysts for  $\text{CO}_2$  hydrogenation (without the presence of CO), 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  $\text{CO}_2$  hydrogenation from a fundamental point of view.

The industrial CZA catalyst serves as a textbook example for understanding how  $\text{CO}_2$  is converted on Cu-based catalysts.<sup>4</sup> 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,<sup>5</sup> 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<sup>+</sup> in the ZnO lattice,<sup>6</sup> lattice strain,<sup>7</sup> Schottky junctions,<sup>8</sup> *etc.* However, most of these hypotheses lack clear support from the latest experimental and theoretical results. In 2012, Behrens *et al.*<sup>9</sup> 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 active sites: the CuZn surface alloy model,<sup>10</sup> in which Zn is reduced to form a CuZn alloy phase, and the ZnO<sub>x</sub>/Cu interface model,<sup>11</sup> 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 the CZA catalyst, the exploration of the possibility to apply Cu single-atom catalysts (SACs) as low-temperature  $\text{CO}_2$  hydrogenation catalysts is mainstream in heterogeneous catalysis.<sup>12,13</sup> 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,<sup>14</sup> Ni,<sup>15</sup> Fe,<sup>16–18</sup> *etc.*). Introducing a second metal into the Cu-catalyst can result in the formation of non-methanol products, such as methane,<sup>15</sup> long-chain hydrocarbons,<sup>18</sup> or ethanol.<sup>16</sup> For example, the Cu–Ni catalyst can lead to high selectivity on CH<sub>4</sub>,<sup>15</sup> while the Cu–Fe catalyst tends to produce long-chain hydrocarbons.<sup>17</sup> 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.*<sup>16</sup> in the Cu–Fe catalyst, although the CuFe alloy phase is regarded as the active site for the Cu–Fe bimetallic catalyst, FeO<sub>x</sub> and FeC<sub>x</sub> also exist in the catalyst and thus may still be the active centers.

With encouraging progress in Cu-based catalysts for  $\text{CO}_2$  hydrogenation achieved in recent years, we here aim to overview the current understanding of the active sites of different types of Cu-based catalysts, with a particular emphasis on the atomic structure as revealed by joint theoretical calculations and experimental characterization. This Perspective is organized as follows. The thermodynamics and reaction networks for  $\text{CO}_2$  hydrogenation are first summarized. This follows sequentially the recent advancements in probing the catalytic active sites using advanced theoretical and experimental techniques, including CZA catalysts, Cu SAC catalysts, and their closely related supported Cu cluster catalysts, and bimetallic Cu–M catalysts. Finally, an outlook for future research directions is provided.

## 2. Thermodynamics and the kinetics of $\text{CO}_2$ hydrogenation on Cu surfaces

$\text{CO}_2$  hydrogenation can in principle yield a diverse range of products, including primary reduction products (such as CO, HCOOH, and HCHO), alcohols (CH<sub>3</sub>OH and C<sub>2</sub>H<sub>5</sub>OH), and hydrocarbons (CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, and even long-chain alkanes). It is noteworthy that while methanol is a commonly targeted product in industrial  $\text{CO}_2$  hydrogenation, it is not the most thermodynamically favorable product at a typical operating temperature of 500 K. Fig. 1 illustrates the Gibbs free energy



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interests include methodology development for potential energy surface exploration, theory on heterogeneous catalysis, and machine-learning-based atomic simulation.

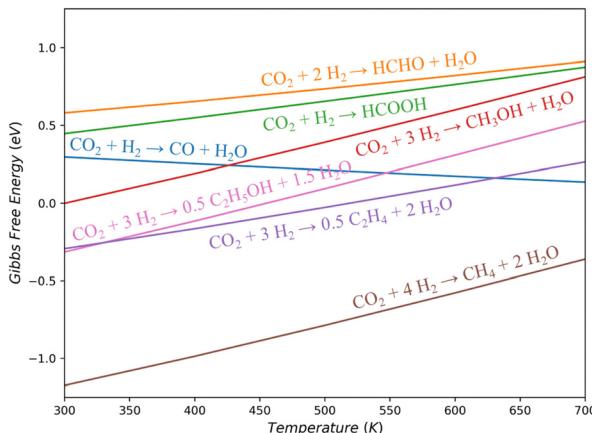


Fig. 1 Gas-phase Gibbs free energy variation against temperature for  $\text{CO}_2$  hydrogenation to low-carbon products. All gas pressures set to 1 bar.

changes ( $\Delta G$ ) for these gas-phase reactions.<sup>19</sup> It shows that CO and  $\text{CH}_3\text{OH}$ , the most frequently observed products, have similar  $\Delta G$  at 500 K (0.21 and 0.39 eV, respectively), both slightly above zero. When the feed gas is compressed to increase the input pressure the reaction can be driven forward, resulting in a more favorable equilibrium conversion of  $\text{CH}_3\text{OH}$  compared to the economically undesirable CO. However, the maximum one-pass conversion of  $\text{CH}_3\text{OH}$  is still limited to 15–35%,<sup>20</sup> which can be increased by decreasing the temperature and increasing the pressure. Consequently, the methanol synthesis industry tends to favor lower reaction temperatures as long as the reaction rate remains acceptable.

Products other than  $\text{CH}_3\text{OH}$  and CO are less frequently reported on Cu-based catalysts. HCOOH and HCHO are thermodynamically unfavorable than  $\text{CH}_3\text{OH}$  across the entire temperature range ( $\Delta G$  is 0.26/0.34 eV higher than that of  $\text{CH}_3\text{OH}$  at 500 K, respectively). They exhibit low selectivity, likely due to their instability and susceptibility to further hydrogenation into  $\text{CH}_3\text{OH}$ . Products like  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ , and  $\text{C}_2\text{H}_5\text{OH}$  are consistently thermodynamically more favorable than  $\text{CH}_3\text{OH}$  ( $\Delta G$  is 1.18/0.42/ 0.30 eV lower at 500 K), but the hydrocarbon and multi-carbon

products are rarely reported in the products using Cu-based catalysts. On Cu metal, a model system,  $\text{CO}_2$  hydrogenation only produces CO and  $\text{CH}_3\text{OH}$ .<sup>21</sup>

The answer to the conflict of product selectivity with thermodynamics preference lies in the reaction kinetics in catalysis. Fig. 2 summarizes the generally-regarded  $\text{CO}_2$  hydrogenation mechanism on Cu surfaces obtained from density functional theory (DFT) studies.<sup>22–27</sup> Three general findings are outlined in the following.

(i) A most-mentioned  $\text{CO}_2$  hydrogenation pathway to  $\text{CH}_3\text{OH}$  follows the sequence:  $\text{CO}_2^*$  (superscript \* indicates the adsorbed state)  $\rightarrow \text{HCOO}^*$   $\rightarrow \text{HCOOH}^*$   $\rightarrow \text{H}_2\text{COOH}^*$   $\rightarrow \text{HCHO}^*$   $\rightarrow \text{CH}_3\text{O}^*$   $\rightarrow \text{CH}_3\text{OH}^*$ , termed the formate pathway.<sup>22</sup> The rate-determining step occurs in the first half of the reaction before  $\text{CH}_2\text{O}$  formation, involving the hydrogenation of  $\text{CH}_x\text{O}_2$  ( $x = 0–3$ ) species, such as  $\text{CO}_2$  to  $\text{HCOO}^*$ ,  $\text{HCOOH}^*$  to  $\text{H}_2\text{COOH}^*$ , or  $\text{H}_2\text{COOH}$  to  $\text{HCHO}^*$ . If the overall barrier for the further hydrogenation of  $\text{HCOOH}^*$  and  $\text{HCHO}^*$  is not higher than that for the formation of  $\text{HCOO}^*$ , the reaction will show low product selectivity to HCOOH or HCHO, which is the case in most Cu surfaces. For example, the Gibbs free energy barriers on Cu(211) surfaces is 1.4 eV with the rate-determining steps (RDS) being  $\text{CO}_2$  and  $\text{HCOO}^*$  hydrogenation.<sup>25</sup>

(ii) Another mechanism for  $\text{CO}_2$  to  $\text{CH}_3\text{OH}$  is the reverse water-gas shift (r-WGS) coupling with CO hydrogenation.<sup>28</sup> In the pathway,  $\text{CO}_2$  is first hydrogenated to CO through  $\text{CO}_2^* \rightarrow \text{COOH}^* \rightarrow \text{CO}^*$ , termed the carboxyl pathway, and then CO\* is further hydrogenated to  $\text{CH}_3\text{OH}^*$  through  $\text{CO}^* \rightarrow \text{CHO}^* \rightarrow \text{HCHO}^* \rightarrow \text{CH}_3\text{O}^* \rightarrow \text{CH}_3\text{OH}^*$ , termed 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  $\text{CO}_2^* \rightarrow \text{COOH}^*$ , e.g.  $>1.8$  eV for Cu(111),<sup>22</sup> Cu(100)<sup>23</sup> and Cu(211).<sup>27</sup> Additionally,  $\text{COOH}^*$  is less stable than  $\text{HCOO}^*$  on Cu surfaces, leading to a lower rate of 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.<sup>29</sup> This is likely due to the high barrier associated

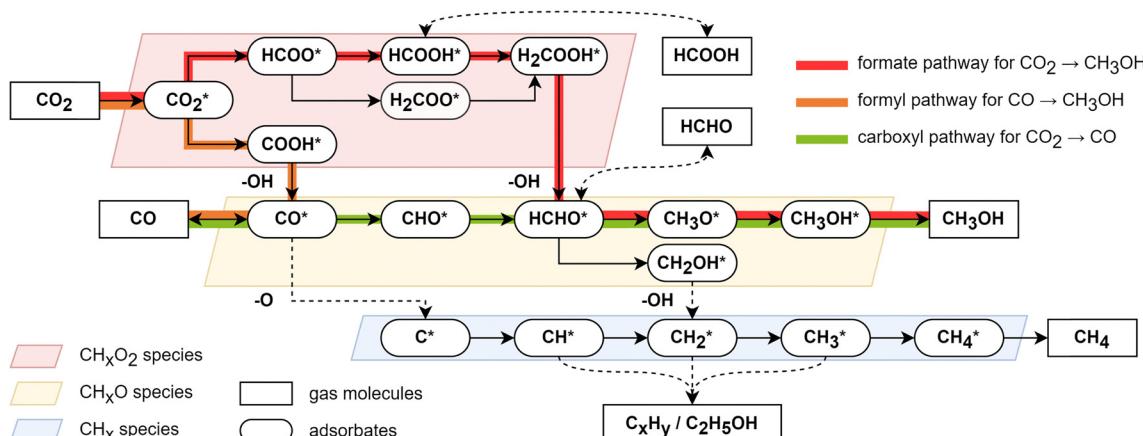


Fig. 2 The possible reaction network and reaction pathway on the Cu surface for  $\text{CO}_2$  hydrogenations.

**Table 1** The reaction and structure information of the Cu cluster and surface.  $E_a$  represents the overall barrier. RDS represents the rate determining steps

Cu surface	RDS	CN	$E_a$ (eV)	Ref.
Cu(111)	$\text{HCOO}^* \rightarrow \text{H}_2\text{COOH}^*$	9	1.27	22
Cu(100)	$\text{HCOO}^* \rightarrow \text{H}_2\text{COOH}^*$	8	1.25	23
Cu(110)	$\text{HCOO}^* \rightarrow \text{H}_2\text{COOH}^*$	7	1.19	23
Cu(111)	$\text{CO}_2 \rightarrow \text{HCOO}^*$	9	1.15	30
Cu(100)	$\text{CO}_2 \rightarrow \text{HCOO}^*$	8	1.03	30
Cu(111) point defect	$\text{CO}_2 \rightarrow \text{HCOO}^*$	8	1.02	30
Cu(100) point defect	$\text{CO}_2 \rightarrow \text{HCOO}^*$	7	0.92	30
Cu(211)	$\text{CO}_2 \rightarrow \text{HCOO}^*$	7	0.92	30

with the C–O bond breaking to produce  $\text{CH}_x$  ( $x = 0\text{--}4$ ) species, which is essential for subsequent C–C coupling.<sup>25</sup> The direct dissociation of  $\text{CO}^*$  to form  $\text{C}^*$  and  $\text{O}^*$ , known to be feasible on Fe catalysts, encounters a high energy barrier ( $>2$  eV) on Cu surfaces, making it unlikely to occur.<sup>22</sup> Another possible pathway of  $\text{CH}_x$  generation is *via* the  $\text{HCHO}^* \rightarrow \text{CH}_2\text{OH}^* \rightarrow \text{CH}_2^*$  route, but its overall barrier is higher than that of  $\text{HCHO}^* \rightarrow \text{CH}_3\text{O}^* \rightarrow \text{CH}_3\text{OH}$ , leading to a low selectivity.<sup>25</sup>

Quantitatively, the low coordination number (CN) of Cu (the number of Cu atoms neighboring the centering Cu) is generally more active in  $\text{CO}_2$  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,<sup>22,23,30</sup> 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  $\text{CO}_2$  hydrogenation, where the rate-determining step is the  $\text{HCHO}^* + \text{H}^*$  step.<sup>22,25</sup> To allow  $\text{CO}_2$  hydrogenation, the introduction of step and point defects is thus a must.<sup>25,30–32</sup> The Cu(211) surface exhibits a significantly lower Gibbs free barrier of 1.40 eV for methanol production. These findings indicate the importance of manipulating the surface structure for enhancing the catalytic activity of Cu-based catalysts in  $\text{CO}_2$  hydrogenation.

### 3. CZA industrial catalyst

As the active site of the CZA catalyst remains highly controversial, we first overview the basic facts of the CZA catalyst. The industrial CZA catalyst is prepared by the traditional co-precipitation method. The precipitate with a molar ratio of Cu:Zn:Al = 7:3:1 turns to composites containing at least nanoparticles (5–10 nm) of metallic Cu, wurtzite ZnO, and amorphous  $\text{Al}_2\text{O}_3$  after air calcination and  $\text{H}_2$  activation. When operated under conditions such as 500–550 K and 50–100 bar, the CZA catalyst exhibits high selectivity for methanol production (*e.g.*, 99.8%) and exceptional long-term stability (design life  $>3$  years).<sup>33</sup> It is worth noting that a mixed  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{H}_2$  feed gas, instead of pure  $\text{CO}_2$  or pure  $\text{CO}$  with  $\text{H}_2$ , is utilized in the fixed-bed catalysis, where the  $\text{CO}_2:\text{CO}$  ratio range is 0.5–4.<sup>1,34,35</sup> Interestingly, the isotopic-labeling experiments revealed that  $\text{CO}_2$  is the dominant carbon source for methanol production, accounting for more than 90% of the carbon in methanol.<sup>24</sup>

On the other hand, the CO-free  $\text{CO}_2/\text{H}_2$  feed gas leads to a more oxidizing atmosphere.

There are two main competing 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 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<sup>36</sup> or 0.22 ML<sup>25</sup>), but not enough to form a CuZn bulk alloy or metallic Zn. In experiments also high content of the CuZn surface alloy is observed under strong reduction conditions, *e.g.*, CO-free  $\text{CO}$  and  $\text{H}_2$  atmospheres.<sup>37–39</sup> Kuld *et al.*<sup>40</sup> found an increasing Zn coverage with an increasing  $\text{CO}/\text{CO}_2$  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.*<sup>41</sup> also found that the maximum turnover frequency (TOF) on a Zn deposited on a Cu(111) model catalyst with 0.19 ML Zn coverage was 10 times faster compared to that on a clean Cu(111) surface. While earlier DFT studies reported that the Zn-doped Cu(211) surface shows a lower energy barrier of  $\text{CO}_2$  hydrogenation to methanol than that without Zn doping, following the same formate pathway,<sup>9,24</sup> the later *ab initio* microkinetics study reveals a negative effect of Zn alloying on  $\text{CO}_2$  hydrogenation activity.<sup>42,43</sup>

Recently, we developed a microkinetic-guided machine learning pathway search (MMLPS) method to explore the reaction network for  $\text{CO}_2$  and CO hydrogenations on thermodynamically favorable Cu–Zn alloy surface structures.<sup>25</sup> Taking Cu(211) as an example, Fig. 3a plots 14 958 reaction pairs (IS, TS, FS) on the Cu(211) surface through automated reaction sampling based on global neural network potential (G-NN) calculations, from which the  $\text{CO}_2$  and CO hydrogenation reaction pathways are resolved and the reaction mechanism is identified to be the formate pathway rather than the r-WGS pathway for  $\text{CO}_2$  hydrogenation on the Cu(111) and Zn-alloyed Cu(211) surface (Fig. 3b). The key intermediates along the pathways on 0.11 ML and 0.22 ML Zn–Cu(211) surfaces are shown in Fig. 3c and d. Interestingly, we found that the Zn decorates at the step-edge of the Cu(211) surface with a coverage of up to 0.22 ML under reaction conditions, and the Zn–Zn dimeric site is thermodynamically unfavorable.  $\text{CO}_2$  and CO hydrogenations occur exclusively at the step-edge of the (211) surface with a Zn coverage of up to 0.11 ML, where the low coverage of Zn (0.11 ML) does not much affect the reaction kinetics (Fig. 3b), demonstrating no activity improvement on the CuZn surface alloy. The microkinetics simulations based on DFT calculation reproduced nicely the experimental finding that  $\text{CO}_2$  hydrogenation dominates methanol synthesis, instead of CO hydrogenation.

Another popular view proposes that Zn species form a  $\text{ZnO}_x(\text{H}_y)$ –Cu interface, where Zn atoms are primarily present as  $\text{ZnO}_x(\text{H}_y)$  clusters of layers on the Cu surface. It was once suggested that the reduced Zn ions migrate to the Cu surface and undergo re-oxidation, forming a few layers of  $\text{ZnO}_x$  on the Cu surface and leading to an SMSI effect.<sup>44</sup> This phenomenon



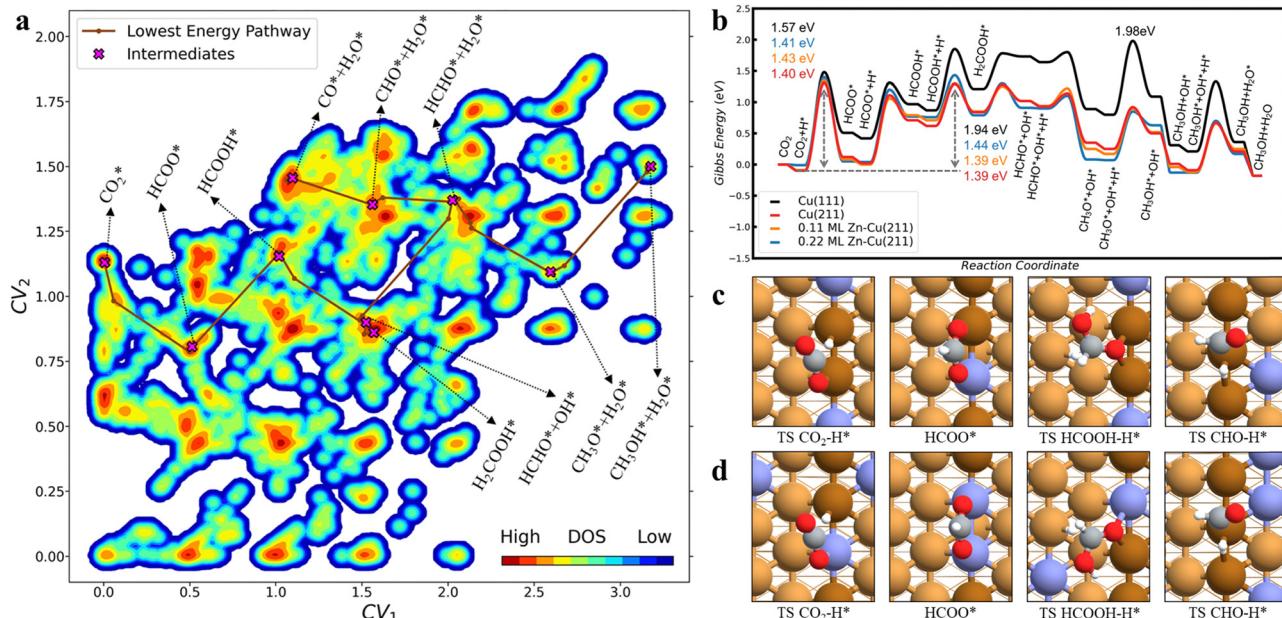


Fig. 3 (a) Contour plot for 14 958 reaction pairs (IS, TS, FS) obtained by MMLPS on the Cu(211) surface. The color indicates the occurrence frequency of the state in reaction pair collection (density of state, DOS). All structures are projected to the plot with two collective variables (CV). Key intermediates along the lowest-energy pathway are highlighted by brown lines. (b) CO<sub>2</sub> hydrogenation Gibbs energy profile on Cu(211) and Zn alloyed Cu(211) surfaces. (c) and (d) The structure of the key reaction step for CO<sub>2</sub> hydrogenation on (c) 0.11 ML Zn–Cu(211) and (d) 0.22 ML Zn–Cu(211). The color scheme for atoms is as follows: H: white; O: red; Cu: yellow; and Zn: blue. Reprinted with permission from ref. 25. Copyright 2022 American Chemical Society.

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 H<sub>2</sub> activation (Fig. 4).<sup>11</sup> This phenomenon was also observed by other research groups.<sup>9,45,46</sup> The presence of cationic Zn as the active site was also suggested by Laudenschleger *et al.*,<sup>47</sup> who conducted a high-pressure pulse experiment in which NH<sub>3</sub> is injected into a high-pressure methanol synthesis. They observed a temporary decrease in methanol yield due to NH<sub>3</sub> poisoning, but the co-fed C<sub>2</sub>H<sub>4</sub> hydrogenates to C<sub>2</sub>H<sub>6</sub> 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 CO<sub>2</sub> hydrogenation, which is poisoned by NH<sub>3</sub>. They also reported that the higher CO<sub>2</sub> content, a more oxidizing condition, may lead to more positively charged Zn on the Cu surface, resulting in more obvious NH<sub>3</sub> 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 ZnO<sub>x</sub>H<sub>y</sub> phase rather than the ZnO<sub>x</sub> phase. Beck *et al.*<sup>36</sup> first showed that the formation of active sites is influenced by the H<sub>2</sub> 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 H<sub>2</sub> pressure was kept beyond 1 bar. However, no significant changes were observed in the zinc (+2) oxidation state until 500 °C under 1 mbar H<sub>2</sub>. In addition, theoretical studies also found the strong adsorption of H on the ZnO<sub>x</sub> cluster supported on Cu(111), stabilizing the ZnO<sub>x</sub> cluster on Cu under the H<sub>2</sub>-rich reaction conditions.<sup>46,48–50</sup> The presence of H may further alter the reaction kinetics. Reichenbach *et al.*<sup>51</sup> showed that the energy barrier of CO<sub>2</sub> hydrogenation on Zn<sub>7</sub>O<sub>3</sub>/Cu(111) is 1.33 eV, which decreases to 1.30 eV when H adsorbs on the ZnO cluster. Kattel *et al.* proposed another Zn<sub>6</sub>O<sub>7</sub>H<sub>7</sub>/Cu(111) model whose CO<sub>2</sub> hydrogenation overall energy barrier is only 1.05 eV (HCOO<sup>\*</sup> → H<sub>2</sub>COOH<sup>\*</sup>), much lower than that of ZnCu(211) (1.49 eV).<sup>52</sup> It should be noted that due to the complexity of the potential energy surface (PES), the structures of ZnO<sub>x</sub>H<sub>y</sub> clusters on Cu surfaces are not explored systematically yet and thus the reported energetics on the manually constructed ZnO<sub>x</sub>H<sub>y</sub> clusters may not be representative.

To date, it is apparent that the catalytic active site of the CZA catalyst, although still in debate, should involve low-coordinated Cu sites. The presence of Zn, as both the 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.

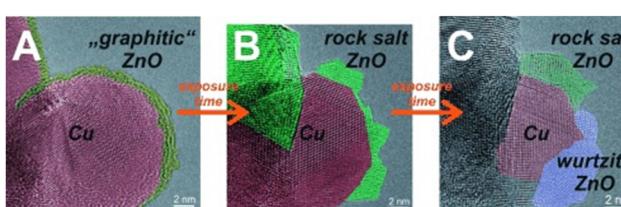


Fig. 4 (A)–(C) HRTEM images of Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> after different times of electron beam exposure. Red-colored sites correspond to Cu particles. Yellow indicates graphitic-like ZnO<sub>x</sub>. Green highlights rock salt ZnO, and blue regions correspond to the wurtzite ZnO structure. Reprinted with permission from ref. 11. Copyright 2015 John Wiley & Sons, Inc.

## 4. Cu SACs

Cu SACs are promising low-temperature catalysts for  $\text{CO}_2$  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 SACs, that is, methanol selectivity decreases with the increase of the Cu–O coordination number. For example, Chai *et al.*<sup>13</sup> reported 89.5% selectivity towards methanol on a faujasite-encaged mononuclear Cu center catalyst that has a higher  $[\text{CuO}_{3.8}]$  coordination environment with a Cu valence state of +2 (Table 2, entry 1). Wu *et al.*<sup>53</sup> conducted a study on  $\text{Cu}_1/\text{ZnO}$  catalysts and found that  $\text{CO}_2$  hydrogenation to methanol had a selectivity of 99.1% with Cu coordination of  $[\text{CuO}_{3.5}]$  and the valence state of  $\text{Cu}^{\delta+}$  ( $1 < \delta < 2$ ) (Table 2, entry 2).

Table 2 The reaction and structure information of Cu SACs

Cu SAC	Temp. (K)	Product (selectivity)	$\text{CN}_{\text{Cu}}$	$\text{Cu}^{\delta+}$	Reaction intermediates	$E_a$ (eV)	Ref.
1 $\text{Cu}_1@\text{FAU}$ zeolite	513	MeOH (89.5%)	$[\text{CuO}_{3.8}]$	+2	$\text{HCOO}$ , $\text{HCOOH}$ , $\text{CH}_3\text{O}$	~2.30	13
2 $\text{Cu}_1/\text{ZnO}$	443	MeOH (99.1%)	$[\text{CuO}_{3.5}]$	$1 < \delta < 2$	$\text{COOH}$ , $\text{CH}_2\text{O}$	1.94	53
3 $\text{Cu}_1/\text{amorphous-ZrO}_2$	453	MeOH (100%)	$[\text{CuO}_3]$	+1.4	$\text{HCOO}$ , $\text{CH}_3\text{O}$	1.46	12
4 $\text{Cu}_1/\text{Zr}_{12}\text{-MOF}$	358	EtOH (> 99%)	$[\text{CuO}_3]$	+1	$\text{CHO}$ , $\text{CH}_2\text{O}$ , $\text{CH}_3\text{O}$		54
5 $\text{Cu}_1/\text{C}_2\text{N}$		HCOOH	$[\text{CuN}_2]$		$\text{HCOO}$	0.57	55
6 $\text{Cu}_1/\text{C}_3\text{N}_4$		HCOOH	$[\text{CuN}_4]$		$\text{HCOO}$	0.86	56
7 $\text{Cu}_1/\text{C}_3\text{N}_4$	423	CO (94.3%)	$[\text{CuN}_3]$	+1.64	$\text{COOH}$		57
8 $\text{Cu}_1/\text{C}_3\text{N}_4$	423	MeOH (95.5%)	$[\text{CuN}_4]$	+1.05	$\text{HCOO}$ , $\text{CH}_3\text{O}$		57
9 $\text{Cu}_1/\text{graphine}$		HCOOH	$[\text{CuC}_3]$		$\text{HCOO}$	1.47, 1.18	58 and 59

Table 3 Catalyst composition, reaction conditions and catalytic performance of various multi-metallic catalysts for  $\text{CO}_2$  hydrogenation. HC represents hydrocarbon

Alloy	Active site	Alloy composition	Temp (K)	Pressure (Mpa)	Conversion (%)	Product (selectivity)	Ref.
CuPd	Pd–Cu/SiO <sub>2</sub>	Cu : Pd = 0.34 : 0.66	523	4.1	6.60	CO (66%) $\text{CH}_3\text{OH}$ (34%)	14
	Pd–Cu/Ti <sub>0.1</sub> Zr <sub>0.9</sub> O <sub>2</sub>	Cu : Pd = 3 : 1	523	4.1	10.10	CO (55.4%) $\text{CH}_3\text{OH}$ (44.6%)	78
	1Pd–10Cu/CeO <sub>2</sub>	Cu : Pd = 1 : 0.06	543	3	17.8	$\text{CH}_3\text{OH}$ (23.7%)	75
CuNi	Ni-in-Cu	Cu : Ni = 4.14 : 1	673	0.1	26	CO (> 99.9%)	81
	CuNi-rGO	Cu : Ni = 2 : 1	498	4.0	7.87	$\text{CH}_3\text{OH}$ (98.7%)	82
	Cu–Ni/CeO <sub>2</sub> -nanotubes	Cu : Ni = 2 : 1	533	4	17.8	$\text{CH}_3\text{OH}$ (76%) CO (~25%)	84
	Cu–Ni/MgAl <sub>2</sub> O <sub>4</sub>	Cu : Ni = 15.5 : 1	623	—	86	$\text{CH}_4$ (> 98%)	15
CuFe	sp-CuFeZn	Cu : Fe = 15.9 : 5.7	613	3.0	33.40	CO (18%) $\text{CH}_4$ (~ 14%) $\text{C}_{2+}$ paraffin (~ 49.5%) $\text{C}_{2+}$ olefin (15.2%)	18
	im-CuFeZn	Cu : Fe = 15.7 : 5.7	613	3.0	28.60	CO (26.5%) $\text{CH}_4$ (~ 10%) $\text{C}_{2+}$ paraffin (~ 10%) $\text{C}_{2+}$ olefin (46.1%)	18
	Cs–Cu <sub>0.8</sub> Fe <sub>1.0</sub> Zn <sub>1.0</sub>	Cu : Fe = 28.9 : 35.7	603	5.0	36.60	$\text{C}_{2+}\text{OH}$ (19.8%) CO (~ 20%) $\text{C}_{2+}$ alkane (~ 43%)	88
HEA	4.6K–Cu–Mg–Zn–Fe	Cu : Fe = 1 : 0.98	593	5	30.40	$\text{C}_{2+}\text{OH}$ (15.7%) CO (30.6%) $\text{C}_{2+}$ alkane (~ 30%)	89
	Fe–Cu–K	Cu : Fe = 8.6 : 69.8	573	2.5	35	$\text{C}_{2+}\text{C}_4\text{HC}$ (~ 26%) $\text{C}_{5+}\text{HC}$ (50.7%) $\text{C}_{2+}$ olefin (72.7%)	16
	CuFeO <sub>2</sub> -24	Cu : Fe = 1 : 1	573	1	16.70	CO (31.4%) $\text{C}_{5+}\text{HC}$ (44.5%)	17
Zr <sub>0.5</sub> (NiFeCuMnCo) <sub>0.5</sub> O <sub>x</sub>	CoNiCuRuPd/TiO <sub>2</sub>	Co : Ni : Cu : Ru : Pd = 1 : 1 : 1 : 1 : 1	673	0.1	~46	$\text{CH}_4$ (68.3%) CO (31.7%)	92
	Co <sub>3</sub> MnNiCuZnO <sub>x</sub>	Zr : Ni : Fe : Cu : Mn : Co = 5 : 1 : 1 : 1 : 1 : 1	673	0.1	~29	CO (90%)	93
		Cu : Co : Ni = 1 : 3 : 1	773	0.1	48	CO (94%)	94



Interestingly, the study revealed that water present at the optimal levels acts as an active chemical reagent, opening the reaction pathways of  $\text{CO}_2 \rightarrow \text{COOH} \rightarrow \text{HCOOH}$ .

Recently,  $\text{CO}_2$  hydrogenation to methanol with 100% selectivity was achieved on an amorphous  $\text{ZrO}_2$  surface ( $\text{Cu}_1/\text{ZrO}_2$ ) Cu SAC, as shown by Zhao and colleagues<sup>12</sup> (Table 2, entry 3). Not only a high selectivity, the catalyst also exhibits exceptional stability over 100 hours under 453 K reaction conditions (Fig. 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 Fig. 5b-d. Furthermore, DFT calculations prove that the amorphous  $\text{ZrO}_2$  plays a key role in stabilizing the Cu single atom. The formation of Cu SACs is exothermic on amorphous  $\text{ZrO}_2$  but endothermic on  $\text{ZrO}_2$  flat (111) and terrace (112) surfaces, indicating that the amorphous  $\text{ZrO}_2$  support is instrumental in maintaining the high stability of the Cu atom. The  $\text{CO}_2$  hydrogenation on the isolated  $\text{Cu}^{\delta+}$  cation site follows the  $\text{CO}_2 \rightarrow \text{HCOO} \rightarrow \text{H}_2\text{COO} \rightarrow \text{H}_2\text{COOH} \rightarrow \text{H}_2\text{CO} \rightarrow \text{H}_3\text{CO} \rightarrow \text{H}_3\text{COH}$  pathway with the rate-determining step being the  $\text{HCOO}^*$  species hydrogenation (Fig. 5e). The calculated TOF for  $\text{CO}_2$  hydrogenation to  $\text{CH}_3\text{OH}$  on the isolated  $\text{Cu}^{\delta+}$  cation is

approximately  $2.89 \text{ h}^{-1}$ , consistent with the experimental TOF of  $1.37 \text{ h}^{-1}$  and being about two orders of magnitude larger than the  $\text{CO}_2$  hydrogenation to the CO product ( $0.03 \text{ h}^{-1}$ ).

By coupling neighboring  $[\text{CuO}_3]$ ,  $\text{CO}_2$  hydrogenation can also produce ethanol with high selectivity, as shown by An *et al.*<sup>54</sup> (Table 2, entry 4). They synthesized Cu single atoms at a  $[\text{CuO}_3]$  coordination supported on a  $\text{Zr}_{12}$  cluster in a metal-organic framework (MOF). With the assistance of a  $\text{Cs}^+$  alkali cation, the catalyst exhibited  $>99\%$  selectivity towards EtOH in tetrahydrofuran solution at 358 K. The proposed mechanism involved the coupling of  $\text{CHO/CH}_3\text{O}$  on two cooperative  $\text{Cu}^{1+}$  sites for ethanol synthesis.

Compared to the common  $[\text{CuO}_x]$ , the  $[\text{CuN}_x]$  and the  $[\text{CuC}_x]$  patterns in Cu SACs are much less reported in the literature. The DFT calculations first reveal the low reaction barriers ( $<0.9 \text{ eV}$ ) for  $\text{CO}_2$  hydrogenation to  $\text{HCOOH}$  on the  $[\text{CuN}_x]$  pattern (Table 2, entries 5-8).<sup>55-59</sup> The energy barrier on the  $[\text{CuC}_x]$  pattern is higher than that on the  $[\text{CuN}_x]$  pattern, but still lower than that on the  $[\text{CuO}_x]$  pattern (Table 2, entry 9).<sup>58,59</sup> This suggests that the  $[\text{CuN}_x]$  and  $[\text{CuC}_x]$  sites may exhibit even higher  $\text{CO}_2$  hydrogenation activity than the  $[\text{CuO}_x]$  sites. Indeed, Yang *et al.*<sup>57</sup> demonstrated the high selectivity and activity of a  $\text{C}_3\text{N}_4$ -supported Cu SAC with  $[\text{CuN}_4]$  and  $[\text{CuN}_3]$  coordinations for  $\text{CO}_2$  hydrogenation at low temperatures ( $<150 \text{ }^\circ\text{C}$ ). The  $[\text{CuN}_3]$  site with the valence state of  $\text{Cu}^{+1.64}$  tends to catalyze  $\text{CO}_2$  hydrogenation to CO, while the  $[\text{CuN}_4]$  site with the valence state of  $\text{Cu}^{+1.05}$  favors producing methanol *via* the formate pathway. This catalyst achieves a methanol selectivity of 95.5% at a  $\text{CH}_3\text{OH}$  productivity of  $4.2 \text{ mmol g}^{-1} \text{ h}^{-1}$  (Table 2, entries 7 and 8), which surpasses that of the state-of-the-art CZA catalyst by 3.2 times ( $1 \text{ mmol g}^{-1} \text{ h}^{-1}$ ). Overall, the Cu SAC exhibits excellent methanol selectivity in  $\text{CO}_2$  hydrogenation, but the conversion rate is still too low due to the low concentration of the active site. New synthetic approaches are pursued to precisely disperse Cu single sites and inhibit the subsequent catalyst sintering.

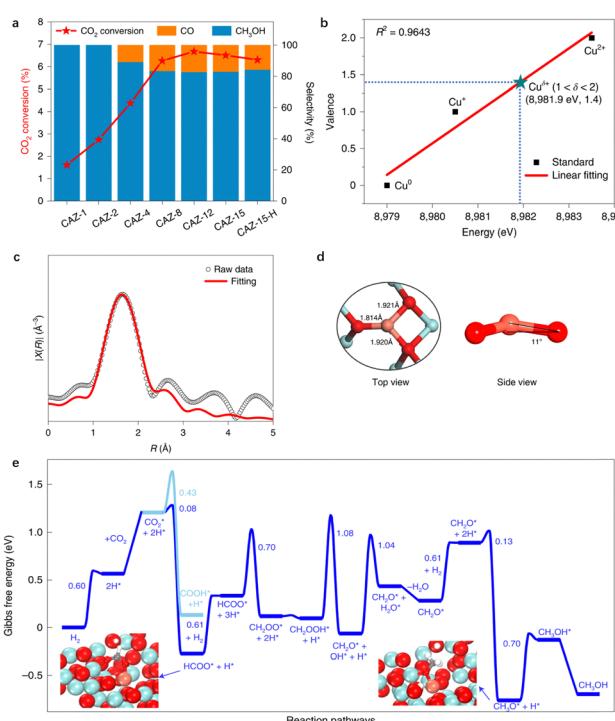


Fig. 5 The structure and catalytic performance of  $\text{CO}_2$  hydrogenation to methanol on Cu SAC supported on the amorphous  $\text{ZrO}_2$  surface (CAZ-1). (a) The catalytic performance of  $\text{CO}_2$  conversion and selectivity. (b) The mean chemical valence of  $\text{Cu}^{\delta+}$  species under *in situ* test conditions detected using XANES spectra. (c) Fitting of  $k^2$ -weighted *in situ* extended X-ray absorption fine structure (EXAFS) data. (d) The identified  $[\text{CuO}_3]$  configuration from SSW-NN simulation. (e) Gibbs free energy profile of  $\text{CO}_2$  hydrogenation to  $\text{CH}_3\text{OH}/\text{CO}$ . Reprinted with permission from ref. 12. Copyright 2022 Springer Nature.

## 5. Supported/confined Cu nanoclusters

Utilization of metal clusters is a common strategy to enhance the 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  $\text{CO}_2$  hydrogenation, theoretical calculations indeed show that  $\text{Cu}_4$  clusters possess a lower activation barrier of  $1.18 \text{ eV}$  for formate formation.<sup>60</sup> In practice, it is a major concern on how to stabilize these Cu nanoclusters to achieve long-term catalyst stability.

Various supports, such as  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ , and  $\text{CeO}_2$ , have been tested and demonstrated to have good catalytic performances. 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  $\text{Cu}^{2+}$ ,  $\text{Cu}^+$ , and  $\text{Cu}^{\delta+}$  that coexist with  $\text{Cu}^0$  of nanoparticles. It was believed that  $\text{Cu}^0$  is responsible for dissociating  $\text{H}_2$ , while  $\text{Cu}^+$  polarizes the C–O



bond to promote intermediate conversion. The product selectivity can thus be tuned by adjusting the  $\text{Cu}^0/\text{Cu}^+$  ratio.<sup>61–63</sup> For example, Yu *et al.*<sup>64</sup> demonstrated that a Cu cluster catalyst supported on inert  $\text{SiO}_2$  prepared using flame spray pyrolysis, results in five times more  $\text{Cu}^+$  species than the traditional catalyst made using ammonia evaporation, and increases the methanol selectivity by inhibiting CO desorption and promoting  $\text{CO}^*$  hydrogenation to  $\text{CH}_3\text{OH}$ . DFT calculations by Sun *et al.*<sup>65</sup> also showed that CO adsorption on  $\text{Cu}^+$  sites is stronger than that on  $\text{Cu}^0$ , and CO can be further hydrogenated to  $\text{CHO}^*$  species.

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.*<sup>66</sup> investigated the effect of different Zn contents on  $\text{CO}_2$  hydrogenation and found that the catalyst with  $\text{Zn}:(\text{Zn} + \text{Cu}) = 0.62$  shows the highest methanol activity of  $4.6 \text{ mol h}^{-1} \text{ kg}^{-1}$  at 523 K. The adsorbed H amount on  $\text{ZnO}$  shows a volcano-like profile against the  $\text{Zn}:(\text{Zn} + \text{Cu})$  content, consistent with the activity variation, pointing to the synergistic effect between Cu and  $\text{ZnO}$ . Song *et al.* unveiled the remarkable activity (11.3%) and methanol STY ( $242 \text{ g}_{\text{CH}_3\text{OH}} \text{ kg}_{\text{cat}}^{-1} \text{ h}^{-1}$ ) of 8 wt% Cu/ $\text{ZnAl}_2\text{O}_4$  at  $220^\circ\text{C}$  and 3 MPa, far surpassing that of conventional 8 wt% Cu/ $\text{ZnO}/\text{Al}_2\text{O}_3$  composite oxides (6.8% for  $\text{CO}_2$  conversion and  $144 \text{ g}_{\text{CH}_3\text{OH}} \text{ kg}_{\text{cat}}^{-1} \text{ h}^{-1}$  for methanol yield). They believed that the  $\text{ZnAl}_2\text{O}_4$  dispersed the Cu cluster with a small particle size of  $\sim 3.2 \text{ nm}$ , quite smaller than that on  $\text{ZnO}/\text{Al}_2\text{O}_3$  ( $\sim 6.4 \text{ nm}$ ). And the higher  $\text{H}_2$  dissociation ability on  $\text{ZnAl}_2\text{O}_4$  strongly enhanced the  $\text{CO}_2$  conversion and methanol yield.<sup>67</sup> The Cu/ $\text{ZrO}_2$  catalyst has been widely reported with high methanol yield, where  $\text{ZrO}_2$  can facilitate the formation and transformation of formate, thereby enhancing methanol synthesis.<sup>68–71</sup> Especially, the crystalline phase of  $\text{ZrO}_2$  can significantly affect the catalytic performance. As reported by Tada *et al.*, the active sites on Cu/a- $\text{ZrO}_2$  (a: amorphous) with a TOF of  $29\text{--}39 \text{ h}^{-1}$  were more suitable for  $\text{CO}_2$ -to-methanol than those on Cu/t- $\text{ZrO}_2$  (t: tetragonal) with a TOF of  $16\text{--}23 \text{ h}^{-1}$  and Cu/m- $\text{ZrO}_2$  (m: monoclinic) with a TOF of  $6\text{--}8 \text{ h}^{-1}$ .<sup>70</sup>

Confining Cu nanoclusters in small cages is another approach to stabilizing nanoparticles and achieving high

catalytic performance. Zhu *et al.* have demonstrated that the Cu nanoclusters encapsulated into MOF materials with  $\text{Zr}_6$  oxide nodes show a high methanol yield. By subtly tuning the  $\text{Zr}-\text{O}-\text{Cu}$  interface, it is found that the  $\text{Zr}-\text{O}-\text{Cu}$  interface is at least part of the active site that strongly adsorbs  $\text{CO}_2$ . As illustrated in Fig. 6, the binding of  $\text{CO}_2$  is not energetically favored on the Cu metal particle with slightly positive adsorption energy. The adsorption of  $\text{CO}_2$  to the  $\text{O}^{2-}$  or  $\text{Zr}^{4+}-\text{O}^{2-}$  sites of the  $\text{Zr}_6\text{O}_8$  node to form a bidentate or tridentate carbonate is considerably stronger, resulting in adsorption energies of  $-42.7$  and  $-51.0 \text{ kJ mol}^{-1}$ , respectively. The adsorption of  $\text{CO}_2$  at the  $\text{Cu}-\text{Zr}^{4+}$  interfacial sites is significantly stronger ( $-80.8 \text{ kJ mol}^{-1}$ ) than the adsorption on the Cu nanoparticles and  $\text{ZrO}_2$  nodes.<sup>72</sup> Cui *et al.* also reported a series of zeolite-fixed Cu/ $\text{ZnO}_x$ @Na-ZSM-5 catalysts. The ultrasmall Cu/ $\text{ZnO}_x$  nanoparticles ( $\sim 2 \text{ nm}$ ) in the Na-ZSM-5 zeolite exhibit the space-time yield of methanol of  $44.88 \text{ g}_{\text{MeOH}} \text{ g}_{\text{Cu}}^{-1} \text{ h}^{-1}$ , much more higher than those of the supported Cu/ $\text{ZnO}_x$ /Na-ZSM-5 catalyst ( $13.32 \text{ g}_{\text{MeOH}} \text{ g}_{\text{Cu}}^{-1} \text{ h}^{-1}$ ) and industrial Cu/ $\text{ZnO}/\text{Al}_2\text{O}_3$  catalyst ( $8.46 \text{ g}_{\text{MeOH}} \text{ g}_{\text{Cu}}^{-1} \text{ h}^{-1}$ ) under identical conditions. The zeolite was suggested to prevent the separation of Cu- $\text{ZnO}_x$  interfaces.<sup>73</sup> Ding *et al.* prepared a high-performance Cu@Na-Beta catalyst which shows a high ethanol yield of  $\sim 14\%$  at  $300^\circ\text{C}$   $\sim 12\,000 \text{ mL g}_{\text{cat}}^{-1} \text{ h}^{-1}$ , and 2.1 MPa, corresponding to a space-time yield of  $\sim 398 \text{ mg g}_{\text{cat}}^{-1} \text{ h}^{-1}$ . They proposed the reaction key step as the reaction of  $\text{CO}_2^*$  with the surface methyl species at step sites of Cu nanoparticles to form  $\text{CH}_3\text{COO}^*$ , which finally leads to ethanol after the hydrogenation steps.<sup>74</sup>

The supported/confined Cu nanocluster offers convenient ways to access rich chemical environments of Cu, leading to low-coordination Cu, positively charged  $\text{Cu}^{\delta+}$  and different interface-contacted Cu. While more adjustable variables in synthesis enable the fine tune of the catalytic performance for catalytic reactions such as  $\text{CO}_2$  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.

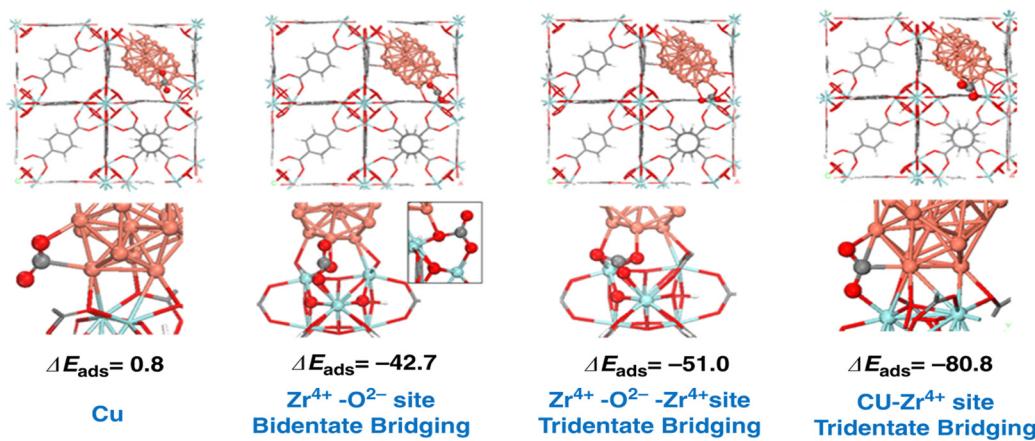


Fig. 6 Adsorption energies ( $\Delta E_{\text{ads}}$  in  $\text{kJ mol}^{-1}$ ) of  $\text{CO}_2$  at different Cu/UiO-66-a interface sites. Reprinted with permission from ref. 72. Copyright 2020 Springer Nature.



## 6. Bimetallic Cu-based and high entropy alloy catalysts

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 alloy (HEA) catalysts. At elevated temperatures (mostly 500–700 K) and pressures (mostly 1–5 MPa), the main products of these catalysts span a large range, including not only common CO and CH<sub>3</sub>OH but also CH<sub>4</sub>, long-chain hydrocarbon (HC) and even alcohols.

CO<sub>2</sub> hydrogenation on the Pd–Cu system produces methanol with the CO byproduct.<sup>75</sup> Song *et al.*<sup>14,76</sup> 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 selectivities of the two corresponding monometallic catalysts. Further screening of catalyst supports led to an improved methanol selectivity of 44.6% on the Pd–Cu/Ti<sub>0.1</sub>Zr<sub>0.9</sub>O<sub>2</sub> catalyst.<sup>77,78</sup> Catalyst characterization studies by using X-ray diffraction (XRD) and TEM confirm the formation of a Pd–Cu alloy nanoparticle comprising bcc PdCu and fcc PdCu<sub>3</sub> phases.<sup>14</sup> Nie *et al.*<sup>79</sup> suggested that the catalytically active site is the bcc PdCu(111) surface with unsaturated Pd, as shown in Fig. 7a. The reaction proceeds through a water-assisted formate pathway with an overall Gibbs energy barrier of 1.23 eV, which is more active than the fcc PdCu<sub>3</sub>(111) surface. Microkinetics simulations show that CO formation from CO<sub>2</sub> through the r-WGS pathway is faster than CH<sub>3</sub>OH synthesis, consistent with the experimental results of a high CO selectivity (>70%).

Cu–Ni alloys can catalyze CO<sub>2</sub> hydrogenation to CO,<sup>80,81</sup> CH<sub>4</sub>,<sup>15</sup> or CH<sub>3</sub>OH.<sup>82–86</sup> Originally, monometallic Ni is known as an active CO<sub>2</sub> methanation catalyst. Wang *et al.*<sup>81</sup> demonstrated that a Cu–Ni catalyst synthesized through a hydrothermal method (with a Cu/Ni ratio of 4.14) exhibits a high selectivity (>99.9%) for CO production during the r-WGS reaction at 1 bar pressure, due to the high dispersion of Ni on the Cu–Ni alloy as detected by high angle annular dark-field scanning transmission

electron microscopy (HAADF-STEM). Indeed, DFT calculations confirmed that the H-assisted CO<sub>2</sub> dissociation has a lower energy barrier of 1.30 eV on Ni-doped Cu(111) compared with plain Cu(111). Tan *et al.*<sup>84,86</sup> synthesized a Cu–Ni alloy on CeO<sub>2</sub>-nanotubes and achieved CO<sub>2</sub> hydrogenation to CH<sub>3</sub>OH with a maximum CH<sub>3</sub>OH space-time yield at a Cu:Ni ratio of 2 and a CH<sub>3</sub>OH selectivity of 76%. Summa *et al.*<sup>15</sup> used a Cu promoted Ni–Mg–Al hydrotalcite-derived catalyst with a low loading of 1.4 wt% for CO<sub>2</sub> hydrogenation to methane, achieving selectivity above 98% and CO<sub>2</sub> conversion up to 86%. XRD and XANES suggest the formation of the Cu–Ni alloy during the reduction step. Furthermore, compared with the Cu-free catalyst, promotion with Cu strongly increased the number of medium-strength basic sites revealed by CO<sub>2</sub> temperature programmed desorption, which is crucial for methanation.

Catalysts with Cu and Fe can lead to a distribution of multi-carbon products in CO<sub>2</sub> hydrogenation. Fe alone serves as a famous Fischer–Tropsch catalyst that converts CO to hydrocarbon, and its combination with Cu allows direct conversion of CO<sub>2</sub> to a multi-carbon product.<sup>17,87–89</sup> Their product and selectivity are listed in Table 3. For example, Si *et al.*<sup>18</sup> developed an FeCu nanoalloy catalyst supported on ZnO by a sputtering method (sp-CuFeZn), which demonstrated a high paraffin selectivity of 63.5% (containing ~14% of CH<sub>4</sub>). *In situ* XRD reveals that in sp-CuFeZn the metal mainly exists as an FeCu<sub>4</sub> nanoalloy under the reaction conditions. Hwang *et al.*<sup>16</sup> synthesized an Fe–Cu–K catalyst that exhibited superior selectivity towards liquid hydrocarbons (50.7% toward C<sub>5+</sub> hydrocarbons and 72.7% toward olefin), with a 1.7-fold increase in CO<sub>2</sub> conversion and higher chain growth probability compared to the Fe–K catalyst. The observed phases include the Cu–Fe alloy, Fe<sub>3</sub>O<sub>4</sub>, and a small amount of iron carbide (Fe<sub>5</sub>C<sub>2</sub>) after the reaction.

Theoretical calculations have been utilized to provide insights into the activity of the Cu–Fe alloy. Nie *et al.*<sup>90,91</sup> utilized Fe(100) and Cu-alloyed Fe(100) to investigate the reaction mechanism of CO<sub>2</sub> hydrogenation towards C<sub>1</sub> and C<sub>2</sub> hydrocarbons. On the Cu-alloyed Fe(100) surface, the adsorption strength of CO<sub>2</sub> decreases as the surface Cu coverage increases, increasing the CO<sub>2</sub> dissociation barrier.<sup>91</sup> At medium Cu coverage ( $\theta_{\text{Cu}} = 0.4$  ML), the CO<sub>2</sub> hydrogenation to HCOO\* occurs with a low hydrogenation

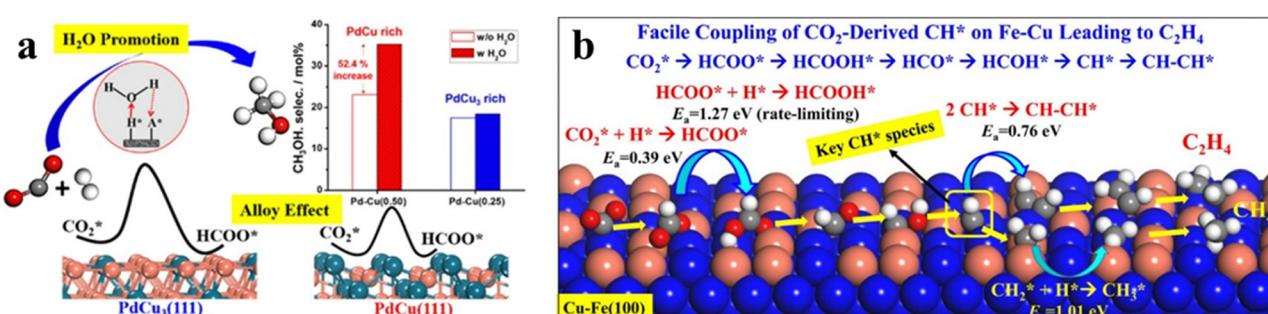


Fig. 7 (a) Methanol selectivity of different Pd–Cu bimetallic catalysts with and without H<sub>2</sub>O. The *in situ* produced water can accelerate CO<sub>2</sub> conversion to methanol. The stepped bcc PdCu(111) active site shows a lower barrier than fcc PdCu<sub>3</sub>(111) and shows higher methanol selectivity. Reprinted with permission from ref. 79. Copyright 2018 American Chemical Society. (b) Cu-alloyed Fe(100) active sites for the Cu–Fe bimetallic catalyst and its reaction mechanism of CO<sub>2</sub> hydrogenation toward C<sub>2</sub>H<sub>4</sub>. Reprinted with permission from ref. 90. Copyright 2017 American Chemical Society.



barrier of 0.39 eV. The  $\text{HCOO}^*$  species then undergoes a series of steps, including  $\text{HCOO}^* \rightarrow \text{HCOOH}^* \rightarrow \text{HCO}^* \rightarrow \text{HCOH}^* \rightarrow \text{CH}^* \rightarrow \text{CHCH}^* \rightarrow \text{CH}_2\text{CH}^* \rightarrow \text{CH}_2\text{CH}_2^*$ , to produce ethylene with a low energy barrier of 1.27 eV (Fig. 7b).<sup>90</sup> 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  $\text{CO}_2$  hydrogenation. Mori *et al.*<sup>92</sup> synthesised a  $\text{TiO}_2$  supported  $\text{CoNiCuRuPd}$  nanoparticle catalyst, which is found to be both active and extremely durable during  $\text{CO}_2$  hydrogenation. The main product leads to  $\text{CH}_4$  (selectivity 68.3%) and CO (31.7%) at 673K, 1 bar with a conversion of  $\sim 46\%$ , which retained 96% of its original activity after 72 h. Hou *et al.*<sup>93</sup> reported a high entropy cubic  $\text{Zr}_{0.5}(\text{NiFeCuMnCo})_{0.5}\text{O}_x$ , where the configuration entropy leads to observation of *in situ* reversible exsolution–dissolution of supported metallic species in multi redox cycles. In  $\text{CO}_2$  hydrogenation, the  $\text{CO}_2$  conversion is 29% and CO selectivity is over 90%, with no obvious activity loss during the 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  $\text{CH}_4$ ), their ultrahigh thermal stability in long-term  $\text{CO}_2$  hydrogenation may provide useful hints to improve catalyst durability in general. As experimental reports of HEA's applications in  $\text{CO}_2$  hydrogenation are limited, more research work is needed to identify how Cu cooperates with other metals during the HEA catalysis.<sup>92,94</sup>

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 research studies are required for probing the active site structure and resolving the reaction intermediates during  $\text{CO}_2$  hydrogenation.

## 7. Perspectives

This perspective provides an overview of the current understanding of active sites in copper-based catalysts for  $\text{CO}_2$  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  $\text{CO}_2$  hydrogenation main product of a mono-metallic Cu catalyst, *e.g.* CZA, Cu SACs and supported/confined Cu clusters, is either CO or methanol. Once the second metal is introduced to form a Cu-X alloy catalyst, the  $\text{CO}_2$  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 a 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 are highlighted as follows.

The SMSI effect observed during CZA catalyst activation is long believed to be the key reason for creating the active site and resulting in a high activity of the CZA catalyst. There is

growing interest in the *in situ* atomic structure of  $\text{ZnO}_x\text{H}_y$  on Cu surfaces. As mentioned in Section 3, the traditional techniques of structure characterization face great difficulties due to the essentiality of reaction conditions ( $\text{H}_2/\text{CO}$  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<sup>95</sup> (ASOP) to explore the stable  $\text{Zn}_x\text{O}_y\text{H}_z/\text{Cu}(111)$  structure.<sup>25</sup> Fig. 8a and b plot the PES of  $\text{Zn}_x\text{O}_y\text{H}_z/\text{Cu}(111)$  under typical reaction conditions (500 K,  $p_{\text{H}_2} = 40$  bar,  $p_{\text{CO}} = p_{\text{CO}_2} = 10$  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) ( $n_{\text{cell}} = 4\text{--}12$ ) with varied  $\text{Zn}_x\text{O}_y\text{H}_z$  composition ( $\theta_{\text{Zn}} = x/n_{\text{cell}} = 0\text{--}1$ , the same for  $\theta_{\text{O}}$  and  $\theta_{\text{H}}$ ). This shows that besides clean Cu and CuZn surface alloys (where  $\theta_{\text{O}} \approx 0$ ), a stable region is located where the coverage is  $\theta_{\text{Zn}} : \theta_{\text{O}} : \theta_{\text{H}} \approx 1 : 1 : 1$ . 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  $(\text{Zn}_6\text{O}_8\text{H}_8/\text{Cu}(111) - (2\sqrt{3} \times 3))$  whose free energy is  $-0.043$  eV per Cu(111) unit cell, being more stable than clean Cu(111) and bulk ZnO. Many other structures with a similar energy are available, including  $\text{Zn}_6\text{O}_8\text{H}_8/\text{Cu}(111) - (\sqrt{19} \times \sqrt{7})$  (denoted as I, free energy  $-0.038$  eV per unit cell),  $\text{Zn}_4\text{O}_5\text{H}_5/\text{Cu}(111) - (3 \times \sqrt{7})$  (denoted as II, free energy  $-0.029$  eV per unit cell), as well as  $\text{Zn}_3\text{O}_3\text{H}_3/\text{Cu}(111) - (\sqrt{13} \times \sqrt{3})$  ( $-0.042$  eV per unit cell). Apparently, these structures share a similar  $[-\text{Zn}-\text{OH}-\text{Zn}-]$  repeating unit and the multiple degenerate structures suggest the amorphous nature of the  $\text{ZnO}_x\text{H}_y$  overlayer on the Cu(111) surface (Fig. 8c). Further work is required to clarify the  $\text{ZnO}_x\text{H}_y$  structures on the

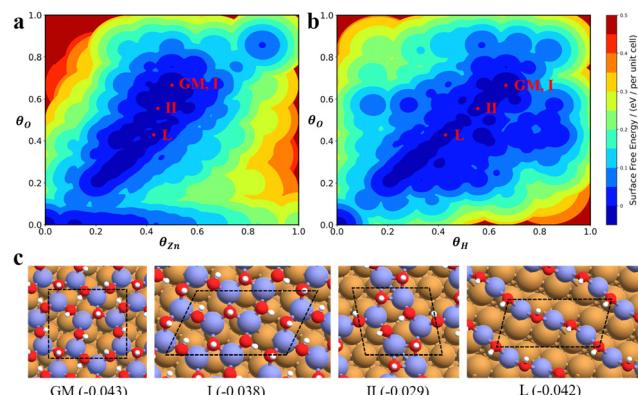


Fig. 8 The PES contour map for  $\text{Zn}_x\text{O}_y\text{H}_z/\text{Cu}(111)$  from ASOP simulation, using (a) coverage of O and Zn as axes, or (b) coverage of O and H as the axes. (c) The identified stable  $\text{Zn}_x\text{O}_y\text{H}_z/\text{Cu}(111)$  structures. From left to right, GM:  $\text{Zn}_6\text{O}_8\text{H}_8/\text{Cu}(111) - (2\sqrt{3} \times 3)$ , I:  $\text{Zn}_6\text{O}_8\text{H}_8/\text{Cu}(111) - (\sqrt{19} \times \sqrt{7})$ , II:  $\text{Zn}_4\text{O}_5\text{H}_5/\text{Cu}(111) - (3 \times \sqrt{7})$ , L:  $\text{Zn}_3\text{O}_3\text{H}_3/\text{Cu}(111) - (\sqrt{13} \times \sqrt{3})$ . The color scheme for atoms is as follows: H: white; O: red; Cu: yellow; and Zn: blue.



stepped Cu surfaces and determine the CO<sub>2</sub> hydrogenation mechanism over these overlayer structures.

In addition, the role of the Al<sub>2</sub>O<sub>3</sub> component in the CZA catalyst needs to be revisited. While Al<sub>2</sub>O<sub>3</sub> was traditionally viewed as a support material, it may still act as an active component in methanol synthesis. In particular, the presence of the ZnAl<sub>2</sub>O<sub>4</sub> spinel has been mentioned in recent literature as a factor for promoting CO hydrogenation.<sup>96,97</sup>

For the Cu SAC catalyst, the low conversion rate (for example, <2%<sup>12,53</sup>) limits its practical applications, which calls for increasing the metal loading and the concentration of active Cu SAC sites. Moreover, as the [CuN<sub>x</sub>] active sites have shown lower reaction barriers, it is fascinating to increase the concentration of [CuN<sub>x</sub>] active sites by immobilizing Cu SACs on nitrides such as GaN or Ta<sub>2</sub>N<sub>3</sub>, which may achieve better catalysis performance for CO<sub>2</sub> hydrogenation than [CuO<sub>x</sub>] and [CuC<sub>x</sub>] active sites.

For the supported/confined Cu cluster catalyst, optimizing the Cu-oxide interface is an effective approach to improving the activity of CO<sub>2</sub> hydrogenation. Recent studies have shown that the inverse oxide/metal configuration can enhance interfacial reactivity in well-defined CeO<sub>x</sub>/Cu(111), ZnO/Cu(111), and ZrO<sub>x</sub>/Cu models used as catalysts for the water-gas shift and methanol synthesis reactions.<sup>98–100</sup> 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 the electron transfer and adsorption of CO<sub>2</sub> and H<sub>2</sub> molecules. The active site structures for these inverse catalysts are however unclear.

Overcoming the above challenges in the future should benefit 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,<sup>72</sup> and to search for unknown reactions,<sup>25,101</sup> 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 centers using 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* a machine learning database of materials with essential catalytic properties and then utilized to predict the activity. Recent years have seen efforts to establish a database for key catalytic properties,<sup>102</sup> such as the adsorption energy of key intermediates, the morphology and acidity of zeolites.<sup>103</sup> These approaches can be applied in the design of HEA (Cu, Co, Ni, Zn, and Sn) catalysts for CO<sub>2</sub> hydrogenation.<sup>104,105</sup>

We note that electrochemical CO<sub>2</sub> hydrogenation has attracted more and more attention in recent years, which is not the focus of the current perspective, and there has been significant and interesting progress. For example, the electrochemical C–N coupling of CO<sub>2</sub> and nitrogenous small molecules (*e.g.* NO and NO<sub>2</sub>) can simultaneously eliminate greenhouse gas emissions and environmental pollutants;<sup>106</sup> the CO<sub>2</sub> electrochemical reduction on Cu-based catalysts can produce other high-value products (*e.g.* ethylene or ethanol) under ambient

conditions.<sup>107,108</sup> These new reaction routes together with the thermal approach of CO<sub>2</sub> hydrogenation are going to be the key catalysis hotspots towards greener and more sustainable future.

## Conflicts of interest

The authors declare no competing financial interests.

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