Copper-based catalysts for CO₂ hydrogenation: a perspective on active sites

Yun-Fei Shi, a Sicong Ma b,* and Zhi-Pan Liu a,*

CO₂ 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 CO₂ 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 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 ZnOₙHₓ 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 CO₂ hydrogenation catalysts.

Broader context

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 Cu-based catalyst structures, the most important type of CO₂ 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 (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 industry through the low-pressure methanol synthesis process with a Cu-based catalyst, i.e. a Cu/ZnO/Al₂O₃ (CZA) catalyst. The global CH₃OH production with this technology is massive, reaching 106.89 million metric tons in 2021. This industrial achievement demonstrates the great value of CO₂ conversion in making renewable fuels and chemicals. In recent years, significant efforts have been devoted to developing new types of catalysts for CO₂ 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 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. 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, 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 the ZnO lattice, lattice strain, Schottky junctions, etc. However, most of these hypotheses lack clear support from the latest experimental and theoretical results. In 2012, Behrens et al. 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, in which Zn is reduced to form a CuZn alloy phase, and the ZnO/Cu interface model, 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 CO₂ hydrogenation catalysts is mainstream in heterogeneous catalysis. 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, Ni, Fe, etc.). Introducing a second metal into the Cu-catalyst can result in the formation of non-methanol products, such as methane, long-chain hydrocarbons, or ethanol. For example, the Cu–Ni catalyst can lead to high selectivity on CH₄, while the Cu–Fe catalyst tends to produce long-chain hydrocarbons. 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. in the Cu–Fe catalyst, although the CuFe alloy phase is regarded as the active site for the Cu–Fe bimetallic catalyst, FeOₓ and FeCₓ also exist in the catalyst and thus may still be the active centers.

With encouraging progress in Cu-based catalysts for CO₂ 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 CO₂ 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.
changes ($\Delta G$) for these gas-phase reactions. It shows that CO and CH$_3$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 CH$_3$OH compared to the economically undesirable CO. However, the maximum one-pass conversion of CH$_3$OH is still limited to 15–35%, 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 CH$_3$OH and CO are less frequently reported on Cu-based catalysts. HCOOH and HCHO are thermodynamically unfavorable than CH$_3$OH across the entire temperature range ($\Delta G$ is 0.26/0.34 eV higher than that of CH$_3$OH at 500 K, respectively). They exhibit low selectivity, likely due to their instability and susceptibility to further hydrogenation into CH$_3$OH. Products like CH$_4$, C$_2$H$_4$, and C$_2$H$_5$OH are consistently thermodynamically more favorable than CH$_3$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, CO$_2$ hydrogenation only produces CO and CH$_3$OH.

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

(i) A most-mentioned CO$_2$ hydrogenation pathway to CH$_3$OH follows the sequence: CO$_2^*$ (superscript * indicates the adsorbed state) → HCOO* → HCOOH* → H$_2$COOH* → HCHO* → CH$_3$O* → CH$_3$OH*, termed the formate pathway. The rate-determining step occurs in the first half of the reaction before CH$_2$O formation, involving the hydrogenation of CH$_x$O$_2$ ($x$ = 0–3) species, such as CO$_2$ to HCOO*, HCOOH* to H$_2$COOH*, or H$_2$COOH to HCHO*. If the overall barrier for the further hydrogenation of HCOO* and HCHO* is not higher than that for the formation of 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 CO$_2$ and HCOO* hydrogenation.

(ii) Another mechanism for CO$_2$ to CH$_3$OH is the reverse water–gas shift (r-WGS) coupling with CO hydrogenation. In the pathway, CO$_2$ is first hydrogenated to CO through CO$_2^*$ → COOH* → CO*, termed the carboxyl pathway, and then CO* is further hydrogenated to CH$_3$OH* through CO* → CHO* → HCHO* → CH$_3$O* → CH$_3$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 CO$_2^*$ → 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 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. This is likely due to the high barrier associated
which is essential for subsequent C–C coupling.25 The direct
step.22,25To allow CO2 hydrogenation, the introduction of step
ion, where the rate-determining step is the HCHO* + H*
way of CH
99.8%) and exceptional long-term stability (design life
under conditions such as 500–550 K and 50–100 bar, the CZA
exhibits a significantly lower Gibbs free barrier of 1.40 eV for
the CO2 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.22 Another possible pathway
of CH4 generation is via the HCHO* → CH2OH* → CH2* route, but its overall barrier is higher than that of HCHO* →
CH2O* → CH2OH, leading to a low selectivity.25
Quantitatively, the low coordination 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 1,22,23,30 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 is the HCHO* + H* step.22,25 To allow CO2 hydrogenation, the introduction of step
and point defects is thus a must.25,30–32 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 cata-
lytic activity of Cu-based catalysts in CO2 hydrogenation.

| Cu surface | RDS | CN | $E_a$ (eV) | Ref.
<table>
<thead>
<tr>
<th></th>
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</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(110)</td>
<td>HCOO* → H2COOH*</td>
<td>8</td>
<td>1.25</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>8</td>
<td>1.02</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>

with the C–O bond breaking to produce CHx (x = 0–4) species,
which is essential for subsequent C–C coupling.25 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.22 Another possible pathway
of CH4 generation is via the HCHO* → CH2OH* → CH2* route, but its overall barrier is higher than that of HCHO* →
CH2O* → CH2OH, leading to a low selectivity.25

3. CZA industrial catalyst

As the active site of the CZA catalyst remains highly contro-
sional, 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 nano-
particles (5–10 nm) of metallic Cu, wurtzite ZnO, and amorphous
Al2O3 after air calcination and H2 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).31 It is worth noting that a mixed CO, 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 range is 0.5–4.14,35
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.24
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
thoretical evidence, fueling an ongoing debate. The first view
poses 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 to 0.22 ML), 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., CO2-free
CO and H2 atmospheres.37–39 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 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 CO2
hydrogenation to methanol than that without Zn doping, follow-

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

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. Cu2(211) as an
e 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 CO2 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 CO2 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 condi-
tions, and the Zn–Zn dimeric site is thermodynamically unfavor-
able CO2 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 improve-
ment on the 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
ZnO(xH2)y–Cu interface, where Zn atoms are primarily present as
ZnO(xH2)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 ZnO on the
Cu surface and leading to an SMSI effect.44 This phenomenon

Perspective

EES Catal., 2023, 1, 921–933 © 2023 The Author(s). Published by the Royal Society of Chemistry
is indeed observed in HRTEM photos under \textit{ex situ} conditions, revealing the formation of a graphite-like ZnO overlayer on the surface of Cu nanoparticles after H$_2$ activation (Fig. 4).\textsuperscript{11} This phenomenon was also observed by other research groups.\textsuperscript{9,45,46} The presence of cationic Zn as the active site was also suggested by Laudenschleger \textit{et al.},\textsuperscript{47} who conducted a high-pressure pulse experiment in which NH$_3$ is injected into a high-pressure methanol synthesis. They observed a temporary decrease in methanol yield due to NH$_3$ poisoning, but the co-fed C$_2$H$_4$ hydrogenates to C$_2$H$_6$ 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$_2$ hydrogenation, which is poisoned by NH$_3$. They also reported that the higher CO$_2$ content, a more oxidizing condition, may lead to more positively charged Zn on the Cu surface, resulting in more obvious NH$_3$ 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$_x$H$_y$ phase rather than the ZnO$_x$ phase. Beck \textit{et al.}\textsuperscript{36} first showed that the formation of active sites is influenced by the H$_2$ 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$_2$ pressure was kept beyond 1 bar. However, no significant changes were observed in the zinc (+2) oxidation state until 500 $^\circ$C under 1 mbar H$_2$. In addition, theoretical studies also found the strong adsorption of H on the ZnO$_x$ cluster supported on Cu(111), stabilizing the ZnO$_x$ cluster on Cu under the H$_2$-rich reaction conditions.\textsuperscript{46,48–50} The presence of H may further alter the reaction kinetics. Reichenbach \textit{et al.}\textsuperscript{51} showed that the energy barrier of CO$_2$ hydrogenation on Zn$_x$O$_y$/Cu(111) is 1.33 eV, which decreases to 1.30 eV when H adsorbs on the ZnO cluster. Kattel \textit{et al.} proposed another Zn$_x$O$_y$H$_z$/Cu(111) model whose CO$_2$ hydrogenation overall energy barrier is only 1.05 eV (HCOO$^-$ $\rightarrow$ H$_2$COOH$^*$), much lower than that of ZnCu(111) (1.49 eV).\textsuperscript{52} It should be noted that due to the complexity of the potential energy surface (PES), the structures of ZnO$_x$H$_y$ clusters on Cu surfaces are not explored systematically yet and thus the reported energetics on the manually constructed ZnO$_x$H$_y$ 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.
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.

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>CN₇Cu</th>
<th>Cu⁺⁺</th>
<th>Reaction intermediates</th>
<th>Eₐ (eV)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu₁@FAU zeolite</td>
<td>513</td>
<td>MeOH (89.5%)</td>
<td>[CuO₃₈⁺]</td>
<td>+2</td>
<td>HCOO, HCOOH, CH₃O</td>
<td>~2.30</td>
<td></td>
</tr>
<tr>
<td>Cu₁/ZnO</td>
<td>443</td>
<td>MeOH (99.1%)</td>
<td>[CuO₃₅⁺]</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>[CuO₃]</td>
<td>+1.4</td>
<td>HCOO, CH₃O</td>
<td>1.46</td>
<td>12</td>
</tr>
<tr>
<td>Cu₁/ZrO₂-MOF</td>
<td>358</td>
<td>EtOH (&gt;99%)</td>
<td>[Cu₃]</td>
<td>+1</td>
<td>CHO, CH₂O, CH₃O</td>
<td></td>
<td>57</td>
</tr>
<tr>
<td>Cu₁/C₃N</td>
<td></td>
<td>HCOOH</td>
<td>[Cu₂]</td>
<td></td>
<td>HCOO</td>
<td>0.57</td>
<td>55</td>
</tr>
<tr>
<td>Cu₁/C₃N₄</td>
<td></td>
<td>HCOOH</td>
<td>[Cu₄]</td>
<td></td>
<td>HCOO</td>
<td>0.86</td>
<td>56</td>
</tr>
<tr>
<td>Cu₁/C₃N₅</td>
<td></td>
<td>CO (94.3%)</td>
<td>[Cu₅]</td>
<td>+1.64</td>
<td>COOH</td>
<td></td>
<td>57</td>
</tr>
<tr>
<td>Cu₁/C₃N₆</td>
<td></td>
<td>CO (95.5%)</td>
<td>[Cu₆]</td>
<td>+1.05</td>
<td>HCOO, CH₂O</td>
<td></td>
<td>57</td>
</tr>
<tr>
<td>Cu₁/graphene</td>
<td></td>
<td>HCOOH</td>
<td>[Cu₅]</td>
<td></td>
<td>HCOO</td>
<td>1.47, 1.18</td>
<td>58 and 59</td>
</tr>
</tbody>
</table>

Table 3: Catalyst composition, reaction conditions and catalytic performance of various multi-metallic catalysts for CO₂ hydrogenation. HC represents hydrocarbon.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Active site</th>
<th>Alloy composition</th>
<th>Temp (K)</th>
<th>Pressure (Mpa)</th>
<th>Conversion (%)</th>
<th>Product (selectivity)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuPd</td>
<td>Pd–Cu/SiO₂</td>
<td>Cu : Pd = 0.34 : 0.66</td>
<td>523</td>
<td>4.1</td>
<td>6.60</td>
<td>CO (66%) (34%)</td>
<td>14</td>
</tr>
<tr>
<td>Pd–Cu/Ti₆O₆</td>
<td>Cu : Pd =3 : 1</td>
<td></td>
<td>523</td>
<td>4.1</td>
<td>10.10</td>
<td>CO (55.4%) (44.6%)</td>
<td>78</td>
</tr>
<tr>
<td>1Pd–10Cu/CeO₂</td>
<td>Cu : Pd = 1 : 0.06</td>
<td></td>
<td>543</td>
<td>3</td>
<td>17.8</td>
<td>CH₂OH (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</td>
<td>0.1</td>
<td>26</td>
<td>CO (&gt;99.9%) (98.7%)</td>
<td>81</td>
</tr>
<tr>
<td>CuNi-eGO</td>
<td>Cu : Ni = 2 : 1</td>
<td></td>
<td>498</td>
<td>4.0</td>
<td>7.87</td>
<td>CH₂OH (76%)</td>
<td>82</td>
</tr>
<tr>
<td>Cu-Ni/CO₂-nanotubes</td>
<td>Cu : Ni = 2 : 1</td>
<td></td>
<td>533</td>
<td>4</td>
<td>17.8</td>
<td>CH₂OH (&gt;98%)</td>
<td>15</td>
</tr>
<tr>
<td>Cu-Ni/MgAl₂O₄</td>
<td>Cu : Ni = 15.5 : 1</td>
<td></td>
<td>623</td>
<td>—</td>
<td>86</td>
<td>CH₄ (&gt;98%)</td>
<td></td>
</tr>
<tr>
<td>CuFe</td>
<td>sp-CuFeZn</td>
<td>Cu : Fe = 15.9 : 5.7</td>
<td>613</td>
<td>3.0</td>
<td>33.40</td>
<td>CO (18%) (66%)</td>
<td>18</td>
</tr>
<tr>
<td>im-CuFeZn</td>
<td>Cu : Fe = 15.7 : 5.7</td>
<td></td>
<td>613</td>
<td>3.0</td>
<td>28.60</td>
<td>CH₄ (14%) (49.5%)</td>
<td>18</td>
</tr>
<tr>
<td>Cs-Cu₈ₓFe₄ₓZn₁ₓ</td>
<td>Cu : Fe = 28.9 : 35.7</td>
<td></td>
<td>603</td>
<td>5.0</td>
<td>36.60</td>
<td>CO (20%) (19.8%)</td>
<td>88</td>
</tr>
<tr>
<td>4.6K–Cu–Mg–Zn–Fe</td>
<td>Cu : Fe = 1 : 0.98</td>
<td></td>
<td>593</td>
<td>5</td>
<td>30.40</td>
<td>CO (50.6%) (15.7%)</td>
<td>89</td>
</tr>
<tr>
<td>Fe–Cu–K</td>
<td>Cu : Fe = 8.6 : 69.8</td>
<td></td>
<td>573</td>
<td>2.5</td>
<td>35</td>
<td>C₂–C₄–HC (26%)</td>
<td>16</td>
</tr>
<tr>
<td>CuFeO₂-24</td>
<td>Cu : Fe = 1 : 1</td>
<td></td>
<td>573</td>
<td>1</td>
<td>16.70</td>
<td>CO (31.4%) (45.4%)</td>
<td>17</td>
</tr>
<tr>
<td>HEA</td>
<td>CoNiCuRuPdT/ TiO₂</td>
<td></td>
<td>673</td>
<td>0.1</td>
<td>~46</td>
<td>CH₄ (45.4%) (68.3%)</td>
<td>92</td>
</tr>
<tr>
<td>Zr₂O₃(NiFeCuMnMo)Co₃O₆</td>
<td>Zr : Ni :Fe : Cu : Mn = 5 : 1 : 1 : 1 : 1</td>
<td></td>
<td>673</td>
<td>0.1</td>
<td>~29</td>
<td>CH₄ (45.4%) (68.3%)</td>
<td>92</td>
</tr>
</tbody>
</table>

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.¹³ reported 89.5% selectivity towards methanol on a faujasite-encaged mononuclear Cu center catalyst that has a higher [CuO₃₈⁺] coordination environment with a Cu valence state of +2 (Table 2, entry 1). Wu et al.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 the valence state of Cu⁺⁺ (1<δ<2) (Table 2, entry 2).
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 ZrO\(_2\) surface (Cu\(_x/ZrO_2\)) Cu SAC, as shown by Zhao and colleagues\(^{12}\) (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 \textit{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 ZrO\(_2\) plays a key role in stabilizing the Cu single atom. The formation of Cu SACs is exothermic on amorphous ZrO\(_2\) but endothermic on ZrO\(_2\) flat (111) and terrace (112) surfaces, indicating that the amorphous ZrO\(_2\) support is instrumental in maintaining the high stability of the Cu atom. The \( \text{CO}_2 \) hydrogenation on the isolated Cu\(^{3+}\) cation site follows the \( \text{CO}_2 \rightarrow \text{HCOO} \rightarrow \text{H}_2\text{COO} \rightarrow \text{H}_2\text{COOH} \rightarrow \text{H}_2\text{CO} \rightarrow \text{H}_2\text{CO} \rightarrow \text{H}_3\text{COOH} \) pathway with the rate-determining step being the HCOO\(^*\) species hydrogenation (Fig. 5e). The calculated TOF for \( \text{CO}_2 \) hydrogenation to CH\(_3\)OH on the isolated Cu\(^{3+}\) cation is approximately 2.89 h\(^{-1}\), consistent with the experimental TOF of 1.37 h\(^{-1}\) and being about two orders of magnitude larger than the \( \text{CO}_2 \) hydrogenation to the CO product (0.03 h\(^{-1}\)).

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

Compared to the common [CuO\(_2\)], the [CuN\(_x\)] and the [CuC\(_x\)] patterns in Cu SACs are much less reported in the literature. The DFT calculations first reveal the low reaction barriers (<0.9 eV) for \( \text{CO}_2 \) hydrogenation to HCOOH on the [CuN\(_x\)] pattern (Table 2, entries 5–8).\(^{55–59}\) The energy barrier on the [CuC\(_x\)] pattern is higher than that on the [CuN\(_x\)] pattern, but still lower than that on the [CuO\(_x\)] pattern (Table 2, entry 9).\(^{55,59}\) This suggests that the [CuN\(_x\)] and [CuC\(_x\)] sites may exhibit even higher \( \text{CO}_2 \) hydrogenation activity than the [CuO\(_x\)] sites. Indeed, Yang \textit{et al.}\(^{57}\) demonstrated the high selectivity and activity of a CuN\(_x\)-supported Cu SAC with [CuN\(_x\)] and [CuC\(_x\)] coordinations for \( \text{CO}_2 \) hydrogenation at low temperatures (<150 °C). The [CuN\(_x\)] site with the valence state of Cu\(^{1.64}\) tends to catalyze \( \text{CO}_2 \) hydrogenation to CO, while the [CuN\(_x\)] site with the valence state of Cu\(^{1.05}\) favors producing methanol via the formate pathway. This catalyst achieves a methanol selectivity of 95.5% at a CH\(_3\)OH productivity of 4.2 mmol g\(^{-1}\) h\(^{-1}\) (Table 2, entries 7 and 8), which surpasses that of the state-of-the-art CZA catalyst by 3.2 times (1 mmol g\(^{-1}\) 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.

### 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 Cu\(_4\) clusters possess a lower activation barrier of 1.18 eV for formate formation.\(^{60}\) 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\(_2\), Al\(_2\)O\(_3\), ZrO\(_2\), and 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 Cu\(^{3+}\), Cu\(^{1+}\), and Cu\(^{1+}\) that coexist with Cu\(^0\) of nanoparticles. It was believed that Cu\(^{1+}\) is responsible for dissociating H\(_2\), while Cu\(^{1+}\) polarizes the C–O

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**Fig. 5** The structure and catalytic performance of \( \text{CO}_2 \) hydrogenation to methanol on Cu SAC supported on the amorphous ZrO\(_2\) surface (CAZ-1). (a) The catalytic performance of \( \text{CO}_2 \) conversion and selectivity. (b) The mean chemical valence of Cu\(^{x+}\) species under \textit{in situ} test conditions detected using XANES spectra. (c) Fitting of \( k^2\)-weighted \textit{in situ} extended X-ray absorption fine structure (EXAFS) data. (d) The identified [CuO\(_3\)] configuration from SSW-NN simulation. (e) Gibbs free energy profile of \( \text{CO}_2 \) hydrogenation to CH\(_3\)OH/CO. Reprinted with permission from ref. 12. Copyright 2022 Springer Nature.
bond to promote intermediate conversion. The product selectivity
can thus be tuned by adjusting the Cu⁹/Cu⁺ ratio.⁶¹–⁶³ For example,
Yu et al.⁶⁴ demonstrated that a Cu cluster catalyst supported on
inert SiO₂ prepared using flame spray pyrolysis, results in five
times more Cu⁺ species than the traditional catalyst made using
ammonia evaporation, and increases the methanol selectivity by
inhibiting CO desorption and promoting CO* hydrogenation to
CH₂OH. DFT calculations by Sun et al.⁶⁵ also showed that CO
adsorption on Cu⁺ sites is stronger than that on Cu⁰, and CO can
be further hydrogenated to 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.⁶⁶ investigated the effect of different Zn
contents 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 synergistic
effect between Cu and ZnO. Song et al. unveiled the remarkable
activity (11.3%) and methanol STY (242 gCH₃OH kg⁻¹ h⁻¹) of
8 wt% Cu/ZnAl₂O₄ 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 h⁻¹ for methanol yield).
They believed that the ZnAl₂O₄ 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
ZnAl₂O₄ strongly enhanced the CO₂ conversion and methanol
yield.⁶⁷ 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.⁶⁸–⁷¹ 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 a
TOF of 29–39 h⁻¹ were more suitable for CO₂-to-methanol than
those on Cu/t-ZrO₂ (t: tetragonal) with a TOF of 16–23 h⁻¹ and
Cu/m-ZrO₂ (m: monoclinic) with a TOF of 6–8 h⁻¹.⁷⁰

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 Zr₆
oxide nodes show a high methanol yield. 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 absorbs CO₂. As
illustrated in Fig. 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 Zr⁴⁺–O²⁻ sites of the
Zr₆O₈ node to form a bidentate or tridentate carbonate is con-
siderably stronger, resulting in adsorption energies of ~42.7 and
~51.0 kJ mol⁻¹, respectively. The adsorption of CO₂ at the Cu–Zr⁴⁺
interfacial sites is significantly stronger (~80.8 kJ mol⁻¹) than the
adsorption on the Cu nanoparticles and ZrO₂ nodes.⁷² Cui et al.
also reported a series of zeolite-fixed Cu/ZnO@Na-ZSM-5 cata-
lysts. The ultrasmall Cu/ZnO₅ nanoparticles (~2 nm) in the Na-
ZSM-5 zeolite exhibit the space-time yield of methanol of 44.88
gₘₑₒ₉ gCu⁻¹ h⁻¹, much more higher than those of the supported
Cu/ZnO₅/Na-ZSM-5 catalyst (13.32 gₘₑₒ₉ gCu⁻¹ h⁻¹) and industrial
Cu/ZnO/Al₂O₃ catalyst (8.46 gₘₑₒ₉ gCu⁻¹ h⁻¹) under identical
conditions. The zeolite was suggested to prevent the separation
of Cu–ZnO₅ interfaces.⁷³ 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 h⁻¹, and 2.1 MPa,
corresponding to a space-time yield of ~398 mg g⁻¹ h⁻¹. They
proposed the reaction key step as the reaction of CO₃* with the
surface methyl species at step sites of Cu nanoparticles to form
CH₃COO*, which finally leads to ethanol after the hydrogena-
tion steps.⁷⁴

The supported/confined Cu nanocluster offers convenient
ways to access rich chemical environments of Cu, leading to
low-coordination Cu, positively charged Cu⁹⁺ 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.

Fig. 6 Adsorption energies (ΔE_ads in kJ mol⁻¹) of CO₂ at different Cu/UiO-66-a interface sites. Reprinted with permission from ref. 72. Copyright 2020
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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 CH₄ but also CH₃OH, long-chain hydrocarbon (HC) and even alcohols.

CO₂ hydrogenation on the Pd–Cu system produces methanol with the 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 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/Ti₀.1 Zr₀.9 O₂ catalyst. 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 PdCu₃ phases. Nie et al. 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 PdCu₃(111) surface. Microkinetics simulations show that CO formation from CO₂ through the r-WGS pathway is faster than CH₄ OH synthesis, consistent with the experimental results of a high CO selectivity (> 70%).

Cu–Ni alloys can catalyze CO₂ hydrogenation to CO₃, CH₄, or CH₃OH. Originally, monometallic Ni is known as an active CO₂ methanation catalyst. Wang et al. 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 CO₂ dissociation has a lower energy barrier of 1.30 eV on Ni-doped Cu(111) compared with plain Cu(111). Tan et al. synthesized a Cu–Ni alloy on CeO₂ nanotubes and achieved CO₂ hydrogenation to CH₃OH with a maximum CH₃OH space-time yield at a Cu : Ni ratio of 2 and a CH₃OH selectivity of 76%. Summa et al. used a Cu promoted Ni–Mg–Al hydrotalcite-derived catalyst with a low loading of 1.4 wt% for CO₂ hydrogenation to methane, achieving selectivity above 98% and CO₂ 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 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 hydrocarbons, and its combination with Cu allows direct conversion of CO₂ to a multi-carbon product. Their product and selectivity are listed in Table 3. For example, Si et al. 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 CH₄). In situ XRD reveals that in sp-CuFeZn the metal mainly exists as an FeCu₄ nanosheet under the reaction conditions. Hwang et al. synthesized an Fe–Cu–K catalyst that exhibited superior selectivity towards liquid hydrocarbons (50.7% toward C₄, hydrocarbons and 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 the 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 the Cu–Fe alloy. Nie et al. 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 CO decreases as the surface Cu coverage increases, increasing the CO₂ dissociation barrier. At medium Cu coverage (θCu = 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* → HCOO* → CH* → CHCH* → CH₃CH*, to produce ethylene with a low energy barrier of 1.27 eV (Fig. 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. synthesised a TiO₂ supported CoNiCuRuPd nanoparticle catalyst, which is found to be both active and extremely durable during CO₂ hydrogenation. The main product leads 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. reported a high entropy cubic Zr₀.₃(NiFeCuMn)₀.₇O where the configuration entropy leads 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 the 500 h reaction, affording ultrahigh thermal stability. It is worth noting that besides clean Cu and CuZn surface alloys (where θ₀ ≈ 0), a stable region is located where the coverage is θ₂:θ₄:θ₅ ≈ 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 (Zn₆O₈H₈/Cu(111) – (2√3 × 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 (Zn₆O₇H₆/Cu(111) – (√19 × √7)) (denoted as I, free energy −0.038 eV per unit cell), Zn₆O₇H₆/Cu(111) – (3 × √7) (denoted as II, free energy −0.029 eV per unit cell), as well as Zn₆O₇H₆/Cu(111) – (√13 × √3) (−0.042 eV per unit cell). Apparently, these structures share a similar [Zn–OH–Zn–] repeating unit and the multiple degenerate structures suggest the amorphous nature of the ZnO₄H₂ overlayer on the Cu(111) surface (Fig. 8c). Further work is required to clarify the ZnO₄H₂ structures on the growing interest in the in situ atomic structure of ZnO₄H₂ on Cu surfaces. As mentioned in Section 3, the traditional techniques of structure characterization face 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 the stable Zn₆O₇H₆/Cu(111) structure. Fig. 8a and b plot the PES of Zn₆O₇H₆/Cu(111) under typical reaction conditions (500 K, p₃H₂ = 40 bar, p₁CO = p₂CO = 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) (nₑₐₐ₈ = 4–12) with varied Zn₆O₇H₆ composition (θ₂:θ₄:θ₅ = 0–1, the same for θ₄ and θ₅). This shows that besides clean Cu and CuZn surface alloys (where θ₀ ≈ 0), a stable region is located where the coverage is θ₂:θ₄:θ₅ ≈ 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 (Zn₆O₇H₆/Cu(111) – (2√3 × 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 (Zn₆O₇H₆/Cu(111) – (√19 × √7)) (denoted as I, free energy −0.038 eV per unit cell), Zn₆O₇H₆/Cu(111) – (3 × √7) (denoted as II, free energy −0.029 eV per unit cell), as well as Zn₆O₇H₆/Cu(111) – (√13 × √3) (−0.042 eV per unit cell). Apparently, these structures share a similar [Zn–OH–Zn–] repeating unit and the multiple degenerate structures suggest the amorphous nature of the ZnO₄H₂ overlayer on the Cu(111) surface (Fig. 8c). Further work is required to clarify the ZnO₄H₂ structures on the
stepped Cu surfaces and determine the CO₂ hydrogenation mechanism over these overlayer structures.

In addition, the role of the Al₂O₃ component in the CZA catalyst needs to be revisited. While Al₂O₃ was traditionally viewed as a support material, it may still act as an active component in methanol synthesis. In particular, the presence of the ZnAl₂O₄ spinel has been mentioned in recent literature as a factor for promoting CO₂ hydrogenation.⁹⁶,⁹⁷

For the Cu SAC catalyst, the low conversion rate (for example, <2%¹²,⁵) limits its practical applications, which calls for increasing the metal loading and the concentration of active Cu SAC sites. Moreover, as the [CuN₄] active sites have shown lower reaction barriers, it is fascinating to increase the concentration of [CuN₄] active sites by immobilizing Cu SACs on nitrides such as GaN or Ta₂N₃, which may achieve better catalysis performance for CO₂ hydrogenation than [CuO₃] and [CuC₃] active sites.

For the supported/confined Cu cluster catalyst, optimizing the Cu-oxide interface is an effective approach to improving the activity of CO₂ hydrogenation. Recent studies have shown that the inverse oxide/nitrogen configuration can enhance interfacial reactivity in well-defined CeOₓ/Cu(111), ZnO/Cu(111), and ZrO₂/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 the electron transfer and adsorption of CO₂ and H₂ 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.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 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,¹⁰² such as the adsorption energy of key intermediates, the morphology and acidity of zeolites.¹⁰³ These approaches can be applied in the design of HEA (Cu, Co, Ni, Zn, and Sn) catalysts for CO₂ hydrogenation.¹⁰⁴,¹⁰⁵

We note that electrochemical CO₂ 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 CO₂ and nitrogenous small molecules (e.g. NO and NO₂) can simultaneously eliminate greenhouse gas emissions and environmental pollutants;¹⁰⁶ the CO₂ electrochemical reduction on Cu-based catalysts can produce other high-value products (e.g. ethylene or ethanol) under ambient conditions.¹⁰⁷,¹⁰⁸ These new reaction routes together with the thermal approach of CO₂ 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.

Acknowledgements
This work received financial support from the National Natural Science Foundation of China (2188101, 22033003, and 22203101), the Tencent Foundation for XPLORER PRIZE, Youth Innovation Promotion Association CAS (No. 2023265), Science & Technology Commission of Shanghai Municipality (23ZR1476100) and the Fundamental Research Funds for the Central Universities (2072022001).

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