

## CRITICAL REVIEW

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[rsc.li/rscsus](https://rsc.li/rscsus)The engineering of CO<sub>2</sub> hydrogenation catalysts for higher alcohol synthesisAngie F. J. Tan,<sup>a</sup> Muhammad Dody Isnaini,<sup>ab</sup> Muenduen Phisalaphong<sup>b</sup>  
and Alex C. K. Yip <sup>\*a</sup>

Anthropogenic CO<sub>2</sub> emissions have drawn significant attention in recent years. Using CO<sub>2</sub> as feedstock for chemical processes has become a key solution in overall closed carbon cycles for a vision of a circular carbon economy. CO<sub>2</sub> hydrogenation to higher alcohols has emerged as one of the most promising CO<sub>2</sub> conversion pathways for mitigating CO<sub>2</sub> emissions and producing value-added chemicals. The present review critically discusses the most recent cutting-edge catalyst development in higher alcohol synthesis (HAS), focusing on the influence of different metals, promoters, and supports according to the contributions of different active species in modern catalyst configurations. Particularly, the critical roles of oxygen vacancies and the reaction mechanisms shed light on the rational design of the next-generation CO<sub>2</sub> hydrogenation catalysts.

## Sustainability spotlight

Utilizing CO<sub>2</sub> as feedstock integrated with renewable H<sub>2</sub> is one of the most promising pathways for a closed carbon loop cycle for the circular carbon economy. This review provides a critical assessment on the most emerging CO<sub>2</sub> hydrogenation catalyst designs, discussing the importance of appropriate combination of metal active sites, supports, and promoters for tailoring metal interfaces, metal support interactions, and acid–base sites, *etc.* The review also delves into the reaction pathways that balance between dissociative and nondissociative CO activation, and promote CO insertion and C–C coupling for higher alcohol formation. We believe the readers will find the insights in this review paper enlightening and useful for tailoring advanced catalysts with precise design.

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## Introduction

Excessive carbon dioxide (CO<sub>2</sub>) emissions, one of the primary greenhouse gases, have caused serious environmental concerns, which result in global warming and climate change.



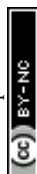
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The atmospheric CO<sub>2</sub> concentration has continued to rise over the past decades, exceeding 410 ppm.<sup>1</sup> Establishing a practical framework for mitigating CO<sub>2</sub> emissions has been periodically discussed at the governmental level. Most nations have signed the Paris Agreement during the UN Climate Change Conference (COP21), which emphasizes limiting global warming to well below 2 degrees Celsius by restricting cumulative CO<sub>2</sub> emissions to less than one trillion tons of CO<sub>2</sub>.<sup>2</sup> According to recent climate reports, the global average temperature is projected to rise by over 2 °C by 2050 and more than 4 °C by 2100.<sup>3</sup> Considerable attention has been directed towards stabilizing atmospheric CO<sub>2</sub> levels, not only by reducing CO<sub>2</sub> emissions but also by effectively utilizing CO<sub>2</sub>. CO<sub>2</sub>, as the main industrial C<sub>1</sub> carbon source, can be utilized in a wide range of applications.

Over the past few decades, there has been a significant rise in research studies on CO<sub>2</sub> hydrogenation, demonstrating the effectiveness of CO<sub>2</sub> hydrogenation reactions in reducing CO<sub>2</sub> emissions. CO<sub>2</sub> hydrogenation of valuable chemicals has been widely explored using catalytic CO<sub>2</sub> conversion technologies such as thermocatalytic conversion, photocatalytic conversion, and electrocatalytic conversion.<sup>4</sup> Thermocatalytic conversion, among these technologies, is the most promising due to its high efficiency and great opportunities in large-scale applications.<sup>5,6</sup> Thermocatalytic CO<sub>2</sub> conversion also promotes a more sustainable approach by utilizing renewable green hydrogen generated *via* wind power, photovoltaic cells, or excess nuclear power from water electrolysis systems.<sup>7–9</sup>

CO<sub>2</sub> hydrogenation is an excellent strategy that mitigates CO<sub>2</sub> release from chemical processes and produces valuable chemicals and fuels, including methane, methanol, ethanol, C<sub>2</sub>–C<sub>4</sub> alcohols, *etc.*, depending on the nature of the specific catalytic active sites and the reaction conditions.<sup>10</sup> Particularly, the CO<sub>2</sub>-to-methanol route has been a promising industrial process due to the significant demand for methanol.<sup>11</sup> On the other hand, higher alcohols (C<sub>2</sub>–C<sub>4</sub> alcohols) offer benefits over

methanol, including greater energy density,<sup>12</sup> lower azeotropic behaviour,<sup>13</sup> and less water affinity,<sup>12</sup> making them strong alternatives for methanol substitutes in fuels and fuel additives. Also, synthesizing higher alcohols, especially ethanol, at low temperatures is thermodynamically more desirable than methanol due to lower Gibbs free energy and a greater equilibrium constant value.<sup>14</sup> Additionally, higher alcohols are used as solvents for resins, fats, waxes, ethers, and gums, as well as useful feedstock and intermediates for various chemicals and pharmaceuticals.<sup>15</sup>

Despite these benefits, achieving high conversion of CO<sub>2</sub> and high selectivity of higher alcohols has remained challenging. An advanced catalyst design is required to promote carbon chain growth and overcome the high kinetic energy barrier associated with CO insertion through C–C coupling into the carbon chain, ultimately facilitating the formation of ethanol and higher alcohols.<sup>16,17</sup> To increase CO<sub>2</sub> conversion and selectivity for higher alcohols, it is essential to modify the metal active sites, the metal–metal interfaces, the metal–support interactions, and the physical and chemical characteristics of the catalysts to promote key reaction intermediates through balancing, suppressing or synchronizing reactions including reverse water–gas shift (RWGS), Fischer–Tropsch (FT) synthesis, CO<sub>2</sub> hydrogenation to alkanes and alkenes, methanol synthesis, and higher alcohol synthesis (HAS).

There have been critical reviews regarding CO<sub>2</sub> hydrogenation for HAS.<sup>14,18,19</sup> Cui *et al.*<sup>18</sup> centered on the various catalytic systems and reaction mechanisms involved by the thermodynamic and kinetic analyses in the conversion of CO<sub>2</sub> into alcohols with discussion focusing on the structure–activity relationship, which was relatively comparable to Latsiou *et al.*<sup>19</sup> but the latter focused solely on HAS. In contrast, Xu *et al.*<sup>14</sup> focused on advancements in catalyst design and performance by categorizing them into different catalyst families with a brief discussion on the promoter and support effect and some



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information on reaction mechanisms. This review aims to provide a comprehensive and systematic analysis of the critical knowledge and research gap that impacts the rational design of effective catalysts for CO<sub>2</sub> hydrogenation to higher alcohols. By summarizing the recent research advancements, we present an integrated and in-depth investigation into the roles of different types of metals, promoters, and supports in catalyst system development in HAS through extensive case-by-case studies. We attempt to address this from the viewpoint of stabilizing active phases and structure–performance relationships to improve the production of higher alcohols, hoping that this review may provide insights on the precise engineering of the interplay between active metal sites, supports and promoters at an atomic scale for optimizing HAS catalytic performance. In addition, this review also underlines the influence of oxygen vacancies and emphasizes the reaction mechanism based on *in situ* characterizations and theoretical calculations. Finally, the conclusion and future perspective are explored for future investigation in HAS.

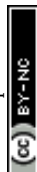
### Catalyst design and development

Research on CO<sub>2</sub> hydrogenation for HAS can be categorized into four main groups: (1) modified Cu-based methanol synthesis catalysts,<sup>20,21</sup> (2) modified Co- or Fe-based FT synthesis catalysts,<sup>22–27</sup> (3) noble metal-based (Rh, Pd, Ir, Au, and Pt) catalysts,<sup>28–32</sup> and (4) Mo-based catalyst,<sup>33,34</sup> as listed in Table 1. Cu-based catalysts are well-known candidates in methanol synthesis and RWGS due to their superior performance and cost-effectiveness.<sup>54–56</sup> It is now widely recognized that metallic Cu promotes non-dissociative CO activation and its insertion step, thus producing mainly CO and methanol instead of higher alcohols. Modifications of Cu-based catalysts have been developed to enhance the selectivity of higher alcohols.<sup>18</sup> Highly dispersed Cu nanoparticles embedded in the Na-beta zeolite (Cu@Na-beta) were synthesized and tested for CO<sub>2</sub> hydrogenation reaction in a fixed bed reactor.<sup>35</sup> The Cu@Na-beta catalyst showed an excellent ethanol selectivity of 79% at 300 °C and 2.1 MPa and a space-time yield (STY) of 398 mg g<sub>cat</sub><sup>−1</sup> h<sup>−1</sup> at a CO<sub>2</sub> conversion of approximately 18%. The authors proposed that the Na-beta can result in the confinement effect of Cu nanoparticles and restrict the formation of unwanted byproducts. Electropositive Cu species were detected in small amounts in the complex Cu@Na-beta catalyst using X-ray photoelectron spectroscopy (XPS) and Cu LMM auger spectra analysis, but none were found in the other prepared catalysts, confirming the cooperative interaction between Cu and Na-beta. The high catalytic performance can be attributed to the synergistic interaction between Cu nanoparticles and the zeolite framework. An *et al.*<sup>21</sup> reported that the combination of cooperative Cu<sup>I</sup> sites on a Zr<sub>12</sub> cluster with a metal–organic framework (MOF) exhibited a high ethanol selectivity of >99% with the addition of alkali metal as promoters. Cu<sup>I</sup> species are identified as the active sites for ethanol formation, and the role of intimate Cu<sup>I</sup>–Cu<sup>I</sup> dual sites stabilized by MOF is crucial for inducing the H<sub>2</sub> activation in ethanol synthesis, resulting in the formation of (Cu<sup>2+</sup>–H<sup>−</sup>)<sup>2</sup> followed by promoting the C–C

coupling of methanol and formyl species. Meanwhile, alkali cation (Cs<sup>+</sup>) creates an electron-rich environment for the Cu center to stabilize the formyl intermediates. This results in the formation of CH<sub>3</sub>CHO, which can undergo reductive elimination, producing methanol, ethanol, and water and regenerating the Cu<sup>I</sup>–Cu<sup>I</sup> sites.

Co-based catalysts have been extensively developed as FT synthesis catalysts due to their strong hydrogenation ability.<sup>57</sup> Interestingly, several studies suggested that the co-existence of Co<sup>0</sup> and CoO<sub>x</sub> phases in Co-based catalysts can promote the synthesis of ethanol. For instance, Wang *et al.*<sup>27</sup> demonstrated that the co-existing phases of Co<sup>0</sup> and CoO<sub>x</sub> in CoAlO<sub>x</sub> catalysts are favored in ethanol synthesis. The authors discovered that the different reduction temperatures significantly affected the catalyst performance. CoAlO<sub>x</sub>-600 catalyst, which the catalyst reduced at 600 °C, exhibited an outstanding ethanol selectivity of 92.1% and a space-time yield of 0.444 mmol g<sub>cat</sub><sup>−1</sup> h<sup>−1</sup>, achieving the best catalytic performance compared to other CoAlO<sub>x</sub> catalysts, which were reduced at a temperature between 300 °C and 650 °C (Fig. 1). Moreover, methanol, *n*-propanol and *n*-butanol were also obtained in this catalyst, further validating the effectiveness of Co-based catalysts in CO<sub>2</sub> hydrogenation to higher alcohols. Using the extended X-ray absorption fine structure (EXAFS) spectroscopy, it was observed that the characteristic peak of metallic Co<sup>0</sup> showed up after reduction at 600 °C with the co-existence of CoO<sub>x</sub> species. This suggests that more hydrogen activation can occur due to the presence of metallic Co<sup>0</sup>, resulting in higher catalytic performance. However, CoAlO<sub>x</sub> catalysts reduced at temperatures higher than 600 °C, with more metallic sites and a relatively small amount of CoO<sub>x</sub> species, encountered an increase in methanol yield but a decrease in ethanol yield.

Similar findings were reported by Ding *et al.*,<sup>42</sup> indicating the significance of co-existing Co<sup>0</sup> and CoO<sub>x</sub> species in facilitating ethanol formation. The authors successfully synthesized silicalite-1 (S-1) with abundant silanols supported on Co species with 5 wt% and 15 wt% of Co loadings, while the sample synthesized using the same procedure but without the addition of NaOH in the precursor gel was denoted as S–S. Of interest is the capability of this novel approach to utilize strong metal-support interaction (SMSI), thus forming Si–O–Co chemical bonds that can stabilize the co-existence Co<sup>0</sup> and CoO species. The co-existence Co<sup>0</sup> and CoO on Co/S-1 was evidenced using characterization techniques such as X-ray diffraction (XRD), CO adsorption (CO-IR), and quasi *in situ* XPS analysis. The catalytic performance of the 5 wt% and 15 wt% Co loadings supported on S-1 showed similar results (Fig. 2). This is consistent with the comparable amount of exposed active sites, *i.e.*, 38.4 μmol g<sup>−1</sup> and 38.2 μmol g<sup>−1</sup> for 15Co/S-1 and 5Co/S-1, respectively, calculated from H<sub>2</sub>-TPD. Besides, 15Co/S-1 and 5Co/S-1 also showed similar results for ethanol selectivity (26% and 27%) and CO<sub>2</sub> conversion (12.1% and 13.9%). A volcano-shaped relationship between CO<sub>2</sub> conversion and the reduction temperature was concluded, highlighting the importance of an optimal reduction temperature to balance the metallic Co<sup>0</sup> and CoO sites. CO<sub>2</sub> conversion increased as the reduction temperature rose from 200 °C to 300 °C but decreased at higher





**Table 1** Summary of reaction conditions and comparison of HAS over selected catalysts

| Catalyst                                                 | T<br>(°C) | P<br>(MPa) | CO <sub>2</sub> /H <sub>2</sub><br>ratio | GHSV<br>(mL g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> ) | X <sub>CO<sub>2</sub></sub><br>(%) | S <sub>CO</sub><br>(%) | S <sub>C<sub>2</sub>H<sub>6</sub></sub><br>(%) | S <sub>MeOH</sub><br>(%) | S <sub>HA</sub> <sup>a</sup><br>(%) | STY <sub>HA</sub> <sup>a</sup>                                              | Ref. |
|----------------------------------------------------------|-----------|------------|------------------------------------------|--------------------------------------------------------------|------------------------------------|------------------------|------------------------------------------------|--------------------------|-------------------------------------|-----------------------------------------------------------------------------|------|
| Cu@Na-beta                                               | 300       | 2.1        | 1:3                                      | 12 000                                                       | 18.0                               | 21.0                   | —                                              | —                        | 79.0 (ethanol)                      | 398 mg g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> (ethanol)             | 35   |
| Na-CuCo-9                                                | 330       | 4.0        | 1:1                                      | 5000                                                         | 20.1                               | 26.5                   | 53.8                                           | —                        | 26.8 (ROH)                          | 80.8 mg g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> (C <sub>3</sub> ,OH) | 36   |
| 4.6 K-CuMgZnFe                                           | 320       | 5.0        | 1:3                                      | 6000                                                         | 30.4                               | 30.6                   | 52.4                                           | 1.3                      | 15.9                                | 69.6 mg g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>                      | 20   |
| CuFeZn-0.7PDA                                            | 310       | 4.0        | 1:3                                      | 7200                                                         | 10.6                               | 43.2                   | 22.0                                           | —                        | 34.8 (ROH)                          | 58.2 mg g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>                      | 16   |
| Cs-Cu <sub>0.8</sub> Fe <sub>1.0</sub> Zn <sub>1.0</sub> | 330       | 5.0        | 1:3                                      | 4500                                                         | 36.6                               | —                      | —                                              | —                        | 19.8                                | 1.47 mmol g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>                    | 37   |
| CuZnAl/K-CuMgZnFe                                        | 320       | 5.0        | 1:3                                      | 6000                                                         | 42.3                               | 13.8                   | 67.6                                           | 1.3                      | 17.4                                | 2.24 mmol g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>                    | 38   |
| Cr (1%)-CuFe                                             | 320       | 4.0        | 1:3                                      | 6000                                                         | 38.4                               | 14.8                   | —                                              | —                        | 29.2                                | 104.1 mg g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> (ethanol)           | 39   |
| 2% Na-Co/SiO <sub>2</sub>                                | 310       | 5.0        | 1:3                                      | 6000                                                         | 53.2                               | —                      | —                                              | —                        | 12.9 (ROH)                          | 1.10 mmol g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> (ethanol)          | 40   |
| CoAlO <sub>x</sub> -600                                  | 140       | 4.0        | 1:3                                      | Tank                                                         | —                                  | —                      | —                                              | —                        | 92.1 (ethanol)                      | 0.44 mmol g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> (ethanol)          | 27   |
| Co/La <sub>4</sub> Ga <sub>2</sub> O <sub>9</sub>        | 270       | 3.5        | 1:3                                      | 3000                                                         | 4.6                                | 15.4                   | 34.6                                           | 15.3                     | 34.7 (ethanol)                      | —                                                                           | 41   |
| 5Co/S-1                                                  | 250       | 2.0        | 1:3                                      | 4670                                                         | 13.9                               | 0                      | 58.0                                           | —                        | 27.0 (ethanol)                      | 0.83 mmol g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> (ethanol)          | 42   |
| 2.5K5Co-In <sub>2</sub> O <sub>3</sub>                   | 380       | 4.0        | 1:3                                      | 2250                                                         | 36.6                               | 80.8                   | —                                              | —                        | —                                   | 3.73 mmol g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>                    | 43   |
| 2% Na-Fe@C/5% K-CuZnAl                                   | 320       | 5.0        | 1:3                                      | 4500                                                         | 39.2                               | 9.4                    | —                                              | —                        | 35.0 (ethanol)                      | —                                                                           | 25   |
| FeNaS-0.6                                                | 320       | 3.0        | 1:3                                      | 8000                                                         | 32.0                               | 20.7                   | —                                              | —                        | 12.8                                | 78.5 mg g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>                      | 23   |
| K-0.82-FeIn/Ce-ZrO <sub>2</sub> -900                     | 300       | 10.0       | 1:3                                      | 4500                                                         | 29.6                               | 13.4                   | 53.2                                           | 4.7                      | 28.7                                | —                                                                           | 44   |
| ZnFe <sub>2</sub> O <sub>4</sub> /Fe-Zn-Na <sup>#</sup>  | 320       | 5.0        | 1:3                                      | 12 000                                                       | 29.1                               | 21.8                   | —                                              | —                        | 18.6                                | 137.7 mg g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>                     | 45   |
| Ir <sub>1</sub> -In <sub>2</sub> O <sub>3</sub>          | 200       | 6.0        | 1:5                                      | Tank                                                         | —                                  | —                      | —                                              | —                        | 99.7 (ethanol)                      | 0.99 mmol g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> (ethanol)          | 46   |
| Pd <sub>3</sub> Cu NPs/P25                               | 240       | 3.0        | 1:3                                      | 3000                                                         | 9.2                                | —                      | —                                              | 0.8                      | 99.2 (ethanol)                      | 59.2 mg g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> (ethanol)            | 47   |
| PdFe-6.9 (37 nm)                                         | 200       | 3.2        | 1:3                                      | Tank                                                         | —                                  | —                      | —                                              | —                        | 92.0 (ethanol)                      | 41.50 mmol g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> (ethanol)         | 48   |
| 0.3K-1Pd/Fe <sub>2</sub> O <sub>3</sub>                  | 300       | 6.0        | 1:3                                      | 6000                                                         | 33.3                               | 27.9                   | —                                              | —                        | 19.1                                | 86.5 mg g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>                      | 49   |
| 0.19Na-Rh@S-1                                            | 320       | 4.0        | 1:3                                      | 6000                                                         | 30.0                               | 23.0                   | —                                              | —                        | 13.4                                | 52.2 mg g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>                      | 26   |
| 2Rh0.5Fe0.5Na/CeO <sub>2</sub>                           | 250       | 5.0        | 1:3                                      | 6000                                                         | 10.0                               | —                      | —                                              | —                        | 24.0 (ethanol)                      | 72.00 mmol g <sub>rh</sub> <sup>-1</sup> h <sup>-1</sup> (ethanol)          | 50   |
| Na-Rh-FeO <sub>x</sub> /ZSM-5                            | 250       | 3.0        | 1:3                                      | 6000                                                         | 9.8                                | 32.1                   | 15.9                                           | 27.3                     | 21.5 (ethanol)                      | 63.5 mmol g <sub>rh</sub> <sup>-1</sup> h <sup>-1</sup> (ethanol)           | 51   |
| K <sub>0.2</sub> Rh <sub>0.2</sub> /βMo <sub>2</sub> C   | 200       | 1.0        | —                                        | 3600                                                         | 7.0                                | —                      | —                                              | —                        | 97.0 (ethanol)                      | 1.10 mmol g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> (ethanol)          | 52   |
|                                                          | 150       | 6.0        | 1:3                                      | Tank                                                         | —                                  | —                      | —                                              | —                        | 72.1 (ethanol)                      | 0.03 mmol g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> (ethanol)          | 53   |

<sup>a</sup> Selectivity and space-time yield of a specific product are indicated in parentheses.

reduction temperatures. Notably, the Co species in 5Co/S-1 was fully reduced into metallic  $\text{Co}^0$  at 400 °C. The increase in  $\text{CO}_2$  conversion can be explained by the increase in metallic  $\text{Co}^0$  sites, which enhance the dissociation activation of hydrogen on the surface and facilitate the breaking of the C–O bond. However, at higher reduction temperature, aggregation of metals may occur, leading to catalyst deactivation.<sup>25</sup> For the same reason, although 5Co/S-1 exhibited superior catalytic activity during the initial phase of the reaction, but it lost stability over time due to gradual reduction of  $\text{CoO}_x$  to  $\text{Co}^0$  under reaction conditions, causing the aggregation of cobalt nanoparticles. In summary, the so-called protection provided by Si–O–Co bond may be able to postpone the reduction of  $\text{CoO}_x$  to  $\text{Co}^0$ , but it is not capable of completely preventing  $\text{CoO}_x$  from fully reducing into  $\text{Co}^0$ , which ultimately affects the catalyst stability.

Previous studies have shown that Pd-based catalysts are effective for  $\text{CO}_2$  hydrogenation to methanol and have recently gained attention in HAS. For instance, Lou *et al.*<sup>47</sup> reported  $\text{CO}_2$  hydrogenation to ethanol over Pd/CeO<sub>2</sub> catalysts. In their study, Pd dimers ( $\text{Pd}_2/\text{CeO}_2$ ) and Pd nanoparticles (nano-Pd/CeO<sub>2</sub>) were supported on CeO<sub>2</sub> with nanorods morphology.  $\text{Pd}_2/\text{CeO}_2$  catalyst with the unique geometric structure of Pd dimers exhibited impressive catalytic activity with 9.2% of  $\text{CO}_2$  conversion, 99.2% of high ethanol selectivity, and STY of 45.6  $\text{g}_{\text{ethanol}} \text{g}_{\text{Pd}}^{-1} \text{h}^{-1}$  at 240 °C and 3 MPa. The STY of atomically dispersed Pd dimers on the CeO<sub>2</sub> catalyst was 90 times higher than that of nano-Pd/CeO<sub>2</sub> with STY of 0.5  $\text{g}_{\text{ethanol}} \text{g}_{\text{Pd}}^{-1} \text{h}^{-1}$  because CO was the primary product formed over nano-Pd/CeO<sub>2</sub> catalyst. High-angle dark-field scanning transmission electron microscope (HAADF-STEM) images further revealed the absence of Pd clusters and particles on both fresh and used  $\text{Pd}_2/\text{CeO}_2$  catalysts, hypothesizing that Pd species are atomically and uniformly distributed on the CeO<sub>2</sub> support. To the best of our knowledge, the formation of agglomerated Pd clusters and particles can result in a decrease in higher alcohol synthesis. They conclude that the catalytic performance is sensitive to different Pd nanoparticle sizes, with single-atom catalyst (SAC) of Pd dimers exhibiting the best catalytic performance.

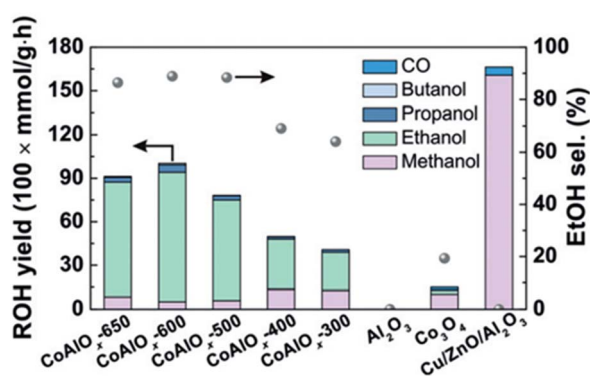


Fig. 1 Catalytic performance of various catalysts based on their alcohols yields and ethanol selectivity. Reprinted with permission from ref. 27. Copyright 2018 John Wiley and Sons, Inc.

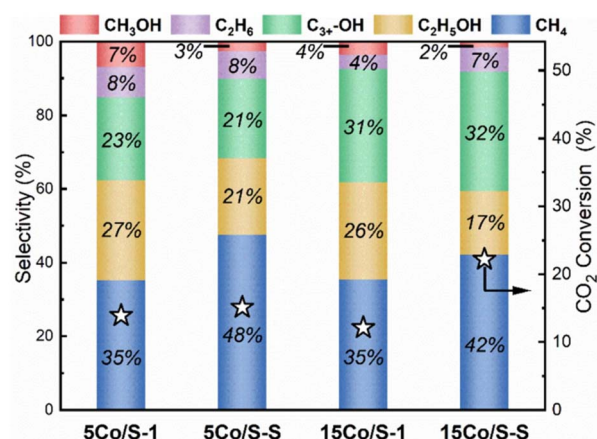


Fig. 2  $\text{CO}_2$  conversion and product selectivity by Co/S-1 and Co/S-S catalysts with different 5 and 15 wt% Co contents. Reprinted with permission from ref. 42. Copyright 2024 Elsevier.

Therefore, this means that tailoring the active sites of a catalyst at an atomic scale can remarkably promote HAS. Meanwhile, the CO adsorption strength, considered the key factor in determining product selectivity, was investigated through *in situ* diffuse reflectance infrared Fourier transform spectroscopy experiments using CO as a probe molecule (CO-DRIFTS). The result demonstrated that the Pd species in  $\text{Pd}_2/\text{CeO}_2$  catalyst were mostly Pd dimers with no neighbouring Pd atoms, which exhibited stronger CO adsorption strength. Claiming that the stronger binding strength of CO over  $\text{Pd}_2/\text{CeO}_2$  catalyst can effectively inhibit CO desorption and trigger the C–C coupling reactions between CO and  $\text{CH}_3$  intermediate, the formation of ethanol is, therefore, enhanced.

A similar concept has been implemented using an Ir-based catalyst to demonstrate that highly dispersed atomic active sites can promote ethanol generation. In particular, bifunctional  $\text{Ir}_1\text{-In}_2\text{O}_3$  SAC was synthesized through a wet-chemical approach, and the  $\text{CO}_2$  hydrogenation reactions were carried out in an aqueous solution.<sup>46</sup> By impregnating Ir onto the  $\text{In}_2\text{O}_3$  support, oxygen vacancy ( $\text{O}_v$ ) is induced by partially reducing  $\text{In}_2\text{O}_3$  in the  $\text{H}_2$  atmosphere, as shown in Fig. 3. As a result, the adjacent oxygen vacancy can bind with monoatomic Ir to form Lewis acid–base pair. The partially reduced  $\text{In}_2\text{O}_3$  and Lewis acid–base pair act as two active sites, which can enhance the  $\text{CO}_2$  adsorption and activation into  $\text{CO}^*$  intermediates. *In situ* DRIFTS experiment results showed further evidence supporting the existence of  $\text{Ir}^{\delta+}\text{-CO}^*$  intermediates, while the *in situ* Fourier transform infrared spectroscopy (FTIR) confirmed the existence of  $\text{CH}_3\text{O}^*\text{-O}_v$  intermediates. It is concluded that  $\text{Ir}_1\text{-In}_2\text{O}_3$  SAC promotes the C–C coupling by coupling the  $\text{Ir}^{\delta+}\text{-CO}^*$  intermediates with the  $\text{CH}_3\text{O}^*\text{-O}_v$  intermediates to enhance ethanol selectivity. The  $\text{CO}_2$  hydrogenation experiment achieved a high selectivity to ethanol (>99%) and a turnover frequency (TOF) of up to 481  $\text{h}^{-1}$  in this study. The authors also discovered that the ethanol formation was suppressed from 85.3% to 5.7% when the Ir loading increased from 0.2 wt% to 1.0 wt%, which can be ascribed to the agglomeration of Ir nanoparticles and the over-reduction of  $\text{In}_2\text{O}_3$ .

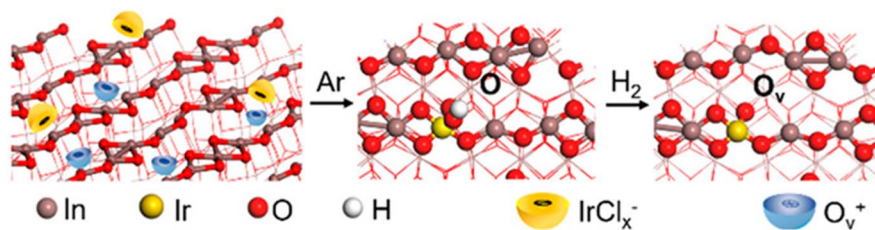


Fig. 3 Schematic illustration of synthesis procedure for  $\text{Ir}_1\text{-In}_2\text{O}_3$  SAC. The diagram depicts the generation of  $\text{O}_\text{v}$  by partially reducing  $\text{In}_2\text{O}_3$  under  $\text{H}_2$  atmosphere prior to impregnating of the Ir. These  $\text{O}_\text{v}$  then act as the anchoring site for single Ir atoms and promote the trapping of  $\text{IrCl}_6^{2-}$ . Reprinted with permission from ref. 46. Copyright 2020 American Chemical Society.

Besides monometallic catalyst systems, bimetallic catalyst systems have recently emerged as promising candidates for  $\text{CO}_2$  hydrogenation to higher alcohols. Several studies have shown that introducing a second metal into Cu or noble metal can alter the electronic structure of the catalyst and improve the catalytic performance. Irshad *et al.*<sup>36</sup> proposed that in the synthesized Cu-Co bimetallic catalyst, Cu and Co active sites each serve their distinct roles. Na-promoted bimetallic Cu-Co- $\gamma$  catalysts, combining the capabilities of methanol synthesis and C-C coupling, were prepared with different Cu loadings ( $\gamma = \text{Cu}/(\text{Cu} + \text{Co}) \times 10$ ) *via* coprecipitation method and investigated for the production of higher alcohols. In simpler terms, the Cu site is accountable for the rapid RWGS to produce CO,<sup>58</sup> and, subsequently, experiencing methanol synthesis. In contrast, Co site is responsible for forming  $\text{CH}_x$  intermediates through C-O dissociation.<sup>59</sup> Subsequently,  $\text{CH}_3\text{CO}^*$  is formed through C-C coupling between the CO produced and  $\text{CH}_x$  intermediates, which, after deep hydrogenation, produce acetaldehyde and, ultimately, ethanol or *n*-butanol.<sup>60,61</sup> Based on their conclusion, acetaldehyde is observed as the key intermediate in the synthesis of *n*-butanol. The “best case” catalyst in their studies was Na-CuCo-9 catalyst, which demonstrated a high  $\text{C}_{3+}\text{OH}/\text{ROH}$  fraction of 73.5%, giving a high  $\text{STY}_{\text{C}_3+\text{OH}}$  of 80.8  $\text{mg g}_{\text{cat}}^{-1} \text{h}^{-1}$  while the overall alcohol selectivity was 58% with  $\text{CO}_2$  conversion of 22.1%. Besides, Na-the CuCo-9 catalyst exhibited superior long-term stability without any detrimental effect on its catalytic performance. However, this study did not explore the role of Na as an alkali promoter. The role of alkali metal as a promoter will be further addressed in a later section. On the other hand, Pd-Cu nanoparticles with different composition ratios and supports for ethanol synthesis were investigated in a slurry batch reactor.<sup>48</sup> By adjusting to the ideal Pd/Cu ratio and catalyst support, the  $\text{Pd}_2\text{Cu}/\text{P25}$  catalyst displayed a high selectivity to ethanol of 92.5% with a TOF value of 359  $\text{h}^{-1}$ . The study, however, did not emphasize the formation of the active phase for HAS; instead, it focused on the presence of charge transfer between Pd and Cu. The formation of electronic interaction caused by charge transfer can improve the reduction of surface oxides to their metallic states, which the authors strongly believed to be the active sites for  $\text{CO}_2$  activation, thus benefitting the overall  $\text{CO}_2$  hydrogenation reaction.  $\text{Pd}_2\text{Cu}$  nanoparticles deposited on various supports such as  $\text{SiO}_2$ ,  $\text{CeO}_2$ ,  $\text{Al}_2\text{O}_3$ , and P25 were also investigated, and the  $\text{Pd}_2\text{Cu}$  supported on the P25 catalyst emerged as the best,

demonstrating the highest TOF and ethanol selectivity out of the four catalysts, which can be attributed to the presence of oxygen vacancies.

Another exciting study is the synthesis of a bimetallic PdFe catalyst.<sup>49</sup> Iron carbides ( $\text{FeC}_x$ ) are well known as one of the active phases, which positively affects HAS activity, although it is not very active at low  $\text{CO}$  partial pressures.<sup>62</sup> Combining  $\text{FeC}_x$  phases with metal species can form metal- $\text{FeC}_x$  interfaces to promote HAS activity. It is presumed that the synergistic effects between PdFe alloy and  $\text{Fe}_5\text{C}_2$  exist, forming PdFe alloy- $\text{Fe}_5\text{C}_2$  interfaces that can eventually promote HAS catalytic performance. Under reaction condition of 300 °C, 5 MPa and  $\text{WHSV} = 6000 \text{ mL g}_{\text{cat}}^{-1} \text{h}^{-1}$ , higher alcohol selectivity of 26.5% and STY of 86.5  $\text{mg g}_{\text{cat}}^{-1} \text{h}^{-1}$  were obtained over PdFe catalyst with Pd loading of 6.9 wt%. The authors demonstrated for the first time that transition metal or alloy could induce the formation of deep iron carbidization without the aid of an alkali ion as a promoter. The presence of PdFe alloy and  $\text{Fe}_5\text{C}_2$  was verified through *in situ* XRD experiments, showing that  $\text{Fe}_2\text{O}_3$  in spent PdFe-6.9% catalyst was instantly converted to  $\text{Fe}_3\text{O}_4$  under hydrogen reduction condition and completely transformed into  $\text{Fe}_5\text{C}_2$  under  $\text{CO}_2$  hydrogenation reaction process within 30 minutes. The XRD analysis also demonstrated that the formation of  $\text{Fe}_5\text{C}_2$  phase appeared when the Pd loading  $\geq 4.3$  wt% under  $\text{CO}_2$  hydrogenation reaction condition. At the same time, PdFe alloy was formed when reduced Fe atoms from  $\text{Fe}_2\text{O}_3$  migrated to the Pd surface. The formation of PdFe alloy- $\text{Fe}_5\text{C}_2$  interfaces was confirmed through HAADF-STEM images of the spent catalyst. Further evidence of the PdFe alloy- $\text{Fe}_5\text{C}_2$  interface formation was shown when the authors compared the HAS activity with the reference catalyst (physically mixing 6.9 Pd/ $\gamma\text{-Al}_2\text{O}_3$  +  $\text{Fe}_2\text{O}_3$  catalyst), which demonstrated no HAS activity. Overall, PdFe alloy mainly generates CO by the RWGS reaction, while  $\text{Fe}_5\text{C}_2$  is essential for CO dissociation and carbon chain propagation. The adsorbed alkyl is then reacted with CO at the PdFe alloy- $\text{Fe}_5\text{C}_2$  interfaces, which is subsequently hydrogenated to ethanol. The authors concluded that PdFe alloy- $\text{Fe}_5\text{C}_2$  interfaces are primarily responsible for HAS in their bimetallic system. A study by Yang *et al.*<sup>45</sup> also observed a similar effect, identifying carburized metal-based catalysts ( $\text{ZnFe}_2\text{O}_4/\text{Fe-Zn-Na}^\#$ ) as active phases for  $\text{CO}_2$  hydrogenation in HAS. Unlike Wang *et al.*<sup>49</sup> research, in which  $\text{Fe}_5\text{C}_2$  was reported to be induced after hydrogen reduction and during the  $\text{CO}_2$  hydrogenation reaction process, Yang *et al.*<sup>45</sup> proposed a tandem



catalysis strategy by synthesizing Fe–Zn–Na<sup>#</sup> catalyst (pre-reduced using H<sub>2</sub> for 8 hours) and physically mixing it with ZnFe<sub>2</sub>O<sub>4</sub> catalyst to generate FeC<sub>x</sub>. However, similar to Wang *et al.*<sup>49</sup> findings, the Fe<sub>5</sub>C<sub>2</sub> phase also appeared after a few hours under reaction conditions as indicated by XRD characterization results. Additionally, CO<sub>2</sub> conversion rapidly increased from 0.3% to 31.8% after 2 h time on stream (TOS) at 300 °C. Higher alcohol selectivity showed a similar pattern, sharply rising from 1.1% to 16.4%. Mössbauer spectroscopy analysis and XRD peaks indicated that the iron species in the spent ZnFe<sub>2</sub>O<sub>4</sub>/Fe–Zn–Na<sup>#</sup> catalyst were primarily Fe<sub>3</sub>O<sub>4</sub>, ZnFe<sub>2</sub>O<sub>4</sub> and Fe<sub>5</sub>C<sub>2</sub>. The authors inferred that Fe<sub>3</sub>O<sub>4</sub> is responsible for CO formation (RWGS reaction), ZnFe<sub>2</sub>O<sub>4</sub> favors the formation of oxygenates, while Fe<sub>5</sub>C<sub>2</sub> enhances C–C coupling reaction and initiates CO insertion to produce higher alcohols.

Wang *et al.*<sup>25</sup> utilized the multifunctional catalyst of 2% Na–Fe@C/5% K–CuZnAl using a tandem catalysis strategy for CO<sub>2</sub> hydrogenation to ethanol. The Fe@C catalyst was synthesized by pyrolyzing the Fe-based MOFs under a nitrogen atmosphere to promote uniformly distributed Fe active sites due to the periodic arrangement of organic linkers and metallic centers and to control the physicochemical properties of the MOF-derived catalyst. Na doping on a Fe-based catalyst is considered to favour alkene synthesis. Na doping enhances the adsorption of acidic CO<sub>2</sub> due to the formation of a Fe–C bond by electron transfer from Na–Fe@C to CO<sub>2</sub> molecules. Thus, the selectivity of ethanol was slightly enhanced with a slight additional amount of HA produced by adding 2% Na to Fe@C (a 2% Na–Fe@C catalyst). The CuZnAl catalyst was combined with the Na–Fe@C catalyst, which was prepared by mixing two catalytic granules, to boost the synthesis of ethanol from CO<sub>2</sub> hydrogenation. The ethanol selectivity increased from 14% (over a 2% Na–Fe@C catalyst) to 35% (over a 2% Na–Fe@C/5% K–CuZnAl multifunctional catalyst), as shown in Fig. 4. The Na–Fe@C catalyst promotes the reaction of RWGS (over iron oxide, Fe<sub>3</sub>O<sub>4</sub>) and FTS (over iron carbide, mainly Fe<sub>5</sub>C<sub>2</sub>), while the addition of the K–CuZnAl catalyst contributes to not only the Fe crystal structure and the catalytic network but also a highly efficient catalyst for the synthesis of methanol to form the intermediate species (formate and CH<sub>x</sub>O\*).

Furthermore, it is possible that the reaction intermediates produced from one catalytic site could diffuse onto the interface of another catalytic site to synthesize the product over

a multifunctional catalyst during the tandem process. The authors suggested that the reaction intermediates (formate and CH<sub>x</sub>O\*) could desorb from K–CuZnAl and diffuse onto the interface of the Fe-based catalyst for the possible formation of ethanol through C–C coupling. Moreover, it is necessary to conduct a more in-depth theoretical analysis and *in situ* characterization for multifunctional catalysts due to the highly complex process. Furthermore, the intimacy mode of the 2% Na–Fe@C/5% K–CuZnAl in the cascade reaction produces the highest selectivity and conversion through the granule-mixing mode with 1 g of quartz sand, which may be attributed to active site coverage in the physical-mixing mode of the 2% Na–Fe@C/5% K–CuZnAl. The granule-mixing mode allows for an increase in the spatial distance between distinct catalytic components. The 2% Na–Fe@C/5% K–CuZnAl multifunctional catalyst achieved an ethanol selectivity of 35% with a CO<sub>2</sub> conversion of 39.2%.

### Role of promoters or additives

In CO<sub>2</sub> hydrogenation, alkali metals, alkaline earth metals, and transition metals can act as promoters or additives to enhance the overall catalytic activity.<sup>63</sup> Some research reported that introducing alkali metals can significantly inhibit hydrocarbon formation by suppressing alkylation reaction, providing opportunities for higher alcohol production.<sup>44</sup> Some reported that alkali metals could promote structural effects by stabilising active sites or interfaces.<sup>40</sup> The promotional effect of alkali metals in HAS was intensively studied by different research groups. For example, Zhang *et al.*<sup>40</sup> synthesized Co/SiO<sub>2</sub> catalysts incorporating alkali metals. Under a CO<sub>2</sub> hydrogenation reaction condition of 250 °C, 5 MPa, and WHSV = 6000 mL g<sub>cat</sub><sup>−1</sup> h<sup>−1</sup>, Co/SiO<sub>2</sub> catalyst without any alkali metal promoter and Li–Co/SiO<sub>2</sub> produced only hydrocarbon. In contrast, high selectivity in alcohols, olefins, and CO was achieved over Na–Co/SiO<sub>2</sub> and K–Co/SiO<sub>2</sub> with a decrease in CH<sub>4</sub> selectivity compared to Co/SiO<sub>2</sub> and Li–Co/SiO<sub>2</sub> catalysts. Among the four catalysts, the Na-doped Co/SiO<sub>2</sub> catalyst exhibited the best alcohol selectivity and was further investigated for its role in HAS. It was demonstrated that CO<sub>2</sub> conversion and hydrocarbon selectivity decreased with higher Na contents increasing from 0 to 5 wt% (Fig. 5). The highest alcohol selectivity (12.5%) was obtained over an optimum Na content of 2 wt% Na–Co/SiO<sub>2</sub> catalyst with

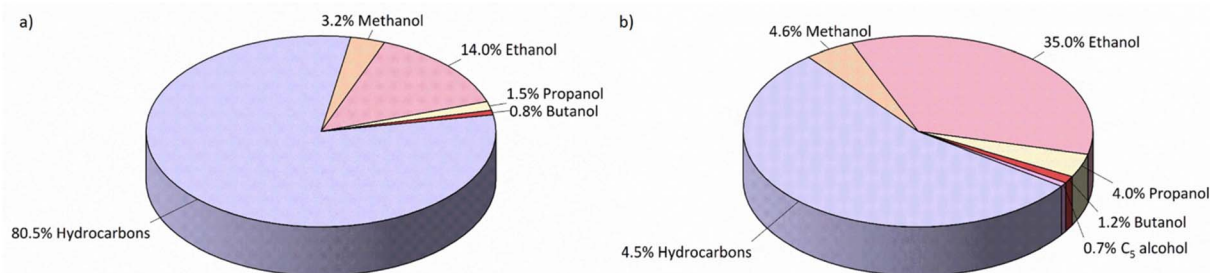
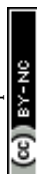


Fig. 4 Product distributions of CO<sub>2</sub> hydrogenation (a) 2% Na–Fe@C catalyst and (b) 2% Na–Fe@C/5% K–CuZnAl multifunctional catalyst (b). Reprinted with permission from ref. 25. Copyright 2021 American Chemical Society.



ethanol STY of  $0.47 \text{ mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$ . The most exciting finding in this study was that CO pulse titration experiments showed that introducing Na content improved  $\text{Co}_2\text{C}$  metal dispersion, which aligned with HAADF-STEM and EDX elemental mapping images. Also, a reduction of corresponding particle size was observed. Other observations, such as EXAFS fitting spectra of Co K-edge, further confirmed the improved metal dispersion and reduced particle size as there was a significant decrease in Co-Co coordination numbers in  $\text{Co}_2\text{C}$  from 6.5 to 1.9 when Na content increased from 0 to 5 wt%. All these characterisation results suggested that the Na promoter has a structural effect on  $\text{Co}_2\text{C}$ , which agrees well with other research, highlighting the exceptional ability of alkali metals to exhibit structural effects that stabilize active metal or interface sites.<sup>64</sup> The authors also concluded that an interaction is formed between Na and  $\text{Co}_2\text{C}$ . This interaction leads to stable Na- $\text{Co}_2\text{C}$  active sites by generating Na-Co bonds, decreasing particle size, and enhancing the metal dispersion. As a result, RWGS reaction and ethanol STY are improved. Furthermore, an optimized amount of Na is also important in HAS because an excess amount of Na with too strong interaction would weaken the CO adsorption strength and hinder CO insertion, thus leading to high CO selectivity, which is unbeneficial to HAS.

A similar trend was observed in the structure-performance relationship between the Na content and ethanol formation by Zhang *et al.*<sup>50</sup> They prepared a series of catalysts with different amounts of Na-promoted Rh nanoparticles embedded in zeolite silicalite-1, denoted as  $x\text{Na-Rh@S-1}$ , where  $x$  was the weight loading of Na. By comparing the catalytic performance with different Na content,  $0.19\text{Na-Rh@S-1}$  with a moderate amount of Na content displayed the best catalytic performance in ethanol generation among all, with  $\text{CO}_2$  conversion of 10% and ethanol selectivity of 24%. Although the results were generally lower than other published works on HAS, the ethanol STY over  $0.19\text{Na-Rh@S-1}$  was surprisingly high, achieving  $72 \text{ mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$ .  $\text{C}_3+$  alcohols were also detected, but the selectivity was not ideal, being less than 5%. Consistent with prior research, an excessive amount of Na can lead to severe deposition of Na species on the surface Rh sites, causing high coverage by  $\text{Na}^+$  on the catalyst surface. Meanwhile, the confinement effect by the rigid framework of zeolite S-1 successfully prevents Rh nanoparticles from agglomeration and restricts the sintering of Na-promoted Rh nanoparticles, supported by TEM results. Hence,  $\text{Na-Rh@S-1}$  achieved exceptional long-term stability under reaction conditions. The experimental results (XPS and  $\text{CO}_2$  chemisorption) also pointed out the role of Na promoter in inducing the  $\text{Rh}^+$  generation, which can coexist with  $\text{Rh}^0$  species in the catalyst, thus causing a promotional effect in ethanol synthesis.  $\text{H}_2$ -TPR profiles observed that the reduction peaks with Na addition became broader and split into two peaks with increasing Na contents. Besides, the reduction peaks also experienced a right shift to a higher temperature with increasing Na loadings. Taken together, this implies that incorporating Na contents can inhibit the complete reduction of Rh species. Besides, the experiment data also showed that the presence of Na as a promoter improved the  $\text{CO}_2$  chemisorption performance, which the presence of strong  $\text{CO}_2$  adsorption

strength and  $\text{Rh}^+$  species can minimize the  $\text{H}_2$  adsorption and dissociation ability, thereby suppressing hydrocarbon formation and enhance C-O bond activation and CO insertion for C-C propagation.<sup>65,66</sup>

Xu *et al.*<sup>20</sup> demonstrated that incorporating a moderate amount of K into CuMgZnFe, abbreviated as K-CMZF catalysts, could effectively boost the production of HAS. It was observed that the selectivity of higher alcohols and STY increased when K loading increased from 0.1 to 4.6 wt% but then decreased at K loading of 17.6 wt%. Optimized K-CMZF catalyst with 4.6 wt% K loading displayed the highest  $\text{CO}_2$  conversion of 30.4% and higher alcohols STY of  $69.6 \text{ mg g}_{\text{cat}}^{-1} \text{ h}^{-1}$ . Based on Anderson-Schulz-Flory (ASF) calculations, the value of chain growth probability ( $\alpha$ ) increased when K loading increased, highlighting that adding K can enhance the chain growth ability of K-CMZF catalysts. The existence of K promoter not only maintains a great balance between non-dissociative and dissociative CO activation but also controls the hydrogenation capacity, thus ensuring the participation of adequate  $^*\text{CH}_x$  and  $^*\text{CO}$  species in C-C coupling reactions while restricting  $^*\text{CH}_x$  hydrogenation termination reaction to promote  $^*\text{CH}_x\text{CO}/^*\text{CH}_x\text{CHO}$  hydrogenation to higher alcohols.

Witoon *et al.*<sup>43</sup> systematically investigated the promoter effect on  $\text{CO}_2$  hydrogenation over K-Co promoted  $\text{In}_2\text{O}_3$  catalysts. Adding K and Co into  $\text{In}_2\text{O}_3$  significantly boosts the C-C chain growth and CO insertion, thus increasing the higher alcohol selectivity, but had only a minor effect on  $\text{CO}_2$  conversion. On the other side, both Co- and K-promoted  $\text{In}_2\text{O}_3$  catalysts showed a clear difference in product selectivity, wherein the K-promoted  $\text{In}_2\text{O}_3$  catalyst was highly selective towards CO and  $\text{CH}_3\text{OH}$  synthesis, while the Co-promoted  $\text{In}_2\text{O}_3$  favored the production of  $\text{C}_{2+}$  hydrocarbons over higher alcohols. The authors postulated that the addition of K reduces the weak and medium  $\text{H}_2$  adsorption, thereby suppressing the hydrogenation of  $\text{CH}_3\text{OH}$  and formation of  $\text{CH}_4$  from CO. Contrarily, characterization results revealed a mixture of  $\text{Co}^0$  and  $\text{CoO}$  in the Co species of Co-promoted  $\text{In}_2\text{O}_3$ .  $\text{CoO}$  sites facilitate the formation of  $\text{C}_x\text{H}_y^*$  species, which subsequently react with migrating  $\text{CO}^*$  on the  $\text{CoO}$  surface to form  $\text{C}_{2+}\text{OH}$  products. However, the faster hydrogenation of  $\text{C}_x\text{H}_y^*$  species over CO insertion owing to weak  $\text{H}_2$  adsorption effectively promotes  $\text{C}_{2+}$  hydrocarbon formation rather than  $\text{C}_{2+}$  oxygenates formation. To enhance the HAS activity, K-Co promoted  $\text{In}_2\text{O}_3$  catalysts with varying weight percent of K and Co were synthesized. As a result, K-Co promoted  $\text{In}_2\text{O}_3$  (2.5 wt% K and 5 wt% Co) demonstrated superior HAS catalytic performance with higher alcohols STY of  $169.6 \text{ g kg}_{\text{cat}}^{-1} \text{ h}^{-1}$  and a higher alcohols distribution of 87.4% among the overall alcohols formed. The improved HAS activity can be attributed to the synergistic interaction between K, Co, and  $\text{In}_2\text{O}_3$ . The introduction of K and Co contributes to generating K-O-Co sites, which reduces weak  $\text{H}_2$  adsorption and causes a stronger interaction of  $\text{H}_2$  with the catalyst surface, hence enabling the manipulation of higher alcohol selectivity.

Zhang *et al.*<sup>39</sup> examined the dependence of  $\text{C}_{2+}\text{OH}$  selectivity on the Cr loading level of the Cr-CuFe catalyst, in which the maximum  $\text{C}_{2+}\text{OH}$  selectivity was obtained at Cr = 1%. In detail, Cr-promoted CuFe-based catalysts with K additive were



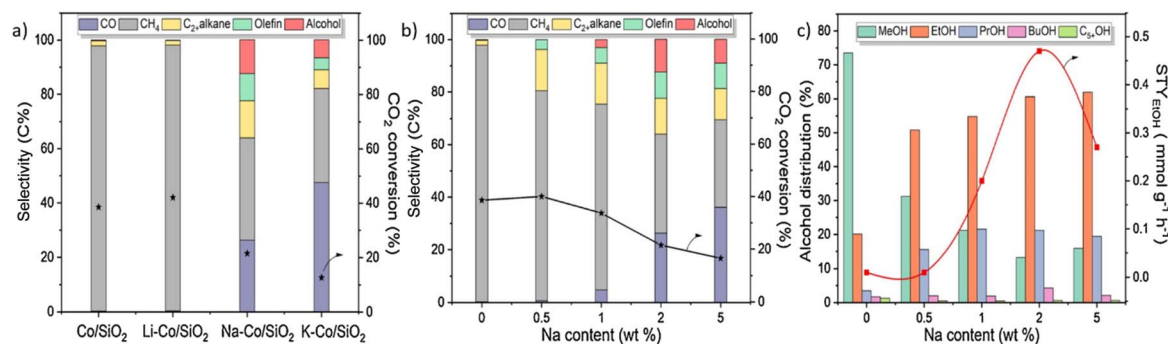


Fig. 5 Catalytic performance over Co/SiO<sub>2</sub> catalysts with different alkali metals and Na contents (a) CO<sub>2</sub> conversion and product selectivity with different alkali metals (b) CO<sub>2</sub> conversion and product selectivity Na contents (c) alcohol distribution and ethanol STY with different Na contents. Reprinted with permission from ref. 40. Copyright 2021 Elsevier.

synthesized *via* the sol-gel method, and the role of Cr as a dopant was further investigated. It was inferred that the interaction between Cu and Fe becomes stronger with the Cr additive. All the CuFe-based catalysts contained the same amount of K as the catalytic performance on Cr (1%)-CuFe catalyst without the K promoter exhibited higher selectivity towards methane and C<sub>2</sub>-C<sub>4</sub> alkanes whereas decrease in olefins and higher alcohols selectivity. This is consistent with previous research, indicating the role of alkali metals in preventing over-hydrogenation and hydrocarbon formation. With the aid of alkali metal, catalyst alkalinity is improved, therefore enhancing CO<sub>2</sub> adsorption and activation.<sup>20</sup> An appropriate Cr loading amount can enhance H<sub>2</sub> adsorption and activation while weakening CO adsorption strength on the CuFe catalyst. This suggests that Cr additives can effectively mitigate CO over-dissociation, inhibiting the formation of excessive iron carbide species (FeC<sub>x</sub>) from metallic Fe. Supported by Fe (2p) XPS and <sup>57</sup>Fe Mössbauer spectroscopy, FeC<sub>x</sub> characteristics were observed over the Cr (1%)-CuFe catalyst compared to the undoped CuFe catalyst. Besides, the amount of Cu<sup>0</sup> (23.2%) was lower, and the amount of Cu<sup>+</sup> and Cu<sup>2+</sup> (76.8%) was higher in Cr (1%)-CuFe catalyst than that of the undoped CuFe catalyst (30.4% of Cu<sup>0</sup>, 69.6% of Cu<sup>+</sup> and Cu<sup>2+</sup>), as indicated by Cu LMM Auger electron spectra. These findings confirmed the improvement of interactions between Cu and Fe species, which are conducive to forming Cu-FeC<sub>x</sub> interfaces, the active sites of the catalyst for HAS.<sup>37</sup> Excessive Cr loading has a negative effect on HAS because the Cr species would heavily cover the catalyst surface, and the interaction of CH<sub>x</sub> with non-dissociative CO over Cu-FeC<sub>x</sub> interfaces will be inhibited. The reaction mechanism proposed that C-C coupling between the interaction between CH<sub>x</sub> and non-dissociative CO over Cu-FeC<sub>x</sub> interfaces produces more acetate and acetaldehyde intermediates, enhancing the synthesis of higher alcohols.

Ji *et al.*<sup>51</sup> explored the effects of different transition metals and alkali metals on Rh/CeO<sub>2</sub> catalyst for CO<sub>2</sub> hydrogenation in ethanol synthesis. Fe and Na doping as dual promoters demonstrated superior catalytic activity for CO<sub>2</sub> hydrogenation with high ethanol selectivity of 29.8% and ethanol STY of 116.7 mmol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> at 250 °C and 3 MPa. The optimum

amounts of Fe and Na in the RhFeNa/CeO<sub>2</sub> catalyst, denoted as 2Rh0.5Fe0.5Na/CeO<sub>2</sub>, were both 0.5 wt%, achieving the highest catalytic performance and Rh dispersions with Rh loading of 2 wt%. H<sub>2</sub>-TPR and CO<sub>2</sub>-TPD profiles showed that adding Fe could enhance the Rh metal dispersion by showing increased H<sub>2</sub> consumption, while adding Na was also shown to increase H<sub>2</sub> consumption and promote the reduction of Rh species to metallic Rh. Other additives such as Li, Cs, and K suppressed the reduction of Rh species. It was concluded that adding Na and Fe as dual promoters improve the overall Rh metal dispersion and form strong interactions with Rh, thus enhancing the SMSI. FTIR studies of chemisorbed CO and XPS results further revealed that Na and/or Fe additions could enhance the CO adsorption ability, which increased the formation of Rh<sup>+</sup> active sites. The mechanism studies observed that there were more intermediates of CO\* and HCOO\* produced on the Fe and Na-promoted Rh/CeO<sub>2</sub> catalysts compared to the unpromoted catalysts, indicating that the doping of Fe and Na promotes dissociation and hydrogenation capacity of CO<sub>2</sub>, hence resulting in higher ethanol production, as shown in Fig. 6. However, there was a slight decrease in catalytic activity in the early stage of the reaction, which then became stable after 50 hours. The characterization results of the spent catalyst remained the same as those of the fresh catalyst. The only difference detected was that thermogravimetric analysis (TGA) showed a relatively small weight loss of 6.4% at temperatures ranging between 150 °C and 250 °C, which can be attributed to the desorption of water and organic compound of the spent catalyst surface.

Yao *et al.*<sup>23</sup> also studied the dual promoter effect by incorporating Na and S into monometallic iron catalysts for HAS. The authors proposed that the sulfur existed in the form of sulfate plays a pivotal role in tuning the CO activation through strong synergistic interaction between Na and S, which increases the amount of adsorbed CO to bind with alkyl species on Na-promoted Fe sites, forming higher alcohols. Experimental results in catalytic performance showed that FeNa catalyst exhibited alcohol selectivity of less than 5% while FeNa catalyst promoted with 0.6 wt% of sulfur through precipitation method, denoted as FeNaS-0.6 catalyst, achieved the maximum alcohol



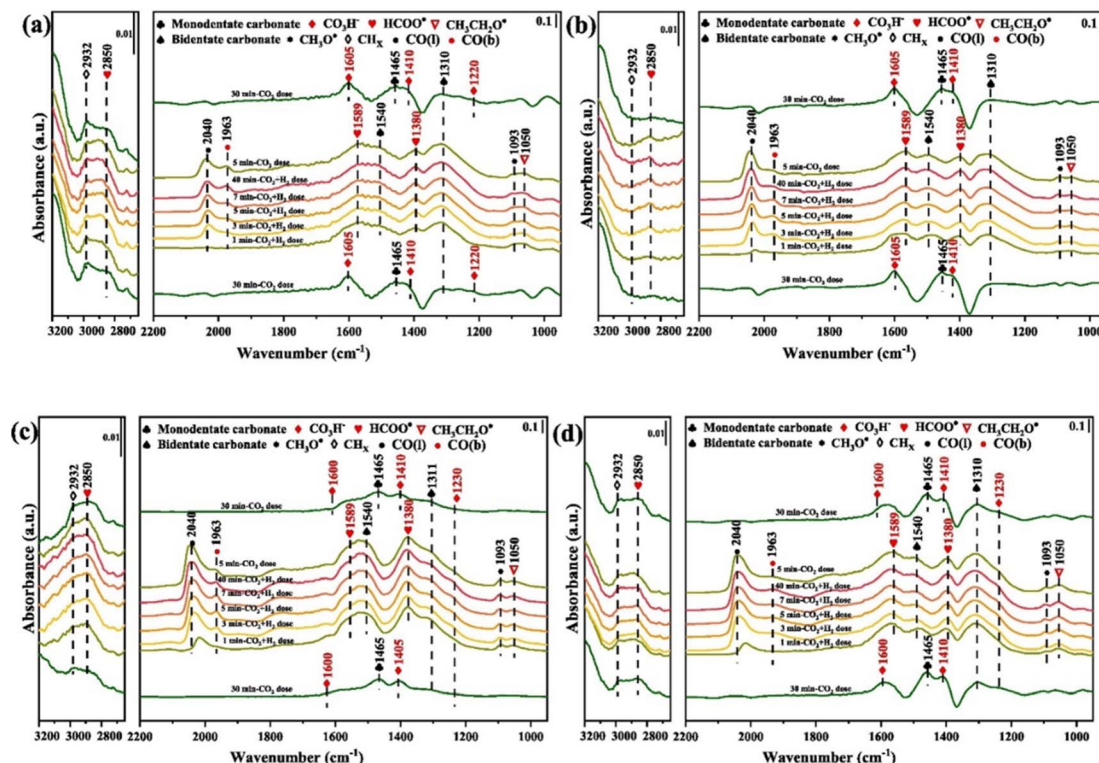


Fig. 6 *In situ* DRIFTS of various catalysts after switching the feed gas from CO<sub>2</sub> to CO<sub>2</sub> + H<sub>2</sub>, followed by returning to CO<sub>2</sub> at 250 °C and 0.1 MPa (a) 2Rh/CeO<sub>2</sub> (b) 2Rh0.5Fe/CeO<sub>2</sub> (c) 2Rh0.5Na/CeO<sub>2</sub> and (d) 2Rh0.5Fe0.5Na/CeO<sub>2</sub>. Reprinted with permission from ref. 51. Copyright 2024 Elsevier.

selectivity of 16.1% with more than 98% of C<sub>2+</sub>OH fraction in total alcohols. The authors also synthesized the FeNaS-*im* catalyst by introducing the same sulfate content as the FeNaS-0.6 catalyst on FeNa *via* the wet impregnation method to study the promotional effects of sulfate. The higher alcohol selectivity of the FeNaS-*im* catalyst was slightly lower than that of the FeNaS-0.6 catalyst, which can be ascribed to the disadvantage of the impregnation method, resulting in non-uniform sulfate distribution and weak interactions between Fe species and sulfate species. It is well-documented that dissociative and non-dissociative CO activation are essential for HAS. In this study, the presence of sulfate with strong electron-withdrawing ability offers additional Fe sites for non-dissociative CO adsorption. At the same time, adding Na helps maintain the CO dissociative ability of Fe sites, highlighting the importance of maintaining a kinetic balance between dissociative and non-dissociative CO activation in HAS.

### Role of catalyst supports

Catalyst support plays a pivotal role in CO<sub>2</sub> hydrogenation by enhancing metal dispersion, stabilizing active sites, regulating catalyst surface interfaces, influencing key intermediates to alter reaction mechanisms, and improving adsorption or activation capabilities.<sup>67</sup> In addition, the construction of SMSI has been demonstrated to effectively stabilize active sites under CO<sub>2</sub> hydrogenation reaction conditions.<sup>68,69</sup> The SMSI effect is widely acknowledged for its significant influence on the stability, activity, chemical state, and morphology of the catalysts.<sup>70</sup> Xin

*et al.*<sup>68</sup> demonstrated that by constructing an SMSI state, it is possible to promote the formation of a defective MoO<sub>3-x</sub> overlayer surrounding Ru nanoparticles (Ru@MoO<sub>3-x</sub>) at a low temperature of 250 °C. This modification favors RWGS, achieving >99% CO selectivity, which could easily revert to CH<sub>4</sub> formation upon O<sub>2</sub> treatment. Therefore, constructing SMSI between active metals and support materials is one of the strategies that could be implemented to increase the higher alcohol selectivity, which also operates under low-temperature reaction conditions. For instance, Zhang *et al.*<sup>71</sup> identified that only SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub> supports managed to stabilize the Co<sub>2</sub>C active sites by generating Si-O-Co bonds. In their study, the influence of different catalyst supports (Al<sub>2</sub>O<sub>3</sub>, ZnO, AC, TiO<sub>2</sub>, SiO<sub>2</sub>, and Si<sub>3</sub>N<sub>4</sub>) in ethanol synthesis over supported Na-promoted cobalt catalysts was investigated, as illustrated in Fig. 7. Na-Co/Al<sub>2</sub>O<sub>3</sub>, Na-Co/ZnO, Na-Co/AC and Na-Co/TiO<sub>2</sub> catalysts exhibited very low alcohol selectivity of less than 1%. In comparison, Na-Co/SiO<sub>2</sub> and Na-Co/Si<sub>3</sub>N<sub>4</sub> catalysts exhibited a total alcohol selectivity of 9%. The experimental result was explained by the formation of the Co<sub>2</sub>C active phase on Na-Co/SiO<sub>2</sub> and Na-Co/Si<sub>3</sub>N<sub>4</sub> catalysts, which remained stable even after the reaction. Although the Co<sub>2</sub>C active phase was also detected on Na-Co/AC and Na-Co/TiO<sub>2</sub> catalysts, the Co<sub>2</sub>C active phase was almost fully decomposed during the reaction condition due to a lack of SMSI. In contrast, no Co<sub>2</sub>C active phase was found on Na-Co/Al<sub>2</sub>O<sub>3</sub> and Na-Co/ZnO catalysts. The authors inferred that Co<sub>2</sub>C is the active phase in CO<sub>2</sub> hydrogenation, with its stability attributed to SMSI facilitated by the



formation of Si–O–Co bonds, which also depends on the nature of the supports utilized.

An *et al.*<sup>41</sup> exploited the SMSI between  $\text{La}_4\text{Ga}_2\text{O}_9$  and cobalt particles, facilitating the formation of active  $\text{Co}^0\text{--Co}^{2+}$  pairs. Perovskite oxides (PTO), with highly tunable composition and structure, can regulate oxygen vacancies through their bulk and surface properties.  $\text{Co}/\text{La}_4\text{Ga}_2\text{O}_9$  catalyst was synthesized using perovskite type  $\text{LaCo}_{1-x}\text{Ga}_x\text{O}_3$  support and investigated for  $\text{CO}_2$  hydrogenation reaction. Ethanol selectivity of 34.7% was obtained over  $\text{Co}/\text{La}_4\text{Ga}_2\text{O}_9$  catalyst under reaction conditions of 270 °C, 3.5 MPa and  $\text{GHSV} = 3000 \text{ mL g}_{\text{cat}}^{-1} \text{ h}^{-1}$ . Co nanoparticles loaded on  $\text{La}_4\text{Ga}_2\text{O}_9$  were formed by reducing the  $\text{LaCo}_{0.5}\text{Ga}_{0.5}\text{O}_3$  precursor. SMSI between Co and  $\text{La}_4\text{Ga}_2\text{O}_9$  are postulated, resulting in electron donation from cobalt to  $\text{La}_4\text{Ga}_2\text{O}_9$ , thus forming  $\text{Co}^0\text{--Co}^{2+}$  pairs as active sites.  $\text{CO}_2$  is adsorbed and activated on the  $\text{La}_4\text{Ga}_2\text{O}_9$  surface, which favors RWGS in producing CO intermediates. Then, the produced CO intermediates migrate to  $\text{Co}^0\text{--Co}^{2+}$  sites to promote ethanol synthesis. However, it is unfortunate that ethanol yield decreased when reaction time increased. This can be attributed to the increase in the  $\text{Co}^0/\text{Co}^{2+}$  ratio, which caused an imbalance in the formation of intermediates over longer periods. Apart from that, SMSI between  $\text{Co}_3\text{O}_4$  particles and isolated silanols, resulting in the formation of Si–O–Co chemical bonds on Co/S-1 catalysts, had also been observed by Ding *et al.*<sup>42</sup> The SMSI was supported by XPS results, which demonstrated an increased number of electronic defects in  $\text{Co}_3\text{O}_4$  on Co/S-1 and a higher electron density of Si–O bonds on S-1. This further consolidates the electron transfers from  $\text{Co}_3\text{O}_4$  to Si–O bonds, contributing to the presence of Si–O–Co chemical bonds. The active sites of the Co/S-1 catalyst can be tuned through Si–O–Co chemical bonds, which stabilize the co-existing phases of  $\text{Co}^0$  and CoO ( $\text{CoO}_x$  sites) by preventing the complete reduction of  $\text{Co}_3\text{O}_4$ . DFT calculations revealed the roles of CoO and CoO sites in  $\text{CO}_2$  hydrogenation to ethanol, respectively. Specifically,  $\text{Co}^0$  sites favor the  $\text{COOH}^*$  species, while CoO sites promote the formation of  $\text{HCOO}^*$  species. The  $\text{COOH}^*$  and  $\text{HCOO}^*$  species are then coupled with  $\text{CH}_x^*$  species on  $\text{CoO}_x$  sites to produce ethanol.

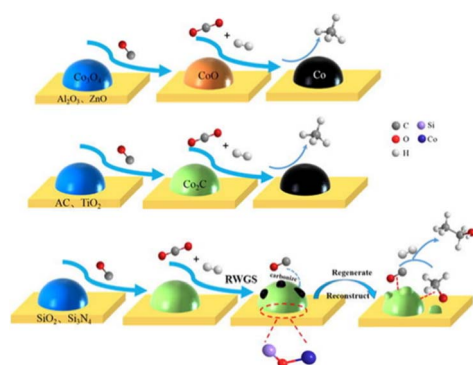


Fig. 7 Schematic of Co phase transformation during CO reduction and  $\text{CO}_2$  hydrogenation reaction on Na–Co catalysts supported on different supports. Reprinted with permission from ref. 71. Copyright 2020 Elsevier.

Moreover, a few studies have investigated the confinement effect of supports to achieve catalyst stability in  $\text{CO}_2$  hydrogenation. Wang *et al.*<sup>72</sup> recently postulated that the confinement effect in  $\text{In}_2\text{O}_3\text{--TiO}_2$  catalysts promotes the dispersion of the  $\text{In}_2\text{O}_3$  guest catalyst onto the  $\text{TiO}_2$  host surface, thereby improving performance in  $\text{CO}_2$  hydrogenation to CO. The formation of In–O–Ti interfacial bonds was crucial in inducing  $\text{In}_2\text{O}_3$  dispersion and stabilizing the metastable  $\text{InO}_x$  layers. Their findings revealed that the confinement effect at oxide/oxide interfaces benefits  $\text{CO}_2$  hydrogenation. For  $\text{CO}_2$  hydrogenation in HAS, Ding *et al.*<sup>35</sup> synthesized the  $\text{Cu@Na-beta}$  catalyst, embedding the Cu nanoparticles in the beta molecular sieve. The authors highlighted that the synergistic interaction between copper nanoparticles and the beta zeolite framework is essential for HAS catalytic performance as this synergy suppresses the  $\text{CO}_2$  adsorption site and prevents the over-reduction of the catalyst. Na-beta zeolite as support in  $\text{Cu@Na-eta}$  catalyst demonstrates a superior confinement effect that shapes the copper nanoparticles into unique configurations with surface sites and limits the reactants along the catalyst surface, thus successfully preventing the formation of by-products such as methanol, formic acid, or acetic acid. In another study, Cu nanoparticles were embedded into BEA and MFI (S-1) zeolites, and their mesoporous equivalents (m-zeolites) were obtained *via* the carbon templating method.<sup>73</sup> Based on the catalytic test result, mesoporous zeolites exhibited a higher  $\text{CO}_2$  conversion and ethanol selectivity than their non-mesoporous counterparts. Besides, the introduction of mesopores facilitated the formation of isopropanol. Cu-based mesoporous S-1 zeolite ( $\text{Cu@m-S1}$ ), which underwent an additional recrystallization procedure, achieved a higher isopropanol selectivity and yielded  $20.51 \text{ mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$ . The authors claimed that the mesoporous effect of zeolites positively affects the production of alcohol by facilitating the accessibility of reactant access to Cu active sites and improving the SMSI to accelerate alcohol formation. Tran *et al.*<sup>52</sup> developed a Na–Rh– $\text{FeO}_x/\text{ZSM-5}$  catalyst, which exhibited a higher ethanol selectivity than a Na–Rh– $\text{FeO}_x$  catalyst without zeolite support. The high specific surface area, smaller pore size, and decrease in iron particle size can be attributed to the excellent synergy between the Na–Rh– $\text{FeO}_x$  and ZSM-5 support. The ZSM-5-supported catalyst showed a suppression effect on hydrocarbon formation. However, the  $\text{CO}_2$  conversion did not increase despite the higher density of active sites due to higher surface area. This indicates that the zeolite support can modify the properties of the active sites.

### Critical roles of oxygen vacancies

Various catalytic materials (*e.g.*, Rh, Co, Fe, Cu, and Au) are active sites to catalyze  $\text{CO}_2$  hydrogenation and produce higher alcohols.<sup>16,29,74,75</sup> However, monometallic catalysts have limitations and restrictions for HAS from  $\text{CO}_2$ , such as low conversion and selectivity. Thus, metal oxides (*e.g.*,  $\text{ZrO}_2$ ,  $\text{TiO}_2$ , and  $\text{CeO}_2$ ) are often used as supports or promoters due to their inherent ability to generate abundant oxygen vacancies. The oxygen vacancy is typically recognized as the active site for  $\text{CO}_2$



adsorption and activation, facilitating the formation of intermediates and promoting SMSI, hence assisting in accelerating  $\text{CO}_2$  hydrogenation.<sup>41,44,76,77</sup> Yang *et al.*<sup>16</sup> synthesized the N-doped CuFeZn catalyst and added an organic ligand, 2,6-pyridine dicarboxylic acid. Accordingly, adding PDA to the CuFeZn catalyst increases the generation of oxygen vacancies, which regulates the electron structure of the catalyst. The oxygen vacancy captures  $\text{CO}_2$  by trapping O, and the nearby Zn or Cu reacts with the captured  $\text{CO}_2$  to form  $\text{CO}_2^{*-}$  or  $\text{CO}^*$  species. This is most likely because O in  $\text{CO}_2$  recharges the oxygen vacancy and strengthens the interaction between O and the active metals of the catalyst, assisting in establishing the pathway for electron transfer, facilitating the activation, dissociation, and reduction of  $\text{CO}_2$  molecules, and thus promoting the formation of higher alcohols. Xi *et al.*<sup>44</sup> reported the K-promoted Fe-In/Ce-ZrO<sub>2</sub> catalyst in which the existence of reduced  $\text{In}_x\text{O}_x$  phases with oxygen vacancies is of great importance for  $\text{CO}_2$  activation; thereby, these oxygen vacancies will assist  $\text{CO}_2$  activation in the formation of key reaction intermediates such as  $\text{HCOO}^*$ ,  $\text{H}_2\text{COO}^*$ , and  $\text{H}_2\text{CO}^*$  species. This study demonstrated that *in situ* pretreatment with CO at 350 °C for 3 h boosted the oxygen vacancy by 348.6% compared to air-calcination treatment. Moreover, Li *et al.*<sup>17</sup> reported tailoring the Fermi level of a Cu-doped Zn catalyst synthesized using the urea homogeneous hydrolysis technique, suggesting that a lower Fermi level promotes better carbon chain growth. The electron trap effect of oxygen vacancy regulates the Fermi level of semiconductors. It influences their catalytic performance *via* charge transfer between the surface and adsorbed substances with an imbalanced electron structure, resulting in fast electron transfer. Thus, oxygen vacancies could boost the formation of higher alcohols. Besides, surface oxygen vacancies also play a key role in promoting  $\text{CO}_2$  adsorption and activation. In the  $\text{Ir}_1\text{-In}_2\text{O}_3$  SAC catalyst, the oxygen vacancies combine with monoatomic Ir to form Lewis acid-base pairs, which serve as active sites for  $\text{CO}_2$  adsorption and activation into  $\text{CO}^*$  intermediates. The

$\text{Ir}^{\delta+}\text{-CO}^*$  intermediates interact with the  $\text{CH}_3\text{O}^*\text{-O}_v$  intermediates, thus enhancing ethanol selectivity.<sup>46</sup>

### Reaction mechanisms of $\text{CO}_2$ hydrogenation for HAS

The reaction mechanisms for the synthesis of higher alcohols from  $\text{CO}_2$  hydrogenation typically involve the following steps: the initial stage for the activation of  $\text{CO}_2$  and  $\text{H}_2$ , resulting in the formation of  $\text{C}_1$  intermediates including  $\text{CO}^*$ ,  $\text{CH}_x^*$ , and  $\text{HCOO}^*$  species; and the second stage for the production of ethanol or higher alcohols with a longer carbon chain ( $\text{C}_{2+}\text{-C}_{4+}$ ) through C-C coupling of  $\text{CH}_x^* - \text{CO}^*$  (a CO-mediated pathway) or  $\text{CH}_x^* - \text{HCOO}^*$  (a formate-mediated pathway).<sup>17,29,37,44,71,78</sup> Yang *et al.*<sup>16</sup> proposed reaction mechanisms for HAS from  $\text{CO}_2$  hydrogenation over N-doped CuZnFe, as illustrated in Fig. 8. The active sites (e.g., Cu<sup>0</sup>, ZnO,  $\text{Fe}_3\text{O}_4$ , and  $\text{Fe}_5\text{C}_2$ ) adsorb the reactant molecules. Through capturing O from  $\text{CO}_2$ , the oxygen vacancies generated on the surface of ZnO facilitate the adsorption and activation of  $\text{CO}_2$  molecules. The weak base of doped N also contributes to activating  $\text{CO}_2$  molecules. This leads to the generation of  $\text{CO}_2^{*-}$  species as  $\text{CO}_2$  captures electrons over the surface of ZnO or N. At the interface of Cu-ZnO,  $\text{H}_2$  is dissociated and activated due to the vacant s orbital of the Cu species. Through the RWGS reaction, at this interface of Cu-ZnO,  $\text{CO}_2$  is dissociated to form  $\text{CO}^*$  species. Subsequently,  $\text{CO}^*$  species may undergo hydrogenation to form methanol or desorb to produce CO. Furthermore, at the Cu- $\text{FeC}_2$  interface, a considerable portion of  $\text{CO}^*$  dissociates, resulting in  $\text{C}^*$  and  $\text{O}^*$  radicals. The  $\text{C}^*$  radical is further hydrogenated to generate the alkyl species ( $\text{CH}_x^*$ ), and carbon chain growth occurs through continuously inserting  $\text{CH}_x^*$  to form hydrocarbons ( $\text{C}_n\text{H}_m$ ). Subsequently,  $\text{CO}^*$  is inserted into  $\text{C}_n\text{H}_m$  on Cu sites to form higher alcohols ( $\text{C}_{2+}$ ).

Zhou *et al.*<sup>26</sup> proposed a reaction pathway for HAS from  $\text{CO}_2$  hydrogenation over a 0.3K-1Pd/ $\text{Fe}_2\text{O}_3$  catalyst, as illustrated in Fig. 9. The authors investigated the reaction intermediates (e.g., CO,  $\text{C}_2\text{H}_5\text{O}^*$ ,  $\text{CH}_3\text{CHO}^*$ ,  $\text{CH}_3\text{CH}_2\text{O}^*$ , and  $\text{CH}_4$ ) after injecting

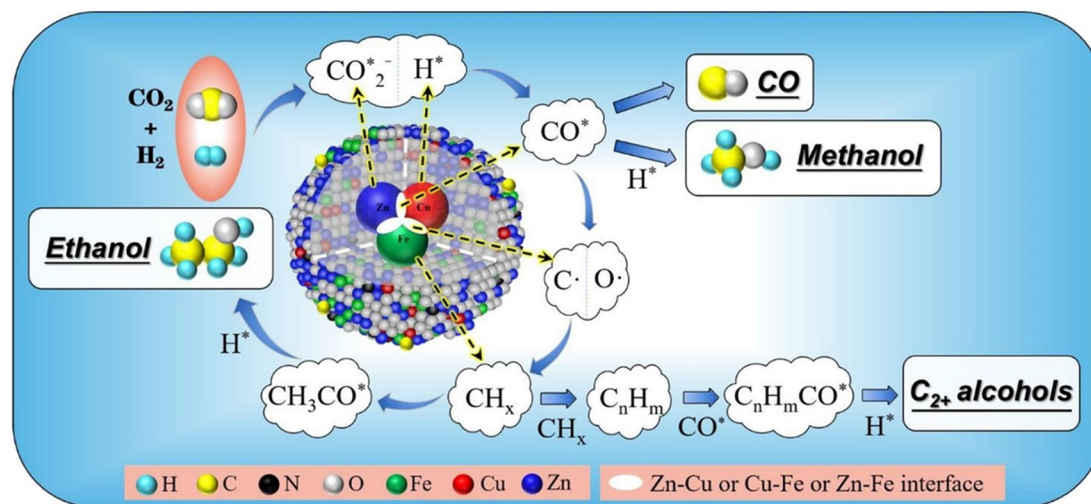


Fig. 8 The weak base of doped N promotes the generation of  $\text{CO}_2^*$  species through  $\text{CO}_2$  activation, which is further regulated by the CuZnFe catalyst to form intermediates including  $\text{CO}^*$ ,  $\text{CH}_x$ , and  $\text{HCOO}^*$  species to form higher alcohols through  $\text{CO}^*$  insertion into  $\text{C}_n\text{H}_m$ . Reprinted with permission from ref. 16. Copyright 2022 Elsevier.

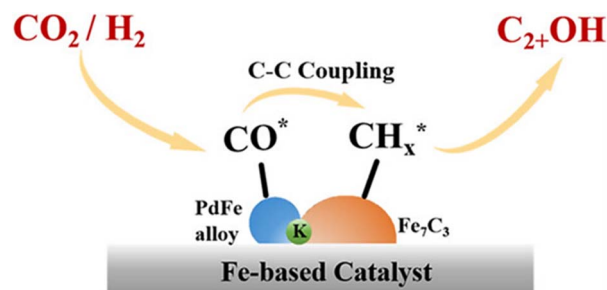


Fig. 9 Proposed reaction pathway that shows the non-dissociative activation of CO regulated by K and Pd to balance the dissociative activation of CO regulated by  $\text{Fe}_2\text{O}_3$  catalyst for promoting the C–C coupling mechanism. Reprinted with permission from ref. 26. Copyright 2024 American Chemical Society.

$\text{CO}_2/\text{H}_2$  over the surface of the catalyst by *in situ* DRIFTS. The introduction of highly dispersed K (0.3 wt%) restricts the hydrogenation of the  $\text{CH}_x^*$  species. It enhances the ratio of  $\text{CO}^*/\text{CH}_x^*$ , promoting the insertion of CO, while introducing 1% Pd increases the formation rate of  $\text{C}_2\text{H}_5^*$  species. The synergy of K and PdFe alloys on a 0.3K–1Pd/ $\text{Fe}_2\text{O}_3$  catalyst can regulate the ratio of  $\text{CO}^*/\text{CH}_x^*$  on the surface of the catalyst. The observed key reaction intermediates by *in situ* DRIFTS suggest the reaction pathway following the CO-mediated

reaction mechanism by the insertion of  $\text{CO}^*$  into  $\text{CH}_x^*$  species to form intermediates ( $\text{CH}_x\text{CO}^*$ ) through C–C coupling, which may instantly conjugate  $\text{CO}^*$  and  $\text{CH}_x^*$  species, resulting in the formation of higher alcohols. Additionally, the study performed CO-TPSR-MS experiments to investigate the influence of K and Pd loading on  $\text{Fe}_2\text{O}_3$  towards the behavior of the dissociative and non-dissociative activations of CO by measuring the ratio of  $\text{CO}_2/\text{CH}_4$  from the desorption peak area. The signals  $\text{CH}_4$  and  $\text{CO}_2$  signify the dissociative activation of CO and the non-dissociative activation of CO, respectively.  $\text{Fe}_2\text{O}_3$  shows a strong dissociative activation of CO. The addition of 1% Pd to 1Pd/ $\text{Fe}_2\text{O}_3$  slightly enhances the non-dissociative activation of CO, which is attributed to the formation of PdFe alloys. However, adding 0.3% K to 0.3K/ $\text{Fe}_2\text{O}_3$  shows a significant non-dissociative activation of CO. The CO-TPSR-MS experiments indicate that the synergy of K and PdFe alloys along with  $\text{Fe}_7\text{C}_3$  regulates a favorable ratio of  $\text{CO}^*/\text{CH}_x^*$  on the surface of the 0.3K–1Pd/ $\text{Fe}_2\text{O}_3$  by balancing the dissociative and non-dissociative activations of CO. This facilitates the C–C coupling of  $\text{CO}^*$  and  $\text{CH}_x^*$  species to produce higher alcohols.

Xu *et al.*<sup>37</sup> proposed an integrated reaction pathway of  $\text{CO}_2$  hydrogenation over a Cs–CuFeZn catalyst with a favorable balance of synergistic sites (Cu–ZnO and copper–iron carbide interfaces), as illustrated in Fig. 10. At the CuZnO interfaces, methanol formation proceeds directly from  $\text{CO}_2$  through

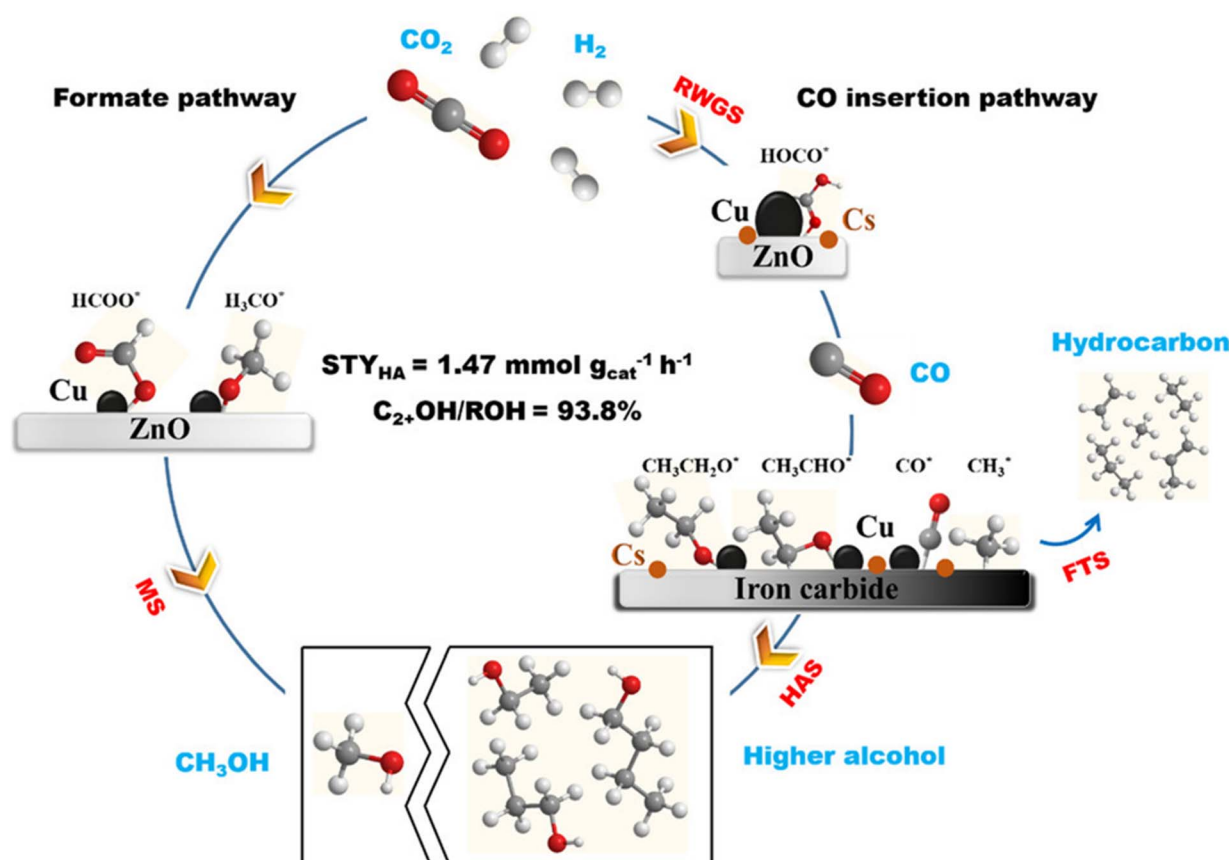
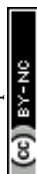


Fig. 10 Proposed reaction mechanism of  $\text{CO}_2$  hydrogenation for higher alcohols through  $\text{C(H)O}^*$  insertion and CO insertion into hydrocarbons over Cs–CuFeZn catalysts. Reprinted with permission from ref. 37. Copyright 2020 American Chemical Society.



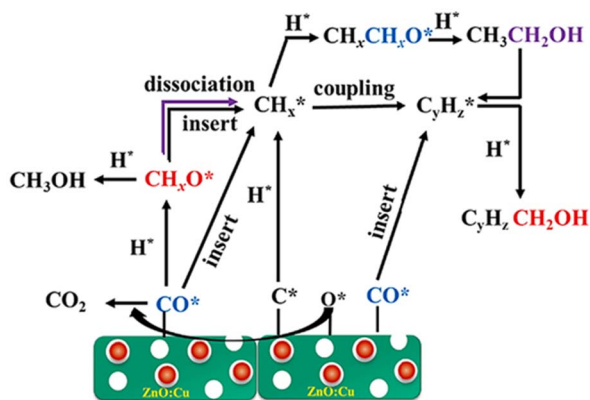


Fig. 11 Electronically modified Fermi level facilitates the formation of alkyl species to promote CO insertion with  $\text{CH}_x\text{-C(H}_x\text{)O}^*$  coupling for higher alcohols. Reprinted with permission from ref. 17. Copyright 2023 Elsevier.

$\text{HCOO}^*$  intermediates following the formate pathway. A proper proportion of the Cs promoter reduces the rate of methanol formation, which is favorable to HAS. Furthermore, at high temperatures, particularly above 300 °C, thermodynamics limits the reaction equilibrium and causes methanol to convert back to  $\text{CO}_2$  and  $\text{H}_2$ , while the formation of CO is considerably accelerated. However, at high temperatures, the formation of higher alcohols is more favorable because Cu–ZnO produces CO through the RWGS reaction. At the same time, copper–iron carbide facilitates the insertion of  $\text{C(H)O}^*$  species to surface hydrocarbon moieties to produce  $\text{C}_{2+}\text{OH}$  at a similar rate. Furthermore, the Cs promoter is essential for driving the CO insertion reaction during the  $\text{CO}_2$ -to-HA process by regulating

the hydrogenation reaction over the CuFeZn catalyst. Since it still does not reach its thermodynamic equilibrium, the rate of  $\text{C}_{2+}\text{OH}$  formation increases as temperature increases. Likewise, a large  $\text{C}_{2+}\text{OH/ROH}$  proportion is produced at high temperatures because of the comparatively slow rate of methanol synthesis in conjunction with the increased rate of  $\text{C}_{2+}\text{OH}$  formation.

Li *et al.*<sup>17</sup> proposed the reaction pathway for HAS from  $\text{CO}_2$  hydrogenation over an electronically modified ZnO catalyst, as illustrated in Fig. 11. According to the analysis of the characterization and the activity of an electronically modified ZnO catalyst, the synergistic effect between ZnO and Cu drives the catalytic activity of  $\text{CO}_2$  hydrogenation, which helps to propose the reaction mechanism for HAS. ZnO plays a critical role in facilitating the activation of CO and  $\text{H}_2$  and promoting the dissociation of the C–O bond. Moreover, the oxygen deficiency species ( $\text{Zn}^{x+}$ ,  $0 < x < 2$ ) promotes carbon chain growth in ZnO. The non-dissociative hydrogenation of CO to generate methoxy species is facilitated by Cu embedded on the ZnO surface. Furthermore, Cu controls the regulation of the electronically modified Fermi level within the ZnO lattice and thus accelerates the electron transfer, facilitating the formation of surface alkyl species ( $\text{CH}_x$ ) by direct C–O dissociation or H-assisted C–O dissociation. As a result, the mechanism of CO insertion with  $\text{CH}_x\text{-C(H}_x\text{)O}^*$  coupling produces higher alcohols ( $\text{C}_{2+}$ ).

Ye *et al.*<sup>53</sup> proposed the reaction pathway for ethanol production from  $\text{CO}_2$  hydrogenation over the  $\beta\text{-Mo}_2\text{C}$  nanowires with a single Rh atom and an alkali metal K ( $\text{K}_{0.2}\text{Rh}_{0.2}/\beta\text{-Mo}_2\text{C}$ ), as illustrated in Fig. 12. An unmodified  $\beta\text{-Mo}_2\text{C}$  catalyst could not convert  $\text{CO}_2$  into ethanol (or limit the conversion to only methanol). Rh loading on the  $\beta\text{-Mo}_2\text{C}$  catalyst promoted the dissociative adsorption of  $\text{CO}_2$ , and the  $\text{CO}^*$  was adsorbed on

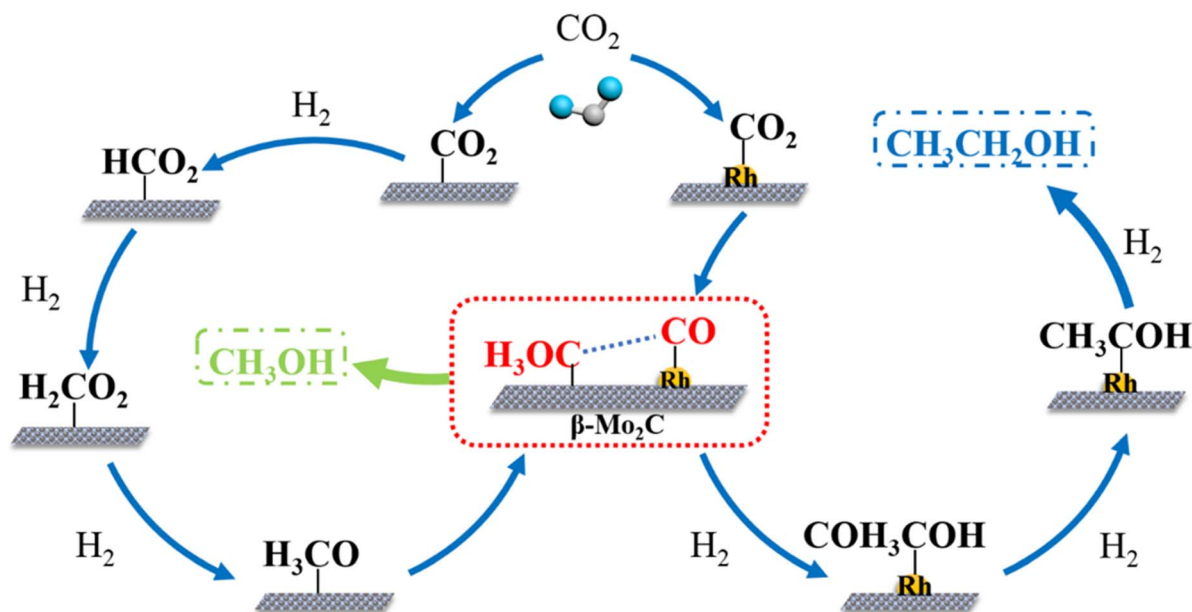


Fig. 12 Proposed reaction mechanism of  $\text{CO}_2$  hydrogenation to ethanol on the  $\beta\text{-Mo}_2\text{C}$  nanowires with a single Rh atom for promoting the C–C coupling mechanism and an introduction of an alkali metal K to regulate the balanced performance of the two active centers for improving the selectivity of ethanol. Reprinted with permission from ref. 53. Copyright 2022 Elsevier.



the monoatomic Rh<sup>δ+</sup>. Moreover, hydrogen was more likely to be adsorbed and activated on Rh, which helped to prevent the production of methanol and methane. Additionally, Mo<sup>δ+</sup>-CO, Mo<sup>2+</sup>-CO, and Mo<sup>4+</sup>-CO exhibited IR peaks at 2094, 2108, and 2129 cm<sup>-1</sup>, respectively. The peaks at 1081, 1053, and 1033 cm<sup>-1</sup> were assigned to strongly adsorbed carbonate species (CO<sub>3</sub><sup>δ-</sup>) formed on the Rh<sub>1.0</sub>/βMo<sub>2</sub>C. Thus, the bifunctional catalyst of monoatomic Rh on βMo<sub>2</sub>C was tailored for promoting the C-C coupling. However, achieving high ethanol selectivity by merely adjusting the Rh content was challenging, as increased Rh led to changes in its dispersion and enhanced oxidation of the carrier, resulting in dominant methanol production under mild conditions. Effective C-C coupling relied on SAC bifunctional active centers, where optimized synergy between the two catalytic pathways was essential for efficient carbon chain growth. To further improve the selectivity of ethanol, introducing K assisted in the adsorption and activation of CO<sub>2</sub> on the βMo<sub>2</sub>C surface by generating more carbonate species. Furthermore, adding an appropriate amount of K assisted in regulating the carrier properties by controlling the H<sub>2</sub> activation, which could effectively reduce the formation of methanol, yielding a higher selectivity of ethanol. In addition, the nature of single atom Rh was retained to promote the C-C coupling, resulting in ethanol formation.

## Conclusions and future perspectives

CO<sub>2</sub> hydrogenation to higher alcohols is a novel strategy to mitigate CO<sub>2</sub> emissions. Efforts have been made to improve the CO<sub>2</sub> conversion and resolve the unsatisfactory selectivity towards higher alcohols. The stability of the catalyst is also a key issue in CO<sub>2</sub> hydrogenation due to catalyst deactivation. The construction of catalysts with various combinations of metals and metal oxides has garnered attention and emerged as a rising trend in enhancing HAS. The introduction of second active metal sites has been proven to hydrogenate the reaction to higher alcohols instead of C<sub>1</sub> product formation, such as methane and methanol. However, designing an ideal catalyst is not easy to achieve. It requires precise control of interplay between active metal sites, supports, and promoters, which could assist in enhanced dispersion of the active metal sites, modify electronic properties, assist in the adsorption and activation of CO<sub>2</sub> on the surface of catalysts, control the activation of H<sub>2</sub>, and promote the carbon chain growth, which could suppress the formation of methane and methanol and thus enhancing the activity and selectivity towards higher alcohols. These factors induce a synergistic interaction among the active metal, the support, and the promoter to facilitate a higher conversion of CO<sub>2</sub> with enhanced selectivity for higher alcohols, as discussed in detail in the case-by-case studies presented in this review. Our understanding remains limited despite significant efforts over the past few years to study catalyst design for product selectivity control and mechanistic investigation in HAS. Unlike the well-established and commercially industrialized C<sub>1</sub> production, such as methanol synthesis, the complexity of these reaction pathways and the challenges in catalyst design (requiring a balance among product selectivity, catalyst

stability, and catalytic activity) pose substantial hurdles. Therefore, in-depth investigations of the nature of active sites and reaction pathways through combining advanced characterization (*e.g.*, *in situ* XPS, *in situ* DRIFTS, and CO-TPSR-MS) with computational catalysts (*e.g.*, DFT calculations and machine learning) are strongly recommended to develop highly efficient and cost-effective catalysts. After all, future trends in catalyst design can focus on tailoring the interaction between the active metal sites and the support through the formation of strong metal support interaction (SMSI) to optimize the catalytic activity of catalysts, adjusting the appropriate amount of promoter to enhance the carbon chain growth, prevent the formation of C<sub>1</sub> products, and boost the selectivity towards higher alcohols. Additionally, promoting the confinement effect of supports to reduce particle size and understanding the reaction mechanism to predict the catalytic reaction pathway are essential for achieving a higher conversion of CO<sub>2</sub> and greater selectivity for higher alcohols.

## Data availability

The data supporting the findings in this study are sourced from existing literature. Citations are given throughout the paper. Readers may contact the corresponding author, A. C. K. Y., to inquire about this review paper.

## Author contributions

A. T.: methodology, investigation, data curation, formal analysis, writing – original draft, writing – review & editing; M. I.: methodology, investigation, data curation, formal analysis, writing – original draft, writing – review & editing; M. P.: formal analysis, writing – original draft, writing – review & editing, funding acquisition; A. C. K. Y.: methodology, investigation, data curation, formal analysis, writing – original draft, writing – review & editing, project administration.

## Conflicts of interest

There are no conflicts to declare.

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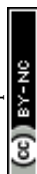
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