

Research progress on the cobalt-based catalysts for the hydrogenation of carbon dioxide to ethanol

BIAN Linghui¹, WANG Jing¹, DING Chenyu¹, SUN Wenjing^{2,*}, WANG Ning^{1,*}

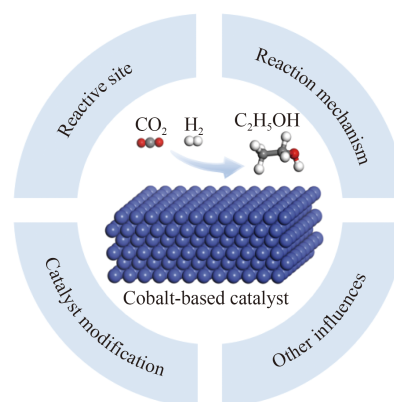
¹ College of Environmental Science and Engineering, Beijing University of Technology, Beijing 100124, China;

² Guangdong Key Laboratory of Medical Molecular Diagnosis, Guangdong Medical University, Dongguan 523808, China

Abstract: The catalytic hydrogenation of CO₂ to ethanol represents a pivotal technology for achieving carbon neutrality and producing high-value fuels and chemicals, where developing the catalysts of high activity, high ethanol selectivity, and long-term stability is vitally important. Currently, the catalysts for the CO₂ hydrogenation to produce ethanol mainly include noble metal-based catalysts (Pt, Pd, Rh, etc.) and Fischer-Tropsch synthesis catalysts (Fe, Co, Mo, etc.); among them, the cobalt-based catalysts have emerged as an ideal candidate for the thermocatalytic hydrogenation of CO₂ to ethanol, owing to their unique electronic structure and tunability. However, the inherent chemical inertness of the relatively stable CO₂ molecule poses a significant barrier to its activation. Furthermore, under high-temperature and high-pressure conditions, the hydrogenation of CO₂ is highly prone to forming undesirable byproducts such as methane or CO, whereas the selective activation of CO₂ and its subsequent conversion into ethanol remain particularly challenging.

Accordingly, current processes for the CO₂ hydrogenation to ethanol are greatly limited by the low single-pass conversion of CO₂, insufficient selectivity toward the target product (ethanol < 60%), and the tendency of catalysts to rapid deactivation. This review aims to conduct a systematic and in-depth analysis of the recent research progress of the cobalt-based catalysts used in the conversion of CO₂ into ethanol. We first establish the basic reaction framework, clarify the thermodynamic boundary conditions, and determine the kinetic steps that control the overall reaction rate. When delving into the molecular-level events, we analyze the complex microscopic mechanisms responsible for the two most critical steps: the initial formation of C–C bonds and the subsequent controlled removal of oxygen. The formation of C–C bonds is a necessary and particularly delicate step for generating ethanol and other C₂₊ products and the reaction mechanism of this step, whether through CO insertion, CO dimerization, or hydroxyl carbonyl (CHOH) coupling, is subject to intense debate and strongly influenced by the properties of the active sites. We then critically assess the synergistic effects among various active sites such as metallic Co, Co₂C, CoO_x and bimetallic configurations on the reaction mechanism; in particular, the structure-activity relationships influenced by the support effects and promoter modifications are thoroughly discussed. Lastly, the application of inverse catalysts and tandem catalytic systems in ethanol synthesis is reviewed. The role of water as a hydrogen source and its impact on the reaction are analyzed in depth. This review tries to integrate current knowledge and identifies existing shortcomings, which presents a forward-looking outlook on the innovative research directions for the cobalt-based catalysts and emphasizes the necessity of conducting complex *in situ*/operational characterization and theoretical modeling in the design of next generation multifunctional catalysts. All these may provide a valuable reference framework to stimulate and guide the development of future efficient cobalt-based catalytic systems, deepen the basic understanding of reaction processes and mechanisms, and ultimately accelerate the progress of CO₂ hydrogenation technology for sustainable ethanol production.

Key words: cobalt-based catalysts; carbon dioxide; ethanol; reaction mechanism; active sites



Since the Industrial Revolution, carbon dioxide emissions have increased dramatically, posing severe challenges to the global ecosystem and social development. Nowadays, we

are facing increasingly serious environmental problems^[1–2], such as climate warming, accelerated glacier melting, and rising sea levels^[3]. Against this background, how to

Received: 2025-10-25; Revised: 2025-12-02

Foundation items: Supported by the National Natural Science Foundation of China (22278008) and the Open Research Fund of Suzhou Laboratory (SZLAB-1308-2024-TS009).

* Corresponding author. Tel: 010-67392430, E-mail: swj_gdmc@163.com, ning.wang.1@bjut.edu.cn.

DOI: 10.1016/S1872-5813(26)60666-4 CSTR: 32157.14.2097-213X.2026.JFCT.0022

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effectively reduce CO₂ emission and achieve a sustainable socio-economic development has become a major global issue^[4–5]. As shown in Figure 1, in the long term, utilizing chemical conversion technologies to valorize CO₂ into high-value-added chemicals not only helps build a sustainable artificial carbon cycle system but also reduces the dependence on traditional fossil fuels. This is widely regarded as a strategic pathway with both economic feasibility and environmental friendliness^[6]. Currently, through catalytic hydrogenation, CO₂ can be transformed into various chemical products such as carbon monoxide, methane, methanol, ethanol, and olefins^[7–8], where “green hydrogen”, produced *via* water electrolysis using renewable energy (wind, solar, etc.), serves as a clean hydrogen source with none carbon emissions and becomes an important energy carrier for promoting CO₂ chemical conversion. Compared to traditional hydrogen production from fossil fuels, green hydrogen can effectively reduce carbon footprint, providing key support for achieving the goal of carbon neutrality^[9–11]. Therefore, CO₂ hydrogenation technology holds broad prospects and warrants further research^[12–13].

Ethanol, as an important fuel additive, disinfectant and solvent, has become one of the widely studied chemicals in the field of chemical synthesis^[15–18], with continuously growing market demand^[19–20]. Traditional ethanol synthesis methods mainly rely on natural feedstock fermentation and ethylene hydration^[21–22]. Fermentation-based ethanol synthesis heavily depends on grain crops and has high costs, whereas ethylene hydration, conducted under strong acidic conditions, may cause equipment corrosion and is limited by equilibrium conversion. With the continuous growth of the global population and socio-economic development, traditional ethanol production methods can no longer meet the production and living demands. Developing low energy consuming, large scale and environmentally friendly ethanol production methods has become an urgent need^[23–25]. Although CO₂ hydrogenation to methanol has made certain progress and is gradually being applied in industrial processes, the synthesis of ethanol from CO₂

hydrogenation is significantly more difficult than the methanol synthesis and requires further in-depth exploration^[26–29]. As ethanol molecules contain a C–C bond and require retention of a C–O bond^[30–33], its synthesis process not only needs to overcome the chemical inertness of CO₂, but also need to achieve precise C–C bond coupling, placing higher demands on catalytic system design^[34–36]. In this reaction, synergistic effects between active sites are crucial for promoting carbon chain growth^[37–39]. Based on existing research, CO₂ hydrogenation to ethanol mainly includes three pathways: electrocatalysis, photocatalysis, and thermocatalysis. Electrocatalysis relies on external electrical current to drive the reaction but is still constrained by high energy consumption and low efficiency^[40–41]. Photocatalysis utilizes photogenerated electron-hole pairs to achieve redox conversion; however, the light absorption efficiency of catalysts and carrier separation capabilities still need improvement^[42–43]. In contrast, thermocatalysis is relatively mature, with fast reaction rates and easy product separation, making it a more practically promising technological direction in current CO₂ hydrogenation to ethanol research^[44–47].

For the hydrogenation of CO₂ to ethanol, the catalyst systems such as noble metal (Pd, Pt, Rh, Ir) and non-noble metal (Fe, Mo, Co) based catalysts have been extensively studied^[48–52], among them, Co-based catalysts offer relatively low cost and are advantageous for CO₂ hydrogenation^[53]. However, current relevant researches mostly focus on the macro-level descriptions of overall progress in CO₂ hydrogenation to ethanol or delve deeply into the significant advantages of cobalt-based catalysts in Fischer-Tropsch synthesis systems. There remains a gap in systematically elaborating on cost-effective cobalt-based catalysts in the field of CO₂ hydrogenation to ethanol, particularly regarding their unique catalytic conversion mechanisms. Therefore, this article aims to review the thermodynamic and kinetic characteristics, reaction mechanistic pathways, and structural features of various catalysts for CO₂ hydrogenation to ethanol over different Co-based catalysts.

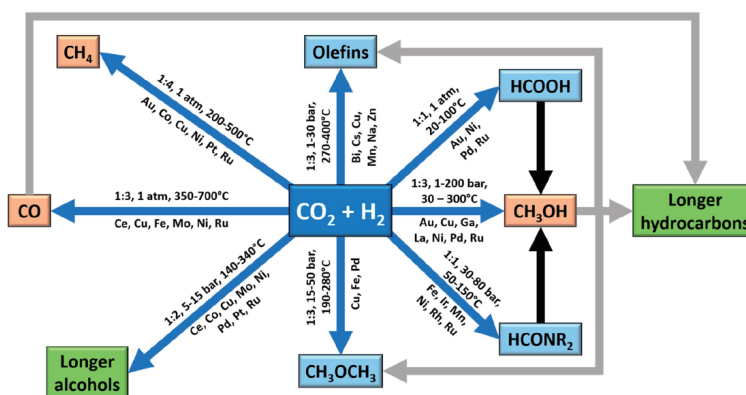


Fig. 1 Conversion of CO₂ to chemicals and fuels through hydrogenation^[14]
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By exploring the correlation between catalyst structure, surface properties, and their roles in the reaction mechanism, this review elucidates how these factors influence the catalytic activity, product selectivity, and stability in CO₂ hydrogenation to ethanol. It is hoped that this review will provide theoretical support for a deeper understanding of the reaction mechanism and offer insights for designing and synthesizing new, efficient, low-cost catalysts, thereby advancing the industrial application of CO₂ catalytic hydrogenation to ethanol technology.

1 Thermodynamic analysis of the carbon dioxide hydrogenation

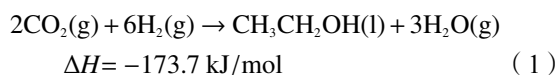
1.1 Characteristics of carbon dioxide

CO₂ is a linear covalent molecule containing two C=O double bonds, with the bond energy of as high as 799 kJ/mol, bond length of 116.3 pm and bond dissociation energy of 531.72 kJ/mol^[54]. As the final oxidation product of carbon, it possesses high thermodynamic stability and is difficult to activate^[55]. The electrons in the CO₂ molecule are concentrated on the two oxygen atoms, with the carbon atom exhibiting strong electrophilicity and can act as an electrophile to attack nucleophilic sites^[56–57]. Additionally, carbon has Lewis acid properties and can be activated by base catalyst. Therefore, designing and developing efficient catalytic centers to improve catalyst activity and product selectivity is key to achieving large-scale industrialization of CO₂ hydrogenation to ethanol^[58–59].

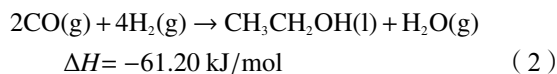
1.2 Thermodynamic analysis

As a complex reaction system, CO₂ hydrogenation involves competition among multiple reactions:

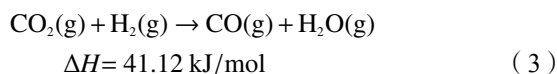
(1) CO₂ hydrogenation to ethanol:



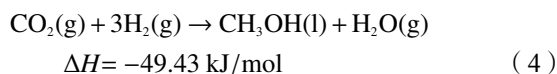
(2) CO hydrogenation to ethanol:



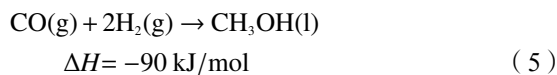
(3) Reverse water-gas shift reaction (RWGS):



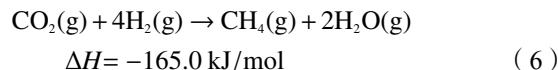
(4) CO₂ hydrogenation to methanol:



(5) CO hydrogenation to methanol:



(6) CO₂ hydrogenation to methane:



Among these, reaction (1), as the primary reaction, is thermodynamically exothermic and accompanied by a decrease in gas volume. To achieve effective conversion of CO₂ hydrogenation, a low-temperature and high-pressure condition is thermodynamically favorable. Reactions (2), (4), (5) and (6) are also exothermic and accompanied by a decrease in gas volume and therefore favorable under low-temperature and high-pressure conditions, meaning that such conditions are also in favor of forming side-products like methanol, methane, etc. The RWGS reaction (3) is endothermic and increasing temperature promotes the forward reaction of RWGS but is detrimental to improving the equilibrium alcohol yield. Therefore, appropriate conditions are essential to achieve a desired reaction result^[60–63].

2 Reaction mechanism for the carbon dioxide hydrogenation to ethanol

In-depth study of the reaction mechanism can facilitate the design of better catalyst. Due to the diversity of CO₂ hydrogenation reaction pathways and the lack of highly active catalysts, the active centers and reaction mechanism for CO₂ hydrogenation to ethanol remain unclear. The lack of theoretical calculations further hinders research on the reaction mechanism for CO₂ hydrogenation to ethanol.

2.1 Mechanism mediated by CO

The route mediated by CO is currently the most widely studied reaction mechanism. The transformation can be viewed as a combination of the RWGS reaction and syngas to ethanol synthesis^[48]. Ethanol synthesis is primarily achieved through the coupling reaction of *CH_x and *CO. Its core mechanism originates from the RWGS process, where CO₂ hydrogenation generates CO that is stably adsorbed on the catalyst. The adsorbed CO then undergoes deep hydrogenation to form *CH_x which is also adsorbed on the catalyst. Subsequently, the adsorbed *CH_x and *CO undergo a *CH_x–*CO coupling reaction under the synergistic action of the catalyst, ultimately forming ethanol^[53,64]. Figure 2 shows three common pathways for CO₂ hydrogenation to ethanol.

Lou et al.^[65] constructed atomically dispersed Pd dimers (Pd₂) on the surface of CeO₂ nanorods to study the CO₂ hydrogenation to ethanol (Figure 3(a)–(d)). Combined with DFT calculations, they found that the reaction pathway on this catalyst follows the *CO–*CH_x path, and the Pd dimer determines the ethanol formation process by forming a unique stable Pd₂–O₄ structure. In this catalytic system, since the dissociation energy barrier for CO₂ is lower than that for the formate pathway, the required CO can be formed by direct dissociation of CO₂. CO undergoes

subsequent hydrogenation and C–C coupling reactions, ultimately generating ethanol (Figure 3(e)).

2.2 Methanol-mediated mechanism

In addition to the above reaction pathway using CO as a key intermediate, methanol, as a common C₁ product, can also serve as an intermediate for ethanol formation. While there has been much research on CO₂ to methanol^[66–67], methanol catalysts cannot extend the carbon chain due to their poor C–C coupling ability. Therefore, methanol catalysts should be modified to impart chain-lengthening functionality^[68–69]. This process involves the CO₂ hydrogenation to *CO, followed by the hydrogenation of *CO to *CH_x. Hydrogenation of *CH_xO accelerates C–O bond cleavage, ultimately forming *CH_x as the main product, which then couples with *CO and undergoes hydrogenation to generate ethanol^[70–71]. Zhao et al.^[72] studied the plasma-promoted process of CO₂ to ethanol over a Cu/ZnO/Al₂O₃ catalyst. Methanol was initially generated on the Cu/ZnO/Al₂O₃ catalyst. When the catalyst was modified by plasma, electrons interacted with methanol, leading to its dissociation into *CH₃ and *OH species. The results confirmed that plasma-modified copper promoted methanol dissociation, and the *CH₃ species generated with copper assistance coupled to form a *CH₃CO intermediate, which was subsequently hydrogenated to ethanol.

2.3 Formate mechanism

Studies show that CO₂ can directly form a formic acid

intermediate (*HCOO) through hydrogenation that participates in subsequent reactions. Specifically, *HCOO is first hydrogenated to *CH_x and *CH_x then couples with *HCOO to form *CH₃COO, which undergoes further hydrogenation to generate ethanol. Zheng et al.^[73] found that over a Co/La₂O₃-La₄Ga₂O₉ catalyst, CO₂ follows the formate-mediated mechanism, where the HCOO–CH_x coupling is the key step for ethanol generation.

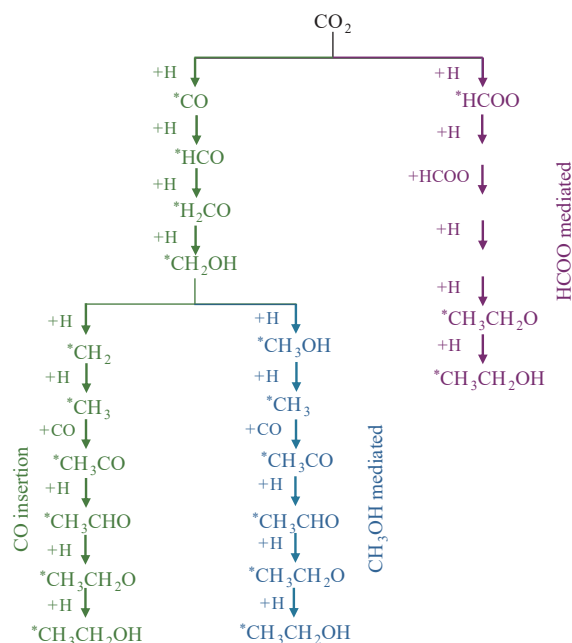


Fig. 2 Three reaction ways of catalytic hydrogenation of carbon dioxide to ethanol

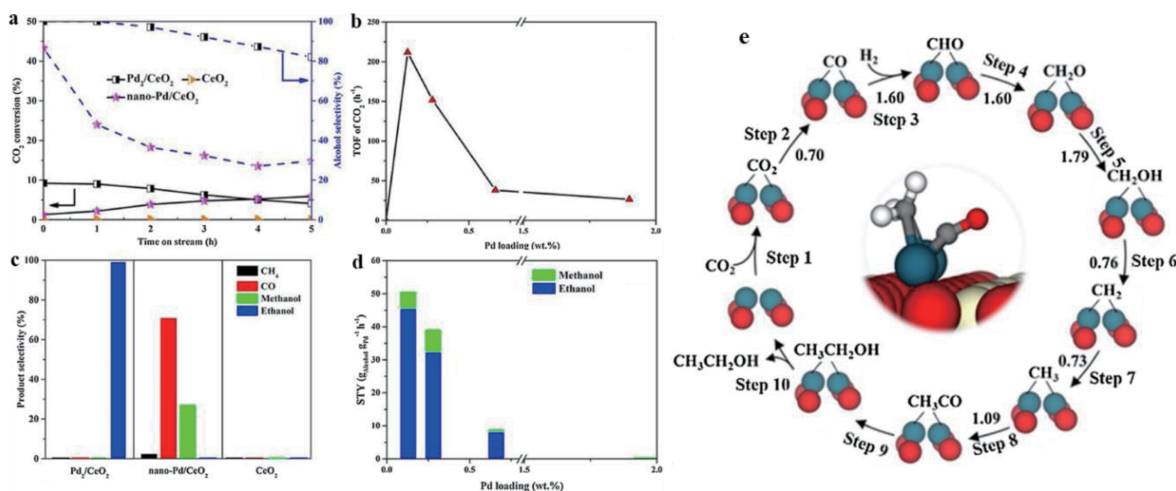


Fig. 3 Catalytic performance of pure CeO₂, nano-Pd/CeO₂ and Pd₂/CeO₂ catalysts for the CO₂ hydrogenation: (a) CO₂ conversion and alcohol selectivity, (b) turnover frequency (TOF) of CO₂ based on the Pd species in Pd/CeO₂, (c) product distribution, (d) space-time yield (STY) of ethanol and methanol over the Pd/CeO₂ catalysts with different Pd loadings (Reaction conditions: H₂/CO₂ = 3, 240 °C, 3 MPa, 3000 mL/(g·h)); (e) Activation barriers of elementary steps involved in the catalytic cycle for the formation of ethanol over Pd₂/CeO₂(110)^[65] (with permission from Elsevier)

3 Catalytically active sites

The active sites of cobalt-based catalysts for the CO₂ hydrogenation to ethanol are mainly divided into metallic Co sites, cobalt oxide sites, cobalt carbide sites, and bimetallic sites. The ethanol formation steps are complex, and a single type of site has limited functionality, making efficient ethanol synthesis unachievable. Therefore, synergistic effects among multiple sites are typically required to promote ethanol formation^[74].

3.1 Co⁰-CoO_x sites

On the cobalt-based catalysts, the C–O bond in CO₂ is easily cleaved, generating hydrocarbons *via* hydrogenation. Cobalt elements in different valence states exhibit different properties: Co⁰ possesses strong hydrogenation ability, while Co^{δ+} plays a key role in adsorbing and activating intermediates. Given the multiple functions of both valence states in ethanol synthesis, research on the cobalt-oxygen composite (Co⁰-Co^{δ+}) active phases has progressed. Wang et al.^[75] prepared a series of Al₂O₃-supported non-noble metal cobalt-based catalysts to investigate their performance for the CO₂ hydrogenation to ethanol (Figure 4(a)). Reducing the precursor Co–Al LDH at 600 °C resulted in the coexistence of Co⁰ and CoO_x phases in the catalyst, with Co⁰ nanoparticles in close contact with CoO_x, generating a large number of Co⁰-CoO_x interfaces (Figure 4(b) and 4(c)). Here, Co⁰ is responsible for H₂ adsorption and dissociation, promoting the formation of C–H bond, whereas CoO_x handles the CO₂ adsorption and activation. The Co⁰-CoO_x interface facilitates subsequent *CH₃ intermediate generation and insertion reactions, converting formate to acetate—a key step for ethanol formation. The synergistic effect of these two sites avoids by-product formation, enabling efficient CO₂ hydrogenation to ethanol^[76].

3.2 Co⁰-Co₂C sites

In addition to the Co⁰-CoO_x active sites that facilitate

C–C coupling *via* the pathway of *CH₃ insertion into formate, the Co⁰-Co₂C metal-carbide active site has garnered widespread attention in recent years due to its unique ability for CO non-dissociative adsorption and directed C–C coupling. Research on Co₂C dates back to 2000 when Volkova et al.^[77] first proposed and verified that Co₂C can promote CO non-dissociative adsorption: at specific temperatures, CO molecules undergo carburization on the surface to form Co₂C, forming a structure where Co metal and Co₂C co-exist. The temperature for high selectivity towards higher alcohols coincides with the stable existence temperature of the Co₂C phase. Once Co₂C decomposes, the catalyst loses its CO non-dissociative adsorption function, and the alcohol selectivity decreases. Building on this, Lebarbier et al.^[78] designed a more complex Co/La₂O₃/AC system to explore the relationship between Co₂C formation and alcohol selectivity (Figure 5(a)). They found that the dual sites formed by Co⁰ and Co₂C at the interface act as the catalytically active sites. CO dissociates on the metallic Co surface, and the resulting carbon atoms penetrate the Co lattice. With the assistance of the La₂O₃ promoter and the AC support, Co₂C can form stably. That is, CO dissociative adsorption and chain growth occur on the metallic Co sites, while Co₂C sites are responsible for CO non-dissociative adsorption. Zhang et al.^[79] deposited carbon species *via* methane catalytic cracking (CDM) on a CoGaAlO₄/SiO₂ catalyst to construct and regulate Co-Co₂C active site pairs (Figure 5(b)). The active site structure consists of Co⁰ nanoparticles in close coexistence with Co₂C species, forming a composite structure. In this structure, the metallic Co⁰ sites are primarily responsible for hydrogen activation and dissociation and provide strong C–C chain growth capability, whereas the Co₂C sites' key function is to promote non-dissociative adsorption of the CO intermediate, stabilizing oxygen-containing intermediates, thereby steering the reaction towards alcohol formation and effectively inhibiting the side reaction of over-hydrogenation to methane, offering new ideas for catalyst design.

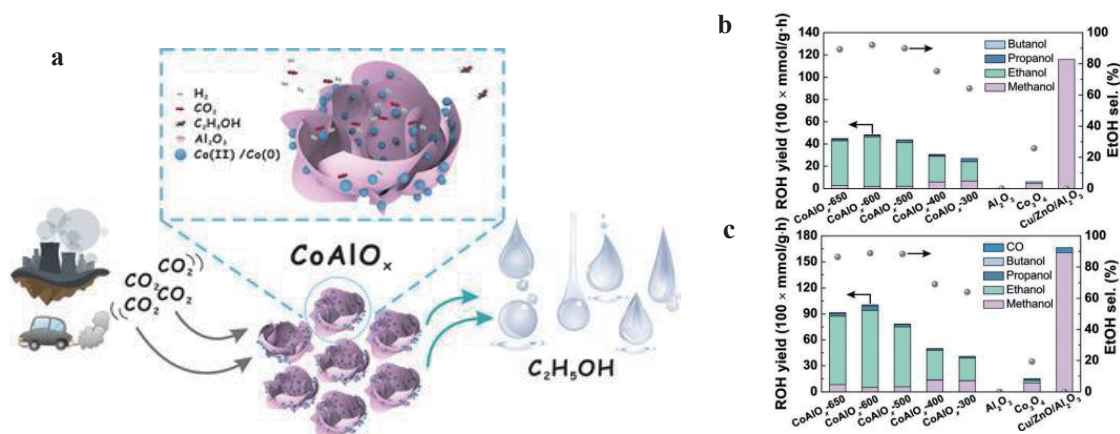


Fig. 4 Schematic diagram of the hydrogenation of CO₂ to ethanol on the CoAl_x catalyst (a); Performance of various catalysts in the CO₂ hydrogenation at 140 °C (b) and 200 °C (c)^[75] (with permission from Wiley)

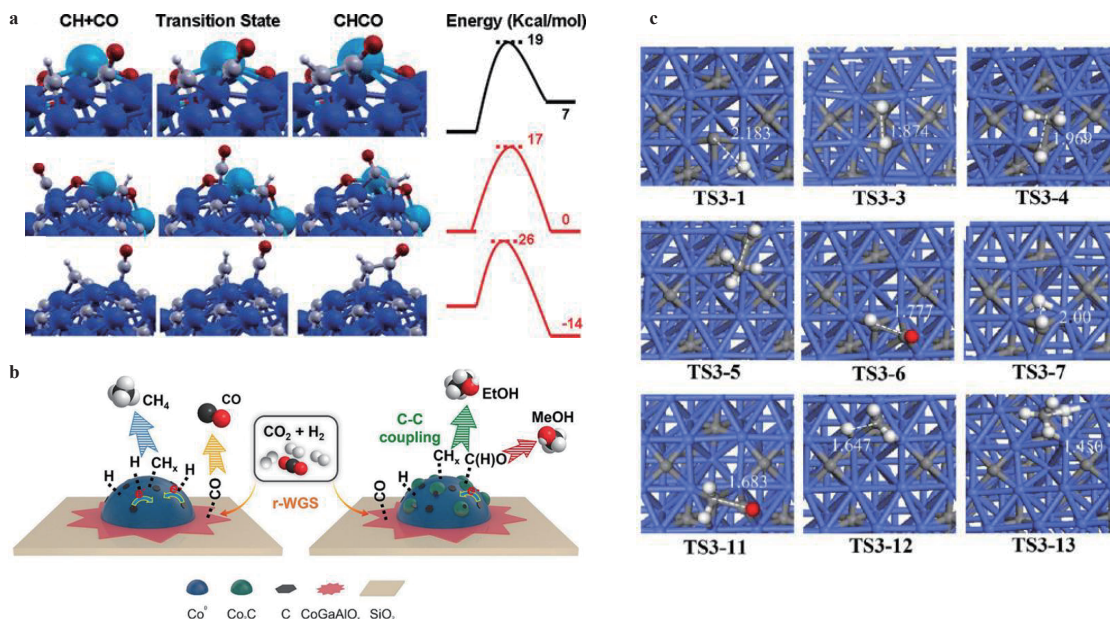


Fig. 5 (a) Calculated energy landscape for $\text{CH} + \text{CO} \rightarrow \text{CHCO}$ on different interface and Co_2C ^[78]; (b) Plausible mechanism of CO_2 hydrogenation for alcohols synthesis over CDM catalysts^[79]; (c) Potential energy profile of Gibbs free energy (493 K) for the first three favorable reactions related to CH_x ($x = 1-3$) species together with transition states (TSs) starting from $^*\text{CH}_3$ species on the Co_2C (111) surface^[80] (with permission from ACS Publications and Elsevier)

Zhang et al.^[80] used theoretical calculations to reveal the reaction mechanism of CO_2 hydrogenation to ethanol on the $\text{Co}/\text{Co}_2\text{C}$ (111) interface (Figure 5(c)). The results indicate that on the metallic Co surface, the C–O bond of the CO molecule breaks, generating surface C atoms, which are further hydrogenated to form the required $^*\text{CH}_x$ intermediates. In contrast, the Co_2C (111) surface exhibits excellent non-dissociative adsorption ability, stabilizing CO in molecular form as $^*\text{CO}$ intermediates. When these intermediates are precisely fixed at their respective active sites, the C atom of $^*\text{CO}$ and the C atom of $^*\text{CH}_x$ undergo C–C coupling, forming the key $^*\text{CHCO}$ intermediate, which is subsequently hydrogenated to ethanol.

3.3 $\text{Co}^0\text{-CoO}_x\text{-Co}_2\text{C}$ sites

As mentioned, $\text{Co}^0\text{-CoO}_x$ and $\text{Co}^0\text{-Co}_2\text{C}$ sites have significant advantages in dissociating/activating CO_2 and stabilizing intermediates to promote the C–C coupling. Building on the different functions of these dual active sites, the idea of functionally complementing them to construct $\text{Co}^0\text{-CoO}_x\text{-Co}_2\text{C}$ sites emerged. Jo et al.^[81] synthesized a sodium and manganese co-promoted $\text{Co}@\text{CoO}_x/\text{Co}_2\text{C}$ catalyst for the CO_2 hydrogenation (Figure 6(a)). They observed that this catalyst can effectively promote carbon chain growth, owing to the clever synergy among different Co phases in the catalyst. The CoO_x shell, rich in oxygen vacancies, is the main activation site for CO_2 , requiring only a 0.15 eV energy barrier for direct dissociation to generate CO. Additionally, CoO_x prevents direct contact between CO_2 and the core Co^0 , effectively inhibiting the deep hydrogenation reaction of CO_2 on Co^0 (Figure 6(b)–(e)). Subsequently, CO migrates to the Co_2C and Co^0 sites at the

interface. Here, Co^0 is the core site for carbon chain growth and CO hydrogenation, ensuring rapid consumption of CO, driving the reaction forward, and reducing CO by-product formation. The Co_2C site assists chain growth and stabilizes the structure. These three Co species synergistically form a complete active site system, achieving efficient CO_2 conversion.

3.4 Bimetallic oxide sites

For the CO_2 hydrogenation to ethanol, to achieve precise regulation of key C_1 intermediate generation and matching, bimetallic-oxide composite active sites are developed that go beyond single-metal sites^[82]. These sites are typically composed of bimetallic alloy nanoparticles and adjacent metal oxides. The bimetallic component optimizes hydrogenation capability through electronic effects, responsible for efficiently generating and stabilizing specific intermediates, while the oxide component mainly handles CO_2 adsorption and activation. The close synergy between them enables precise guidance of the reaction pathway, significantly improving ethanol selectivity and yield. Wang et al.^[83] prepared a series of $\text{Co}_m\text{Ni}_n\text{O}_x$ catalysts for CO_2 hydrogenation to ethanol (Figure 7(a)) and found that the $\text{Co}_{0.52}\text{Ni}_{0.48}\text{O}_x$ catalyst exhibits excellent ethanol selectivity at 200 °C (Figure 7(b)). The $\text{Co}_{0.52}\text{Ni}_{0.48}\text{O}_x$ catalyst contains both CoNi alloy and CoO phases; their synergistic effect enhances the ethanol selectivity. The CoNi alloy promotes the generation of the key $^*\text{CH}_x$ intermediate, whereas the CoO phase favors the formation of the $^*\text{HCOO}$ intermediate. The reaction follows the $\text{CH}_x\text{-HCOO}$ coupling path, where $\text{CH}_x\text{-HCOO}$ is subsequently hydrogenated to ethanol.

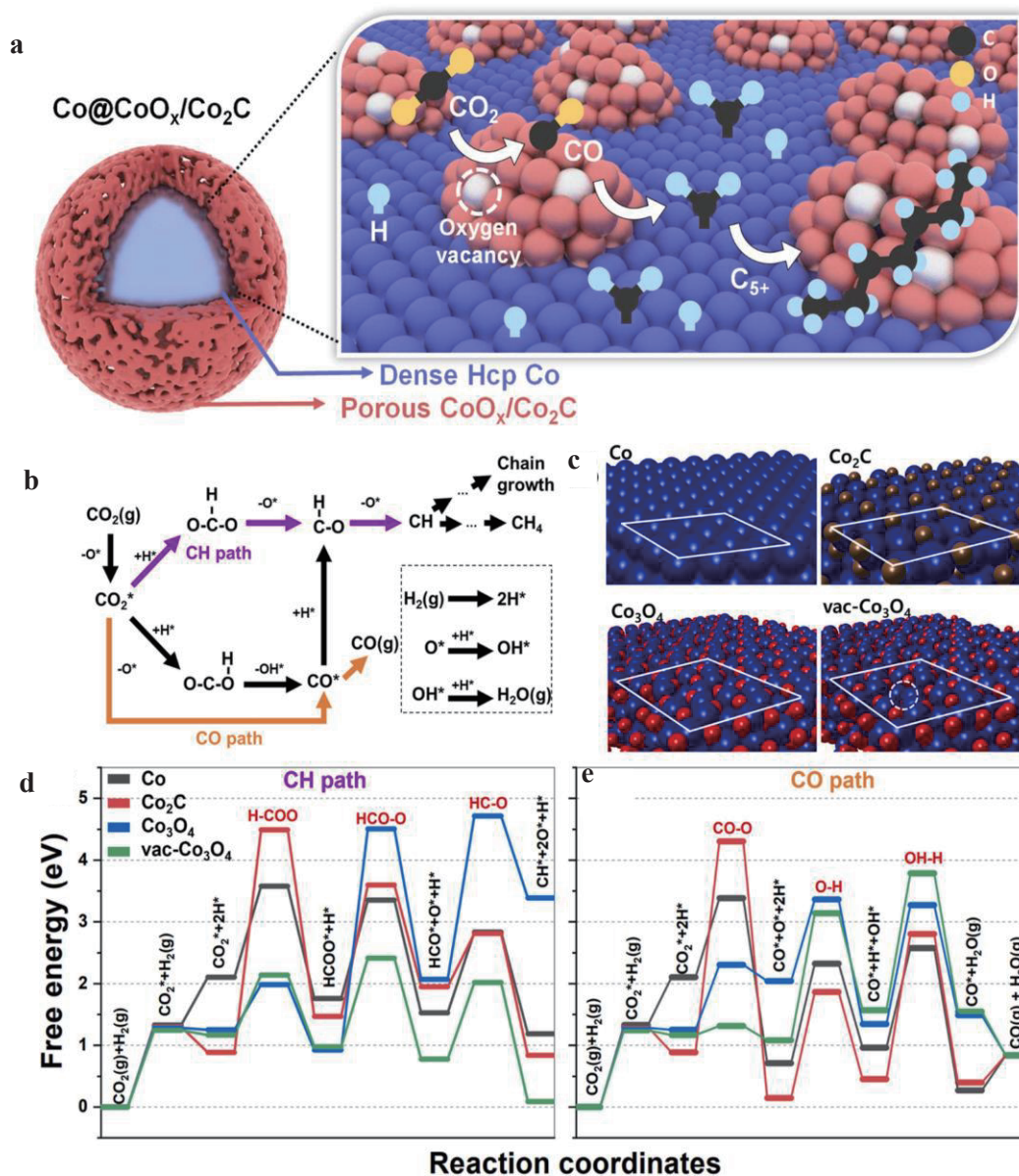


Fig. 6 (a) Schematic reaction mechanism for the direct conversion of CO₂ to long-chain C₅₊ hydrocarbons on the core-shell Co@CoO_x/Co₂C catalyst; (b) CO₂ hydrogenation pathway; (c) Structures of Co(001), Co₂C(101), Co₃O₄(110), vac-Co₃O₄(110) surfaces; (d) and (e) Free energies of CO₂ hydrogenation for CH and CO under 270 °C and 4.0 MPa^[81] (with permission from Elsevier)

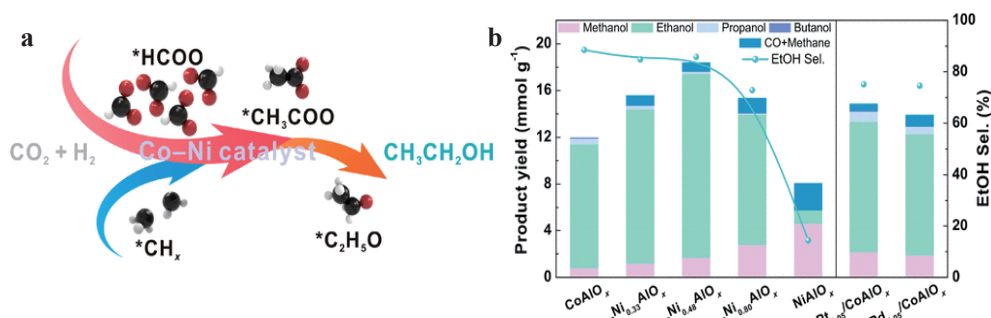


Fig. 7 (a) Schematic illustration of the *CH_x insertion to *HCOO in C₂ oxygenates formation on the CoAlO_x catalyst; (b) Catalytic performance of Co_mNi_nAlO_x catalysts in the CO₂ hydrogenation^[83] (with permission from ACS Publications)

4 Composition of the cobalt-based catalysts for the CO₂ hydrogenation to ethanol

The activity and product selectivity for CO₂ hydrogenation to ethanol are related not only to the construction of different active sites but also to other factors such as supports and promoters. Single active sites are prone to agglomeration, sintering, and coking during the reaction, leading to catalyst deactivation. Therefore, introducing suitable supports and promoters can significantly improve catalyst performance. Table 1 lists the performance of common cobalt-based catalysts for the CO₂ hydrogenation to ethanol in recent years.

4.1 Supports

For the CO₂ hydrogenation to ethanol, the support is an indispensable component of the catalyst and plays a crucial role in its performance^[12, 96–97]. The functions of the support are mainly reflected in the following aspects: first, introducing a support can disperse the active component, increasing the number of active sites; second, it can modify the electronic structure of the active component, influencing intermediate adsorption. In addition, the introduction of a support can also enrich surface Lewis/Brønsted acid-base sites, enabling synergistic catalysis and C–C coupling.

Different supports, due to their varied chemical

properties, significantly impact ethanol selectivity. Das et al.^[84] investigated the influence of three different supports (Al₂O₃, MgO-MgAl₂O₄ and MgO) on the catalytic performance for ethanol synthesis over supported cobalt catalysts, focusing on support structure (Figure 8(a)). The results showed that Co/MgO-MgAl₂O₄ exhibited the best catalytic performance. The Al₂O₃ support promotes the formation of the difficult-to-reduce CoAl₂O₄ phase, favoring CO intermediate formation. The MgO support facilitates the formation of Co⁰ sites, promoting C–C coupling, and enhances the basicity of the support, optimizing CO₂ adsorption and promoting ethanol formation (Figure 8(b)). Zhang et al.^[85] approached from the perspective of inhibiting by-product selectivity, preparing a series of Na-promoted cobalt-based catalysts (Na-Co/X, where X = Al₂O₃, ZnO, AC, TiO₂, SiO₂, Si₃N₄) to study the effect of support type on catalytic performance (Figure 8(c)). The results indicated that SiO₂ and Si₃N₄ supports showed advantages. They form strong Si–O–Co interactions, effectively stabilizing the key Co₂C active phase, preventing its decomposition to metallic Co, thereby inhibiting methane selectivity. In contrast, on the Al₂O₃ and ZnO supports, due to the difficulty in carburizing to form a stable Co₂C phase, the cobalt species exist only as CoO, leading to products being entirely methane. Although TiO₂ and AC supports can form the Co₂C phase, they lack strong metal-support interaction. Co₂C rapidly decomposes during the reaction, also generating methane (Figure 8(d)).

Table 1 Cobalt-based catalysts for the CO₂ hydrogenation to ethanol

Catalyst	H ₂ /CO ₂	p/MPa	t/°C	GHSV /(mL·g ⁻¹ ·h ⁻¹)	CO ₂ conv./%	C ₂ H ₅ OH sel./%	C ₂ H ₅ OH STY /(mmol·g ⁻¹ ·h ⁻¹)
Co/La ₂ O ₃ -La ₄ Ga ₂ O ₉ ^[73]	3	3	240	3000	9.8	65.8	2.16
CoAlO _x -600 ^[75]	3	4	140	20 mg catalyst in 2 mL water for 15 h	—	92.1	0.444
Co/GaAlO ₄ /SiO ₂ ^[79]	3	3	270	3000	3.7	16.9	—
Co _{0.52} Ni _{0.48} O _x ^[83]	3	4	200	25 mg catalyst in 2 mL H ₂ O for 12 h	—	85.7	1.34
Co/MgO-MgAl ₂ O ₄ ^[84]	3	3	270	2000	25.1	17.9	1.04
Na-Co/SiO ₂ ^[85]	3	5	250	4000	18	62	—
Co/La ₄ Ga ₂ O ₉ ^[86]	3	3.5	270	3000	4.6	34.7	—
3K-CuCo-1 ^[87]	3	3	260	—	—	38.8	2.76
1%Na-20%Co/SiO ₂ ^[88]	3	1.9	220	3000	12.4	0.3	—
Cu ⁰ /Cu ⁺ -CoGaO _{0.4} ^[89]	3	3	220	—	17.8	23.8	1.35
CoFeMo10 ^[90]	3	5	320	24000	38.3	21.5	4.37
1wt.%Pt-Co ₃ O ₄ ^[91]	3	3.2	240	—	—	87.9	0.265
Co _m Al _n O _x -R ^[92]	3	4	180	—	—	—	0.123
Co ₂ C CuZnAl ^[93]	3	5	250	12000	20.7	18.3	2.2
FeCo&CZA ^[94]	3	5	320	4500	51.5	49.1	5.34
Ni-In ₂ O ₃ /K-Co ₃ O ₄ ^[95]	3	4	300	4000	38.1	20	1.40

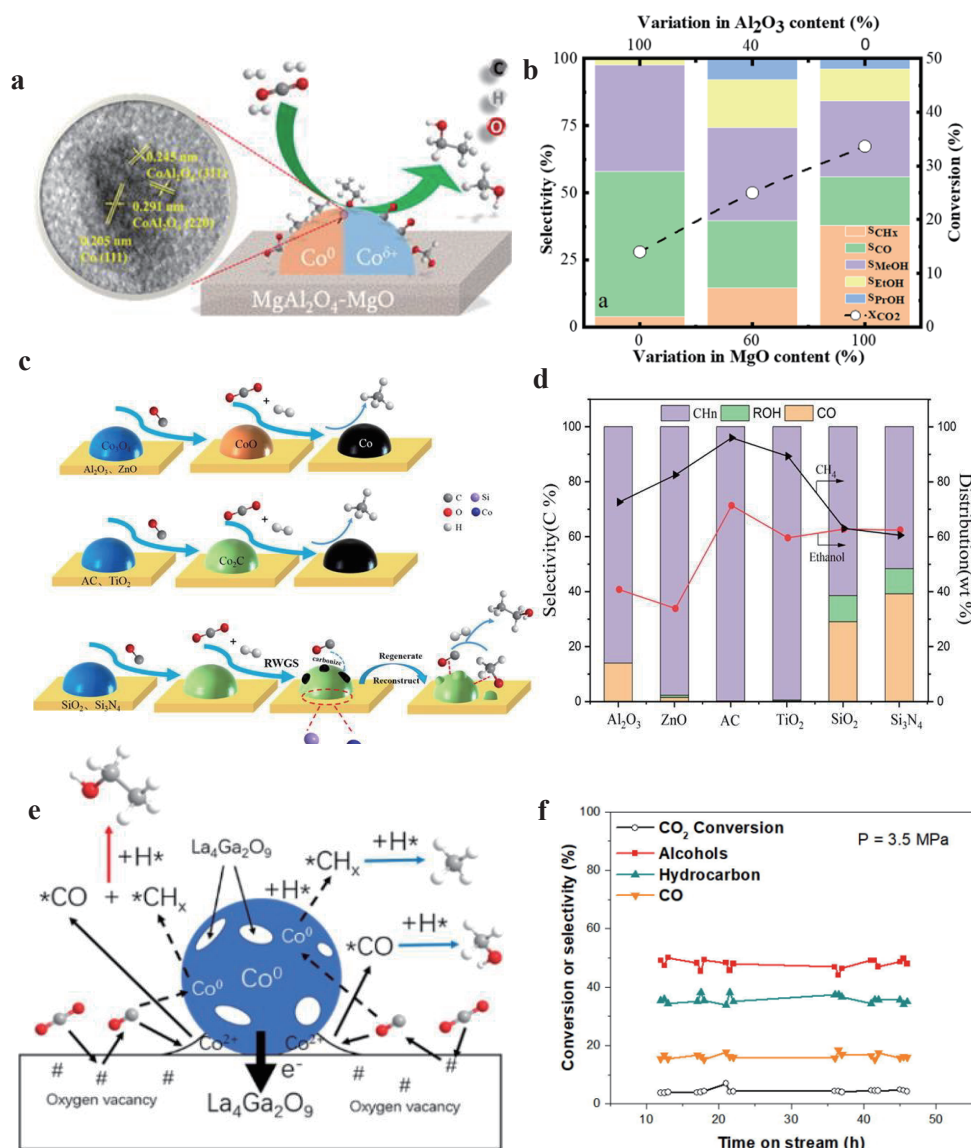


Fig. 8 (a) Schematic diagram of the CO_2 hydrogenation to ethanol over $\text{Co/MgO-MgAl}_2\text{O}_4$ catalyst^[84]; (b) Activity of the calcined catalysts as a function of Co^0 (%) and $\text{Co}^{\delta+}$ (%); (c) Mechanism of stabilizing Co_2C during the reaction; (d) Comparison of various catalysts with different carriers in their performance in the CO_2 hydrogenation^[85]; (e) Schematic diagram of the CO_2 hydrogenation to ethanol over $\text{Co/La}_4\text{Ga}_2\text{O}_9$ catalyst; (f) Performance of the $\text{Co/La}_4\text{Ga}_2\text{O}_9$ catalyst for CO_2 hydrogenation under 3 MPa^[86] (with permission from IOS Press Publications and Elsevier)

This indicates that the ability of different supports to establish strong interactions with the active center directly determines the formation ability of the active phase and the final product distribution. The introduction of SiO_2 and Si_3N_4 supports enabled the catalyst to exhibit about 18% CO_2 conversion and up to 62% ethanol selectivity under 250 °C and 5 MPa, showing that the supports can significantly affect the active phases of Co.

Similarly, Zheng et al.^[73] prepared a $\text{Co/La}_2\text{O}_3\text{-La}_4\text{Ga}_2\text{O}_9$ catalyst using the $\text{LaCo}_{1-x}\text{Ga}_x\text{O}_3$ precursor, investigating the influence of support basic sites on the reactant conversion and the chemical state of active Co species (Figure 8(e)). The La_2O_3 support provides abundant basic sites for adsorbing and activating CO_2 molecules. Ga^{3+} in the $\text{La}_4\text{Ga}_2\text{O}_9$ support interacts electronically with Co, making certain Co species presence in the form of $\text{Co}^{\delta+}$. Two

supports synergistically promote ethanol formation. An et al.^[86] further utilized the $\text{LaCo}_{0.5}\text{Ga}_{0.5}\text{O}_3$ precursor to prepare a $\text{Co/La}_4\text{Ga}_2\text{O}_9$ catalyst, to explore which chemical state of Co can effectively enhance its performance in the CO_2 hydrogenation to ethanol. The results indicated that the constructed $\text{Co}^0\text{-Co}^{\delta+}$ dynamic active sites efficiently achieve triangular electron transfer among $\text{Co}^0 \leftrightarrow \text{support} \leftrightarrow \text{Co}^{\delta+}$, accelerating the subsequent hydrogenation/coupling steps of the CO intermediate rather than desorption into the gas phase. Meanwhile, a strong metal-support interaction exists between the $\text{La}_4\text{Ga}_2\text{O}_9$ support and the active metallic Co species. Its surface is rich in oxygen vacancies, efficiently adsorbing and activating CO_2 molecules to form $^*\text{CO}$. This catalyst exhibited a total selectivity of up to 74.7% to alcohols under mild conditions (270 °C, 3.5 MPa) (Figure 8(f)), which indicates that the

support not only promotes reactant adsorption and activation through oxygen vacancies and basic sites, but also effectively regulates the chemical state of active Co sites, promoting the conversion of intermediates in the CO₂ hydrogenation to ethanol.

4.2 Promoters

To further regulate the reaction pathway and improve target product selectivity, besides adjusting the active center *via* the support, introducing promoters becomes a key strategy. The key to the CO₂ hydrogenation to ethanol reaction lies in balancing CO dissociative and non-dissociative adsorption^[93]. However, on the pure Co-based catalysts, this balance is often difficult to achieve, leading to the over-hydrogenation of CO to methane, making ethanol formation challenging. Therefore, promoters are added to suppress excessive CO hydrogenation to methane^[94]. Simultaneously, CO insertion is the core of C–C bond formation, a key step for ethanol generation. Promoters can stabilize the non-dissociative adsorption state of CO and promote CO insertion into *CH_x species to form the *CH₃CO intermediate, ultimately leading to a high selectivity to ethanol *via* hydrogenation^[98].

Using alkali metals as catalytic promoters can effectively modulate the reaction pathway to some extent. Alkali metals, as strongly electropositive elements, can serve as controllable basic sites. When added to the catalyst surface, they cover the surface, neutralizing acidic sites and enhancing the overall surface basicity, thereby affecting the catalyst performance^[99]. Xu et al.^[100] proposed that K, as a key promoter, can promote electron transfer *via* electronic modulation, strengthen linear CO adsorption, and balance CO dissociative and non-dissociative activation. Adding alkali metals to regulate the reaction pathway inhibits the formation of hydrocarbon by-products, thereby promoting ethanol generation. Zhang et al.^[87] successfully synthesized a series of potassium-doped Cu/CoO_x catalysts using the Cu-Co-Al layered double hydroxide precursors (Figure 9(a)). With a K loading of 3%, the 3K-CuCo-1 catalyst achieved a selectivity of 38.8% to ethanol at 200 °C (Figure 9(b)). K introduction modulates the electronic structure of the active center, transferring electrons to Co and Cu, forming Co–O–K and Cu⁺–O–K bridge structures on the catalyst, thereby stabilizing Cu⁺ species at the interface and enabling CO non-dissociative adsorption. K can further synergize with the Cu⁺–O–K structure to stabilize the key *HCOO intermediate in a bidentate configuration, promoting the C–C coupling with subsequent *CH_x species, generating the crucial *CH₃COO species for ethanol synthesis, and thus enhancing the catalytic performance for ethanol synthesis (Figure 9(c)). This confirms that alkali metal introduction can not only regulate the ethanol synthesis pathway but also affect the chemical environment of the active Co species.

Besides K, Na is also a commonly used alkali metal for improving catalyst performance. Yao et al.^[101] found that

Na, as a key promoter, acts as an electron donor, inhibiting the methanation reaction and thereby promoting the C–C coupling. It is evident that the introduction of the alkali metal Na plays a crucial role in determining the reaction pathway for the CO₂ hydrogenation to ethanol. Davis et al.^[88] further investigated the influence of Na introduction on the active Co species by preparing a 1%Na-20%Co/SiO₂ catalyst. They found that with Na doping, the catalyst exhibited very low selectivity to CH₄ (15.3%) and very high selectivity to alcohols (73.2%, mainly ethanol). Without Na doping, in contrast, the catalyst showed extremely high selectivity to CH₄ (99.7%). This indicates that Na introduction can enhance the interaction between cobalt and the SiO₂ support, modulate the metallic Co species into relatively stable CoO and Co₂C phases, inhibit their reduction and adjust the surface hydrogenation capability, which significantly suppresses the methane formation and improves the ethanol selectivity. In the absence of Na, CoO and Co₂C convert to metallic cobalt, leading to high methane selectivity.

Additionally, transition metals as dopant promoters can indirectly affect ethanol generation through structural effects. Zhang et al.^[89] used the Cu-Co-Ga-Al layered double hydroxide precursor to prepare a Ga-doped CuCo-based catalyst, Cu-CoGa_x (Figure 9(d)). This catalyst can inhibit side reactions and significantly promote the CO₂ hydrogenation to ethanol by constructing Cu⁺/Cu⁰–CoGaO_x interfacial active centers. On one hand, Ga introduction optimizes the ethanol synthesis reaction pathway, effectively increasing the energy barrier for hydrocarbon by-product formation. On the other hand, Ga dispersed on the catalyst surface modulates the electronic structure of Cu and Co, improving the H₂ dissociative adsorption on CoGaO_x to provide more active hydrogen, while simultaneously promoting CO adsorption on Cu⁺, thereby enhancing ethanol selectivity (Figure 9(e) and 9(f)). It suggests that appropriate promoters can not only regulate the catalytic reaction pathway for ethanol generation but also influence the chemical environment around active Co species with their excellent electrophilic properties, effectively inhibiting the formation of light hydrocarbon by-products.

Furthermore, our research group recently proposed a new method for regulating the CO reaction pathway by introducing a Mo promoter to modulate the chemical state of CoFe, thereby indirectly inducing *CH_x and *CO coupling to achieve highly selective CO₂ hydrogenation to ethanol^[90]. When the catalyst lacked Mo promoter, the post-reaction catalyst was almost entirely converted to CoFe carbide, and CO underwent strong dissociative adsorption, easily producing the *CH_x species; due to its strong C–C coupling ability, hydrocarbons appeared as the main products, in particular long-chain C₅₊ olefins, with very low ethanol selectivity (Figure 9(g)). Upon introducing the Mo promoter, the excessive carburization process was suppressed, and the post-reaction catalyst possessed both CoFe carbide and CoFe oxide phases.

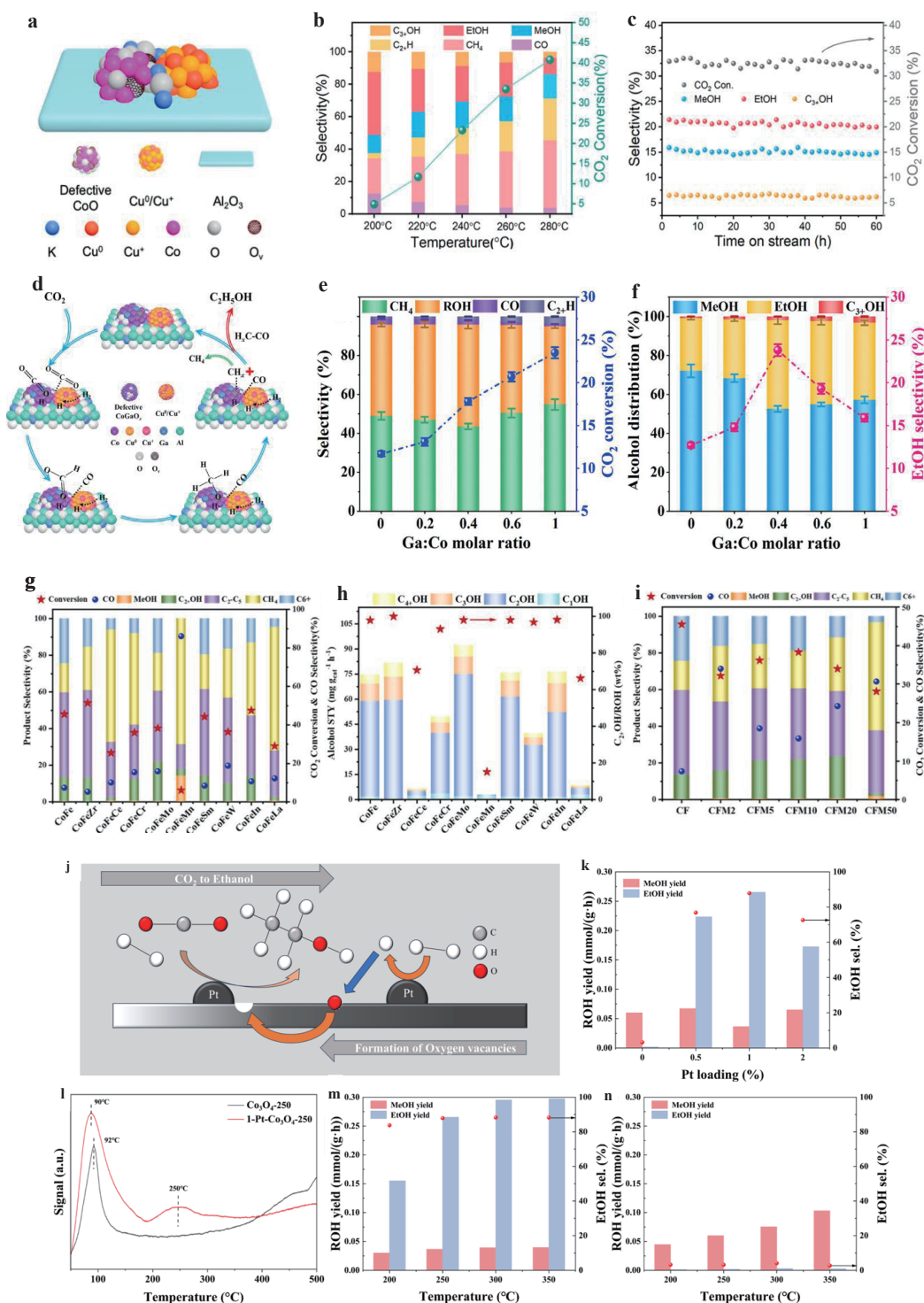


Fig. 9 (a) Schematical structure of K-containing CuCo-1 samples; (b) Conversion of CO₂ and the product selectivity on the 3K-CuCo-1 catalyst at different temperatures; (c) Stability of the 3K-CuCo-1 catalyst in CO₂ hydrogenation^[87]; (d) Proposed mechanism for the CO₂ hydrogenation to ethanol over Ga-promoted CuCo-based catalysts; (e) Changes in CO₂ conversion and product selectivity; (f) Alcohol distributions and ethanol selectivity^[89]; (g) Performance and (h) HA STY of CoFe-based catalysts with different additives at 320 °C, 3 MPa and 6000 mL/(g·h); (i) Performance of CoFeMo catalysts with different Mo loadings at 320 °C, 3 MPa and 6000 mL/(g·h)^[90]; (j) Reaction mechanism on the 1-Pt-Co₃O₄ catalyst; (k) Performance of the catalysts with different Pt loadings in CO₂ hydrogenation; (l) CO₂-TPD of 1-Pt-Co₃O₄-250 and Co₃O₄-250; (m) Performance of the 1-Pt-Co₃O₄ catalyst in CO₂ hydrogenation; (n) Performance of the Co₃O₄ catalyst in CO₂ hydrogenation^[91] (with permission from ACS Publications, IOS Press Publications and Elsevier)

The oxide sites tended towards non-dissociative CO adsorption, generating active $\ast\text{CO}$ intermediates, whereas the carbide sites were primarily responsible for CO dissociative adsorption, generating key $\ast\text{CH}_x$ intermediates. Subsequently, the $\ast\text{CO}$ species migrated to adjacent carbide sites, coupling with the $\ast\text{CH}_x$ species, followed by hydrogenation to generate ethanol. Thus, although the Mo promoter itself does not act as the active site, it can effectively inhibit CO dissociation, thereby curbing excessive carburization of the CoFe alloy and avoiding excessive C_{5+} hydrocarbon generation (Figure 9(h)). The optimal catalyst, CoFeMo10, achieved a selectivity of as high as 22% to ethanol product (Figure 9(i)). Simultaneously, the spontaneously formed Co_3MoO_x species during the reaction exhibited strong CO desorption capacity, further preventing the excessive carburization of active sites. Therefore, the introduction of Mo plays an important role in the product selectivity enhancement.

In summary, introducing promoters into the cobalt-based catalysts is a key strategy for improving their performance in the CO_2 hydrogenation to ethanol. Alkali metal promoters act as electron donors, enhancing catalyst surface basicity and modulating the electronic structure of active centers, thereby effectively suppressing methanation side reactions, stabilizing key oxygen-containing intermediates, and promoting the C–C coupling. In contrast, transition metal promoters primarily regulate the composition and stability of active phases, optimizing the balance between CO adsorption and dissociation, guiding the reaction pathway towards ethanol generation. Both types of promoters enable precise control over reaction selectivity and catalyst stability.

Besides alkali and transition metals, noble metals are also powerful promoters. Noble metal introduction can form synergistic interface structures with Co-based active sites, playing a significant role in regulating electronic properties, stabilizing key intermediates to reduce C_1 by-product formation, and enhancing the C–C coupling, markedly improving the activity and selectivity of the Co-based catalysts in the hydrogenation of CO_2 to ethanol^[102].

Xu et al.^[103] prepared a $\text{Co}/\text{Al}_2\text{O}_3$ Fischer-Tropsch synthesis catalyst and modified it with three noble metals: Pt, Ru and Pd. They found that without noble metals, the catalyst displayed weak C–C coupling ability and hydrogenation appeared as the primary reaction, leading to extremely high selectivity to the C_1 product, i.e., methane. Noble metal introduction significantly promoted the reduction of cobalt oxides, increased the number of surface-active hydrogen species, markedly enhanced the reactivity of adsorbed CO species, and then significantly improved the catalyst activity. As the C–C coupling ability was strengthened, a noticeable decrease in methane selectivity was observed. That is, noble metal introduction plays an important role in inhibiting methane generation and promoting C–C coupling.

In the CO_2 hydrogenation to ethanol, noble metal introduction also noticeably improves the catalyst

performance. Huang et al.^[91] successfully prepared Pt-doped Co_3O_4 catalysts ($\text{Pt-Co}_3\text{O}_4$) via co-precipitation to explore the effect of noble metal modification (Figure 9(j)). Under 240 °C and 3.2 MPa, 1% Pt-modified Co_3O_4 exhibited excellent ethanol selectivity and yield, far outperforming unmodified Co_3O_4 . The unmodified catalyst had low oxygen vacancy concentration and weak CO_2 adsorption ability, primarily producing methanol, with only a selectivity of 3.22% to ethanol. In contrast, the Pt introduction significantly improved the catalyst surface environment, promoting oxygen vacancy concentration on the support surface and completely altering the reaction pathway (Figure 9(k)–(n)). On the advantageous Pt- O_v sites, the formation of $\ast\text{OCH}_3$ was greatly promoted, which coupled with $\ast\text{CH}_3$ species on the Co sites to ultimately generate ethanol. This is entirely different from the pathway from CO_2 to $\ast\text{CH}_x$ and finally to methane or methanol on the pure Co_3O_4 catalyst. Therefore, Pt introduction can not only improve the support to promote oxygen vacancy formation but also induce a shift in the reaction pathway, enhancing C–C coupling, thereby improving catalyst selectivity towards ethanol.

Evidently, noble metal introduction significantly promotes ethanol generation. However, noble metals are expensive. Despite showing high activity and selectivity for ethanol formation, the value of the produced ethanol may not offset the high cost of noble metals, and research on noble metal-modified cobalt-based catalysts is then limited. Therefore, subsequent efforts need to develop cobalt-based catalytic systems that can effectively reduce noble metal content to achieve efficient CO_2 hydrogenation to ethanol^[104].

4.3 Inverse catalysts

To overcome the contradiction between activity and stability faced by traditional catalysts in harsh reaction environments, inverse catalysts provide a novel approach for catalytic material design. Wu et al.^[105] constructed an inverse catalyst ZrO_2/Cu by dispersing ZrO_2 island structures on the Cu particle surfaces, investigating its performance for CO_2 hydrogenation to methanol (Figure 10(a)). The inverse catalyst exhibited powerful advantage through structural inversion. In the inverse catalyst, ZrO_2 , due to its high dispersion, can be partially reduced, forming abundant oxygen vacancies where CO_2 can stably adsorb and undergo subsequent hydrogenation. In the conventional catalyst, in contrast, ZrO_2 serves as the support and is difficult to reduce. Activated CO_2 can form a new $\ast\text{HCOO-Cu}$ intermediate on the inverse catalyst, different from the $\ast\text{HCOO-Zr}$ intermediate on traditional catalysts. The appearance of the $\ast\text{HCOO-Cu}$ intermediate alters the reaction pathway, accelerating the reaction rate. The optimal catalyst, 10% ZrO_2/Cu , showed a methanol formation rate 3.3 times that of the traditional catalyst (Figure 10(b)).

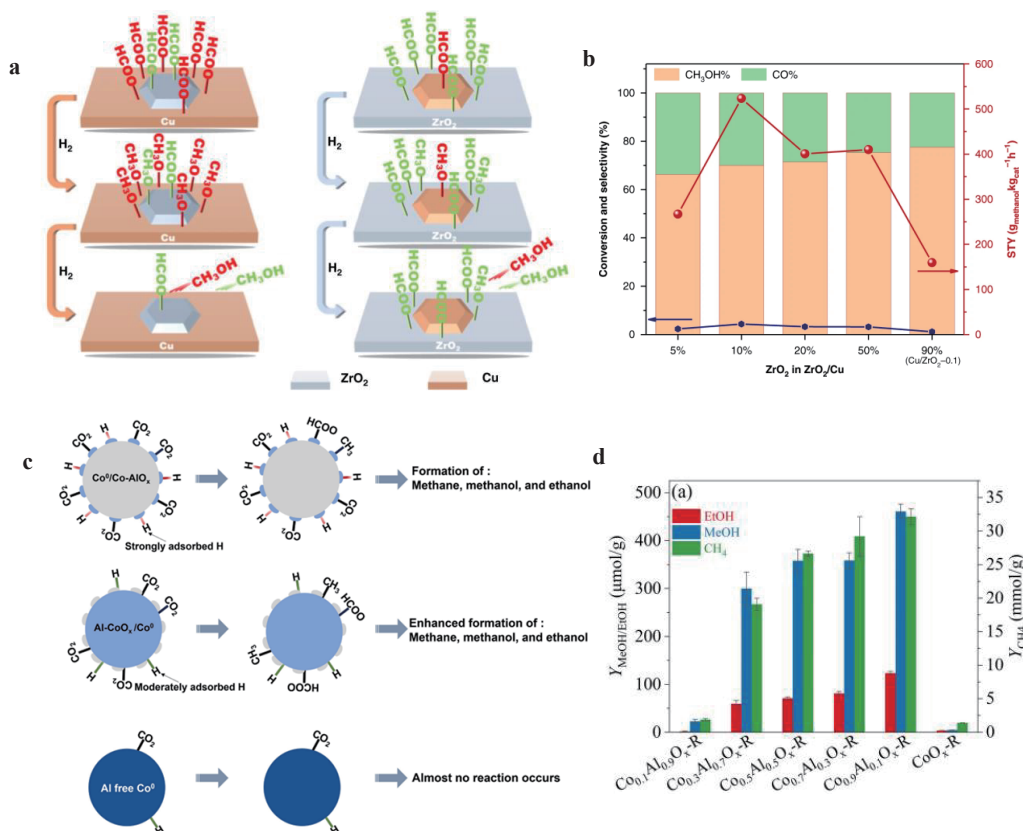


Fig. 10 (a) Scheme of the HCOO-Cu and HCOO-Zr intermediates on the inverse ZrO₂/Cu and Cu/ZrO₂ catalysts; (b) Performance of the ZrO₂/Cu catalysts^[105]; (c) Proposed reaction mechanism for the enhanced CO₂ hydrogenation and ethanol formation over reverse catalyst, a comparison of Co_{0.5}Al_{0.5}O_x-R, Co_{0.5}Al_{0.1}O_x-R and CoO_x-R in the reaction intermediates; (d) Product yield distribution over different catalysts^[92] (with permission from Elsevier and Springer Nature)

The inverse catalysts also exhibit unique advantages in the C–C coupling. Petersen et al.^[106] designed an inverse catalyst to deeply explore metal-support interactions in the cobalt-based Fischer-Tropsch synthesis. Compared to conventional catalysts, the inverse catalyst enhanced CO dissociation ability, further reducing methane selectivity and promoting the formation of higher-carbon products. This advantage shows similar potential in the CO₂ hydrogenation to ethanol. Fu et al.^[92] synthesized an inverse catalyst Co_mAl_nO_x-R by constructing oxide nano-islands on metallic Co surfaces, exploring its catalytic performance in the CO₂ hydrogenation to ethanol (Figure 10(c)). The inverse catalyst exhibited significant performance advantages: its unique metal/metal oxide interface not only provides abundant active sites but also forms moderately adsorbed hydrogen species, significantly promoting the activation of CO₂, generation of key intermediates (*HCOO and *CH₃) and their coupling, thereby efficiently promoting the ethanol synthesis. The optimal Co_{0.9}Al_{0.1}O_x-R catalyst achieved an ethanol yield as high as 123 μmol/g, and its TOF value was also much higher than that of traditional structures, highlighting the powerful capability of inverse structures in regulating reaction pathways and improving product selectivity (Figure 10(d)).

4.4 Tandem catalysts

The CO₂ hydrogenation to ethanol reaction involves the balance between *CO dissociative and non-dissociative adsorption, C–C coupling, and subsequent hydrogenation to ethanol and thus requires precise synergistic effects of multiple active sites. In this connection, tandem catalysts have been widely studied^[107]. They can decompose complex multi-step reactions, allowing different active components to perform their respective functions in the most suitable environments, reshaping and optimizing the reaction pathway, and effectively suppressing the side reactions; those advantages cannot be provided by a single catalyst.

Zhang et al.^[93] synthesized a multifunctional tandem catalyst combining Co₂C nanorods with CuZnAl and compared it with a single Co₂C catalyst to explore its performance advantages in the CO₂ hydrogenation to higher alcohols (Figure 11(a)). They found that on the single Co₂C catalyst, the C–C coupling primarily occurred via CO insertion. On the Co₂C||CuZnAl tandem catalyst, the upstream Co₂C specialized in catalyzing the RWGS reaction and generating olefin intermediates, whereas the downstream CuZnAl was responsible for adsorbing and activating CO₂, generating formate and further hydrogenating it to *CHO species.

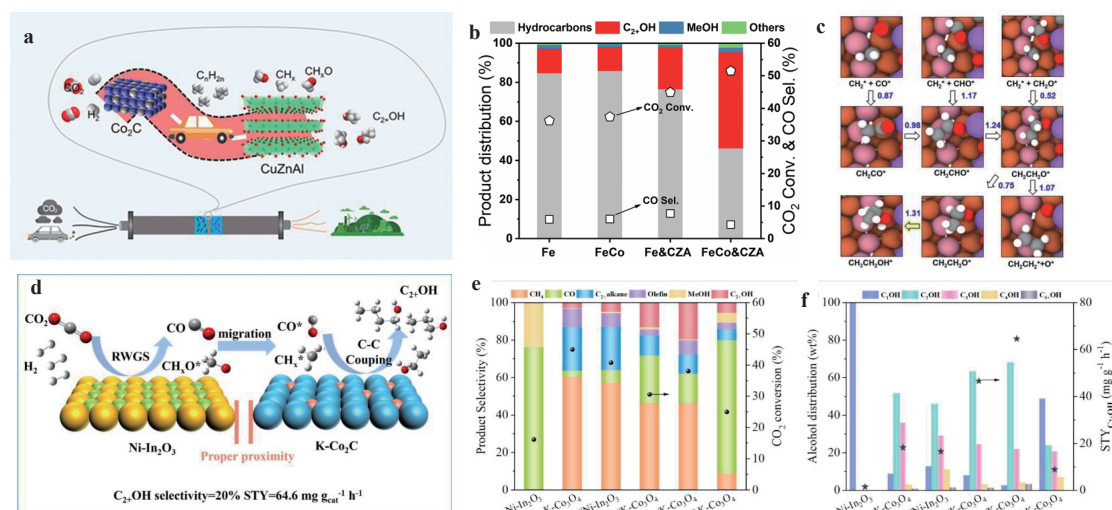


Fig. 11 (a) Schematic diagram of the hydrogenation of CO₂ to ethanol over the Co₂C||CuZnAl catalyst^[93]; (b) CO₂ conversion and product selectivity over four catalysts; (c) Possible C–C coupling pathways and the corresponding energy barriers on the (Fe_{3/4}Co_{1/4})₅C₂(510) surfaces^[94]; (d) Reaction scheme for CO₂ hydrogenation to C₂H₅OH over Ni-In₂O₃/K-Co₃O₄ catalyst; (e) CO₂ conversion and product selectivity; (f) Alcohol distribution and the STY of C₂H₅OH^[95] (with permission from ACS Publications, Springer Nature and Elsevier)

Finally, low-energy-barrier coupling between R–CH₂ from the upstream and *CHO species from the downstream occurred at the Cu/ZnAl₂O₄ interface. This change reflects a shift in the C–C coupling mode. Compared to traditional CO insertion, it has a lower energy barrier, significantly improving ethanol selectivity and achieving a leap in the catalyst performance.

Wang et al.^[94] developed a tandem catalyst composed of FeCo alloy carbide and CuZnAl catalyst, to investigate its performance for the CO₂ hydrogenation to ethanol. They found that on the single-component catalysts, the main products were hydrocarbons or CO, with almost no ethanol produced. On the FeCo&CZA tandem catalyst, the ethanol generation reaction was split into two parts, with specific steps precisely handled by different components (Figure 11(b)). CuZnAl is a widely studied methanol synthesis catalyst, serving to generate oxygen-containing intermediates but lacks C–C coupling ability; CO₂ is directionally converted to *CH₂O here. At this point, the tandem FeCo catalyst showed its advantage. As a common Fischer-Tropsch synthesis catalyst, it possesses strong C–C coupling capability (Figure 11(c)). It can rapidly couple the *CH₂O intermediate with the *CH_x intermediates, subsequently generating ethanol. The two-part catalysts do not interfere with each other and work in their respective domains, achieving high-selectivity ethanol synthesis.

Our research group also conducted in-depth research on a Ni-In₂O₃/K-Co₃O₄ tandem catalyst for the CO₂ hydrogenation to ethanol based on effectively coupling a front-end catalyst with high CO selectivity and a back-end catalyst with strong C–C coupling ability (Figure 11(d)). The single-component Ni-In₂O₃ catalyst had a single function, mainly producing CO or methanol, but lacked the C–C coupling ability and was unable to generate ethanol. On the other single-component catalyst, K-Co₃O₄, although

it had strong C–C coupling ability, CO primarily underwent strong dissociative adsorption, leading to over-hydrogenation of the *CH_x intermediates. The C–C coupling products were hydrocarbons (93.4% selectivity), with very low alcohol selectivity (only 3%, Figure 11(e)). After tandem combination, the value of each catalyst was highlighted. The Ni-In₂O₃ component was primarily responsible for CO₂ activation, generating the key *CO intermediate for subsequent C–C coupling, whereas the K-Co₃O₄ component transformed into the Co₂C phase during the reaction, responsible for CO dissociative adsorption to generate *CH_x intermediates, which reacted with the *CO intermediates generated on the Ni-In₂O₃ catalyst, driving C–C bond coupling, followed by hydrogenation to generate ethanol. On this tandem catalyst, CO₂ conversion increased to 38.1%, hydrocarbon selectivity decreased to 41.0%, and higher alcohol selectivity increased to 20%, strongly proving the great advantage of the tandem catalysts over single catalysts in the higher alcohol synthesis (Figure 11(f)). Therefore, the design of tandem catalysts has a powerful promoting effect on the complex multi-step reactions.

5 Role of water

The CO₂ hydrogenation inevitably produces water, which may affect the yield of the target product and cause partial catalyst deactivation. However, the impact of water on the reaction system is not entirely negative. Wang et al. reported the effect of water on CO₂ hydrogenation to methanol over a Cu/ZnO/ZrO₂ catalyst (Figure 12(a)). The study showed that water promoted the hydrolysis of *CH₃O to generate methanol and altered some properties of the catalyst. Therefore, the presence of an appropriate amount of water in the reaction system can improve product

selectivity, and this also applies to ethanol generation. He et al.^[109] systematically revealed the role of water in the CO₂ hydrogenation to ethanol over a Pt/Co₃O₄ system (Figure 12(b)). They found that in an H₂O/DMI mixed solvent, a higher selectivity of 35.2%–88.1% to alcohol was achieved in the temperature range of 140–220 °C, far exceeding that in the anhydrous system. Additionally, isotope labeling confirmed that deuterium atoms from water entered the ethanol product, proving water's contribution as

a hydrogen source. This indicates that water can act as a promoter to significantly enhance the catalytic performance. Thus, water synergizes with support surface oxygen vacancies and metal interfaces, generating *H species that directly participate in the hydrogenation process. Through protonation, it regulates the reaction pathway, inhibits the hydrocarbon by-product generation, promotes the methanol intermediate dissociation to *CH₃, and thereby facilitates the C–C coupling^[110–112].

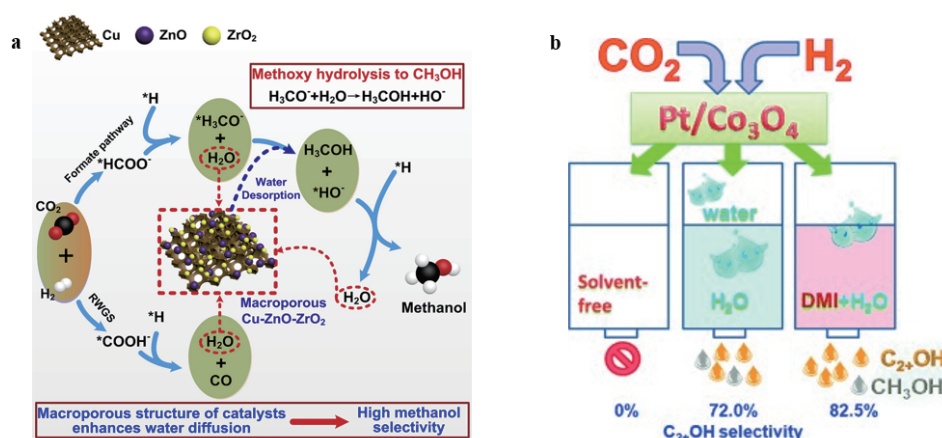


Fig. 12 (a) Influence of water on the selectivity of methanol formation from carbon dioxide hydrogenation over the Cu-ZnO-ZrO₂ oxide catalysts^[108]; (b) Water-assisted synthesis of advanced alcohols on the Pt/Co₃O₄ catalysts^[109] (with permission from Elsevier and Wiley)

6 Influence of the reactor system

Both batch reactors and fixed-bed reactors fundamentally aim to provide the necessary reaction environment for the multi-step catalytic reaction of the CO₂ hydrogenation to ethanol. Regardless of the reactor form, the basic chemical reactions occurring internally are CO₂ activation and C–C bond coupling, which are essentially the same. However, they significantly impact the selectivity for CO₂ hydrogenation to ethanol.

For example, by creating a unique liquid-phase environment in a batch reactor, Wang et al.^[83] significantly increased the local concentration and residence time of CO₂ and key intermediates on the catalyst surface, providing favorable conditions for the C–C coupling step of *CH_x insertion into *HCOO while effectively suppressing the side reaction of *CH_x over-hydrogenation to methane. This enabled the Co_{0.52}Ni_{0.48}AlO_x catalyst to achieve an extremely high selectivity of 85.7% to ethanol. In contrast, Zheng et al.^[73] used a fixed-bed reactor, creating a continuous, stable gas-phase environment, allowing the catalyst to achieve a selectivity of 65.8% to ethanol. Precise control of the reaction temperature, pressure, and space velocity enabled the Co/La-Ga-O catalyst to exhibit excellent resistance to sintering and coking over 100 h. Comparing the two systems, batch reactors are suitable for liquid-phase reaction systems. Their advantage lies in the solvent's ability to effectively dissolve CO₂, forming higher local concentrations and providing a stable reaction environment

for intermediates, which significantly inhibits the side reactions, resulting in higher ethanol selectivity. Fixed-bed reactors, in contrast, are mainly used for gas-phase reactions, are more amenable to continuous, large-scale production, and have high reaction efficiency. However, in the gas-phase environment, intermediates are less stable, and competing reaction pathways increase, typically resulting in lower ethanol selectivity compared to liquid-phase systems.

7 Summary and outlook

Cobalt-based catalysts, due to their low cost and high selectivity, have been widely used in the CO₂ hydrogenation to ethanol. This article summarizes the research progress on the hydrogenation of CO₂ to ethanol over the cobalt-based catalysts. Given the complexity of ethanol generation reactions, the catalytically active sites require synergistic effects between multiple factors to achieve efficient CO₂ hydrogenation to ethanol. The active sites are mainly classified into the following four categories: (1) Co⁰-CoO_x sites: Co⁰ is responsible for the H₂ adsorption/dissociation and promotes the C–H bond formation, whereas CoO_x sites handle the CO₂ adsorption and subsequent C–C coupling steps. (2) Co⁰-Co₂C sites: Co⁰ is responsible for the CO₂ dissociation and enhances the C–C coupling, whereas Co₂C promotes *CO non-dissociative adsorption. (3) Co⁰-CoO_x-Co₂C sites: CoO_x is responsible for *CO and *CHO generation, whereas Co and Co₂C are responsible for the

chain growth and hydrogenation. (4) Bimetallic-oxide sites: The alloy promotes the formation of key $^*CH_x$ intermediates, whereas CoO favors the formation of $^*HCOO$ intermediates, with subsequent hydrogenation generating ethanol.

Regarding the catalyst research progress, single cobalt atoms cannot generate ethanol with high selectivity, necessitating modifications. Current modifications for the cobalt-based catalysts mainly include: (1) Introducing supports such as TiO_2 , Al_2O_3 , SiO_2 , etc., to disperse the active component and increase the number of active sites. (2) Introducing promoters such as K, Na, Ga, etc., which can balance the $^*CO$ dissociative and non-dissociative adsorption, inhibit the by-product formation, promote the C–C coupling, and ultimately generate ethanol. (3) Introducing noble metals: Noble metal addition can regulate electronic properties and stabilize intermediates. (4) Designing inverse catalysts. (5) Designing tandem catalysts.

Although significant progress has been made in the CO_2 hydrogenation to ethanol over the cobalt-based catalysts, their comprehensive performance still faces challenges such as low conversion and high costs, making it difficult to meet the requirements for industrialization. Therefore, future research needs to achieve breakthroughs in the catalyst active site design and reaction mechanism exploration.

First, the formation, evolution, and coupling mechanisms of the reaction intermediates for C_2 products remain unclear. This requires deepening our understanding of dynamic changes during the reaction, breaking current characterization technology limitations, improving the ability to track intermediate evolution during the reaction process, and better understanding their evolutionary pathways. This must be closely integrated with theoretical calculations to reveal energy barriers throughout the reaction process, providing theoretical guidance for the catalyst design.

Second, based on an in-depth understanding of the reaction mechanism and existing research on active sites, exploring more active site combinations in the future can efficiently promote the formation of reaction intermediates and guide the C–C coupling to generate ethanol. Simultaneously, owing to the proved advantages, the concept of tandem catalysts can be extended to design more complex catalysts, achieving spatial separation but functional synergy of active sites, providing more reaction intermediates and new low-energy-barrier reaction pathways for the CO_2 hydrogenation to ethanol.

Finally, regarding the industrial application, a balance between the high economic efficiency and excellent performance must be considered. Current research mostly focuses on the catalyst activity and selectivity, but industrial application requires the catalysts to possess excellent comprehensive performance. During the long-term continuous operation, the catalysts need to resist coking, poisoning, etc., so improving their durability is a key direction for industrial catalyst development. Additionally, many catalysts with high activity in the laboratory are

difficult to prepare on a large scale. Future efforts should develop green and economical methods to prepare industrial catalysts environmentally friendly.

Declaration of Competing Interest

The authors declare no conflict of interest.

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二氧化碳加氢合成乙醇在钴基催化剂上的研究进展

卞伶俐¹, 王 静¹, 丁晨宇¹, 孙文晶^{2,*}, 王 宁^{1,*}

(1. 北京工业大学 环境科学与工程学院, 北京 100124; 2. 广东医科大学广东省医学分子诊断重点实验室, 广东 东莞 523808)

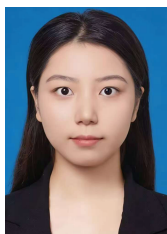
摘 要: CO₂ 催化加氢制乙醇是实现二氧化碳有效利用的关键技术之一, 兼具碳中和与高价值燃料及化学品合成的双重价值, 一直是研究热点。在 CO₂ 加氢制乙醇的技术中, 开发兼具高活性、高乙醇选择性与长期稳定性的催化剂至关重要。目前, 常见的二氧化碳加氢合成乙醇催化剂主要有贵金属基催化剂及费托合成催化剂等。其中, 钴基催化剂因其独特的电子结构与可调控性, 成为热催化 CO₂ 加氢制高价值化学品乙醇的理想选择, 但由于 CO₂ 分子相对稳定, 其化学惰性会对反应产生阻碍; 且经过高温高压活化后, 也极易发生副反应从而生成甲烷或 CO 等副产物。因此, CO₂ 的活化及向乙醇产物的选择性转化极具挑战性, 目前, 仍存在 CO₂ 单程转化效率低 (< 20%)、目标产物选择性不足 (乙醇 < 60%) 和催化剂易失活等关键问题。本综述分析了钴基催化剂在 CO₂ 制乙醇体系中的研究进展, 阐明反应热力学边界条件与动力学控制步骤; 揭示 C–C 偶联与氧脱除的微观反应机制; 评述活性位点 (金属 Co、Co₂C、CoO_x、双金属) 的协同作用对于反应机理的影响; 载体效应及助剂修饰的构效关系; 反相催化剂及串联催化剂在乙醇合成中的应用; 解析水作为氢源对于反应的影响; 对钴基催化剂上 CO₂ 加氢制乙醇的研究进行总结并对催化剂的创新性研究提出展望, 旨在为高效钴基催化剂开发和反应过程与机理研究提供参考, 进而推动 CO₂ 加氢制乙醇技术的开发。

关键词: 钴基催化剂; 二氧化碳; 乙醇; 反应机理; 活性位点

中图分类号: TQ426; TQ223; X701

文献标识码: A

作者简介:



卞伶俐(2001), 硕士研究生, 研究方向为 Fe 基催化剂上二氧化碳加氢制乙醇, s202365287@emails.bjut.edu.cn。



王宁(1986), 博士, 研究员, 研究方向为 C1 小分子催化转化及高碳化学品的合成, ning.wang.1@bjut.edu.cn。



孙文晶(1984), 博士, 副研究员, 研究方向为发展高效、可持续的碳-碳偶联策略及其在复杂功能分子合成中的应用, swj_gdmc@163.com。