

Structure-activity correlation mechanism of additive-modified Cu-based catalysts for methanol synthesis via CO₂ hydrogenation

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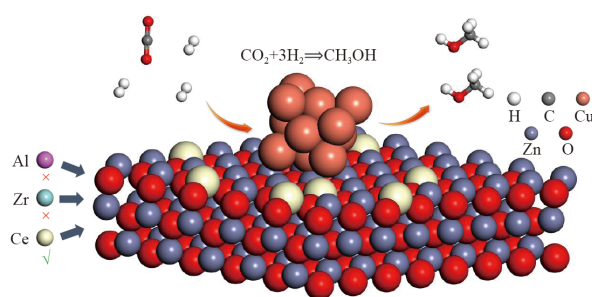
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Abstract: Aiming at the problems of insufficient activity and selectivity of Cu-based catalysts in CO₂ hydrogenation to methanol, Al₂O₃, ZrO₂ and CeO₂ modified Cu-ZnO catalysts by the co-precipitation method were prepared, and the influence mechanism of additives on the structure-performance relationship of the catalysts was systematically explored. Through a variety of characterization methods such as XRD, N₂ physical adsorption-desorption, TEM, H₂-TPR, CO₂-TPD and XPS,

combined with catalytic performance evaluation experiments, the correlation between the microstructure of catalysts and the reaction performance of CO₂ hydrogenation to methanol was analyzed in depth. The results show that metal additives significantly improve the performance of catalysts. After the introduction of additives, the specific surface area and pore volume of the catalysts increase, the grain size of Cu decreases, and its dispersion improves. The Ce-modified CZC catalyst exhibited the best performance, with the grain size of CuO as small as 11.41 nm, and the surface oxygen vacancy concentration ($O_{II}/O_I = 3.15$) was significantly higher than that of other samples. The reaction performance test shows that under the conditions of 2.8 MPa, 8000 h⁻¹ and 280 °C, the CO₂ conversion of the CZC catalyst reached 18.83%, the methanol selectivity was 68.40%, and the methanol yield was 12.88%, all of which are superior to other catalysts. Its excellent performance can be attributed to the fact that CeO₂ enhances the metal-support interaction, increases the surface basicity, promotes the adsorption and activation of CO₂, and simultaneously inhibits the reverse water-gas shift side reaction. This study clarifies the structure-activity regulation mechanism of additive modification on Cu-ZnO catalysts, providing a theoretical basis and technical reference for the development of efficient catalysts for CO₂ hydrogenation to methanol.

Key words: carbon dioxide; catalyst; additive modification; hydrogenation; methanol



Driven by the context of the “dual carbon goals” and the upgrading of the green chemical industry, carbon dioxide (CO₂) catalytic conversion technology has become the core of green transformation in the global energy and chemical sectors. This technology captures industrially emitted CO₂ and converts it into high-value-added chemicals, thereby realizing the cyclic utilization of carbon resources and aligning with the concept of sustainable development^[1].

Among various routes, the hydrogenation of CO₂ to methanol has emerged as a current research hotspot due to its broad application prospects. As a green energy carrier, methanol can not only be directly used as a clean fuel but also serve as a crucial chemical feedstock and hydrogen storage material, holding extensive application value in the energy and chemical industries^[2-3]. However, the current CO₂ catalytic hydrogenation to methanol technology still

Received: 2025-08-01; Revised: 2025-09-02

Foundation items: Supported by National Key R&D Program of China (2022YFA1503400).

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DOI: 10.1016/S1872-5813(26)60632-9 CSTR: 32157.14.2097-213X.2025.JFCT.0187

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faces numerous challenges, primarily manifested in low CO₂ conversion efficiency and poor methanol selectivity. These issues severely restrict the economic competitiveness of the technology and hinder its large-scale industrial application^[4–5]. Therefore, the development of efficient and stable catalysts for CO₂ hydrogenation to methanol, and the breakthroughs of technical bottlenecks in reaction efficiency and product selectivity, are key to advancing the development of this field.

Copper-based (Cu-based) catalysts have been extensively researched and applied in the field of CO₂ hydrogenation to methanol due to their low cost and relatively high catalytic efficiency^[6–10]. Among them, Cu-ZnO catalysts are recognized as highly representative efficient catalytic systems in this field, attributed to the Cu-Zn synergistic effect and the abundant active sites formed at the Cu-ZnO interface. Nevertheless, under high-temperature reaction conditions, Cu particles are prone to agglomeration, leading to a continuous reduction in the number of active sites at the Cu-ZnO interface. This process not only accelerates catalyst deactivation but also promotes the occurrence of the reverse water-gas shift (RWGS) side reaction, thereby significantly reducing methanol selectivity^[11–12]. Consequently, how to maintain a stable Cu-ZnO interface structure and effectively suppress side reactions has become a core issue for improving the performance of this catalytic system.

The introduction of metal oxide promoters to regulate the interfacial interaction and electronic structure of Cu-ZnO catalysts is a mainstream optimization strategy in the current field. However, existing studies still have obvious knowledge gaps and contradictions. The industrially commonly used Cu-ZnO-Al₂O₃ catalyst can inhibit Cu particle agglomeration, increase specific surface area, and enhance thermal resistance through the “skeletal support effect” of Al₂O₃. Nevertheless, the strong hydrophilicity of Al₂O₃ causes water molecules generated during the reaction to accumulate on the catalyst surface, covering active sites and weakening the Cu-ZnO interaction, which in turn reduces catalytic activity. Recent studies have shown that different metal promoters exert unique regulatory effects on the performance of Cu-ZnO catalysts. When ZrO₂ is used as a promoter, some studies have confirmed that its abundant oxygen vacancies can promote CO₂ adsorption and activation, and its weak hydrophilicity can reduce water molecule interference, thereby improving methanol yield^[13]. However, the electron transfer mechanism between Zr⁴⁺ and Cu⁰/Cu⁺, as well as the specific regulatory pathway of ZrO₂ on the Cu-ZnO interface structure, remain unclear, making it difficult to optimize its effect in a targeted manner. The CeO₂ promoter has been reported to increase the capacity of H₂ adsorption on the Cu surface through the “hydrogen spillover effect”, thereby improving methanol activity and selectivity^[14]. Nevertheless, there is a lack of systematic research on whether this effect depends on the crystal phase of CeO₂ and the influence law of the Ce³⁺/Ce⁴⁺ ratio on the charge distribution at the Cu-ZnO interface. More

importantly, most existing literature focus on the modification effect of a single promoter on Cu-ZnO catalysts, and there is no horizontal comparative study on the action mechanisms of three typical promoters (Al₂O₃, ZrO₂ and CeO₂). This makes it difficult to clarify the advantages and disadvantages of different promoters in core functions such as “inhibiting Cu agglomeration”, “regulating interfacial interaction”, and “suppressing side reactions”, and also difficult to establish a universal structure-activity relationship of “promoter type-microstructure-catalytic performance”. As a result, the subsequent catalyst design lacks clear theoretical guidance.

Based on the above research, this study takes Cu-ZnO catalysts as the basis and introduces three metal oxide promoters (Al₂O₃, ZrO₂ and CeO₂) via the co-precipitation method to construct a series of Cu-ZnO-MO_x (M = Al, Zr, Ce) catalysts. It systematically investigates the regulatory laws of different promoters on the phase structure, electronic properties, and surface adsorption performance of the catalysts. Combined with catalytic performance evaluation, the core action mechanisms of different promoters in improving CO₂ conversion efficiency, methanol selectivity, and catalyst stability are clarified. This work aims to provide a clear theoretical basis and technical pathways for the design of Cu-based catalysts for CO₂ hydrogenation to methanol with high activity, high selectivity, and high stability.

1 Materials and methods

1.1 Preparation of Cu-based catalysts modified with different metal promoters

A series of catalysts were prepared by the co-precipitation method. Taking the preparation of Cu-ZnO-CeO₂ catalyst (CZC) as an example, Zn(NO₃)₂·6H₂O, Cu(NO₃)₂·3H₂O and Ce(NO₃)₃·6H₂O were accurately weighed according to the stoichiometric ratio, dissolved in deionized water to prepare a mixed nitrate solution with a concentration of 0.2 mol/L. Meanwhile, a 0.6 mol/L Na₂CO₃ precipitant solution was prepared. Under the condition of stirring in a constant temperature water bath at 70 °C, the above two solutions were synchronously added dropwise into a jacketed beaker. During the dropping process, the pH value of the solution was monitored in real-time and controlled within the range of 8–9. After the precipitation was completed, stirring and aging were continued for 2 h. Subsequently, the precipitate was cooled to room temperature, filtered and washed with deionized water several times until neutral, then dried in an oven for 12 h, and finally calcined in a muffle furnace for 5 h to obtain the CZC catalyst. Using the same preparation process, Cu-ZnO-Al₂O₃ catalyst (denoted as CZA), Cu-ZnO-ZrO₂ catalyst (denoted as CZZr) and Cu-ZnO catalyst without promoter (denoted as CZ) were prepared

respectively. In the series of modified catalysts, the molar ratio of modified metals (Ce, Al, Zr) to active component Cu was 0.4. The obtained catalysts were tableted, granulated, and particles with a particle size of 20–40 mesh were selected for subsequent physicochemical property characterization and catalytic performance evaluation.

1.2 Characterization methods

Crystal structure analysis (XRD): The crystal structure of the catalyst was performed using a DMAX-2400 X-ray diffractometer from Rigaku Corporation, Japan, with Cu $K\alpha$ as the radiation source ($\lambda=0.154$ nm). The scanning range was set to 5° – 90° , and the scanning rate was $2(^\circ)/\text{min}$. The crystalline phase composition and crystal structure of the catalyst were determined by analyzing the diffraction patterns.

Specific surface area and pore size determination (BET): The pore structure of the catalyst was characterized using a Micromeritics ASAP2010 physical adsorption instrument from the United States, with N_2 as the adsorption medium. Before the test, the sample was pretreated under vacuum conditions at 300°C for 2 h. The specific surface area was calculated based on the Brunauer-Emmett-Teller (BET) theory, and the pore size distribution and pore volume were analyzed by the Barrett-Joyner-Halenda (BJH) model.

Determination of Cu specific surface area and dispersion (N_2O titration): The specific surface area (S_{Cu}) and dispersion (d_{Cu}) of Cu in the catalyst were determined by the N_2O titration secondary reduction method using a Chem BET-Pulsar-TPR/TPD chemisorption instrument. The calculation formulas are as follows:

$$d_{Cu}(\%) = 2n_2/n_1 \times 100\% \quad (1)$$

$$S_{Cu} = 2n_2N / (W \times 1.47 \times 10^{19}) \quad (2)$$

where N is the Avogadro constant ($6.02 \times 10^{23} \text{ mol}^{-1}$), W is the mass of the catalyst sample (g), and n_1 and n_2 are the amounts of H_2 consumed in the first and second reduction processes (mol), respectively.

Reduction performance characterization (H_2 -TPR): H_2 temperature-programmed reduction experiments were carried out using a Chem BET pulsar TPR/TPD automatic chemisorption analyzer. 50 mg of catalyst was placed in a quartz tube, and N_2 was first introduced to heat up to 400°C at a rate of $10^\circ\text{C}/\text{min}$ for purging for 30 min. After the temperature was reduced to 70°C , it was switched to 10% H_2/Ar gas mixture (flow rate 15 mL/min) and heated to 450°C at a rate of $10^\circ\text{C}/\text{min}$, and the H_2 signal was recorded to obtain the reduction characteristic curve of the catalyst.

Adsorption performance characterization (CO_2 -TPD): CO_2 temperature-programmed desorption experiments were performed using a Chem BET pulsar TPR/TPD automatic chemisorption analyzer. 50 mg of catalyst was placed in a quartz tube, and N_2 was first introduced to heat up to 400°C

at a rate of $10^\circ\text{C}/\text{min}$ for purging for 30 min. Then, it was switched to 10% H_2/Ar gas mixture (flow rate 15 mL/min), reduced at 400°C for 30 min, cooled to 70°C , and then adsorbed CO_2 for 1 h (CO_2 flow rate 30 mL/min), and then purged with N_2 to remove residual gas. Finally, the temperature was raised to 700°C at a rate of $10^\circ\text{C}/\text{min}$, and the CO_2 desorption signal was recorded to study the CO_2 adsorption performance of the catalyst.

Surface element valence analysis (XPS): The chemical valence states of surface elements of the catalyst were analyzed using an AXISULTRADLD (Shimadzu Corporation) X-ray photoelectron spectrometer with Al $K\alpha$ ray as the excitation source. The test area was $700\mu\text{m} \times 300\mu\text{m}$, and the binding energy error range was ± 0.1 eV.

Crystal structure and morphology characterization (TEM): The microstructure of the active phase of the reduced catalyst was observed using a Tecnai G2 F20 field emission transmission electron microscope. The catalyst was ground into fine powder, dispersed in cyclohexane at a ratio of 1:100, ultrasonicated for 30 min, and the suspension was dropped onto a special carbon film for testing.

1.3 Catalytic test

Catalyst activity evaluation experiments were carried out on a fixed-bed micro-reactor. According to the filling requirements of the reaction tube (volume 33 mL), 16 mL of quartz sand, 1 mL of catalyst, and 16 mL of quartz sand were filled in sequence to ensure that the catalyst was located in the middle of the reaction tube, and the bottom was supported by inert ceramic balls to prevent the quartz sand from blocking the pipeline. After the catalysts were loaded, N_2 (150 mL/min) was first introduced for leak detection and purging for 20 min, then the temperature was raised to 300°C , and the catalyst was reduced with H_2 for 2 h. After the system was cooled to below 220°C , it was switched to CO_2/H_2 gas mixture (volume ratio 1:3), and the reaction pressure and space velocity were adjusted to 2.8 MPa and 8000 h^{-1} , respectively. 5 temperature points (20°C intervals) were set in the range of 220 – 300°C , and the reaction was stabilized for 2 h at each temperature. After condensation, the reaction products were analyzed for composition by gas chromatography. Qualitative analysis was performed with reference to the retention times of CO , CO_2 , N_2 , H_2 , H_2O , methane and methanol standards, and the content of each component was calculated according to the peak area, and then the CO_2 conversion rate, methanol selectivity and methanol yield were calculated. Since the amount of methane generated in the reaction was extremely low, it was ignored in this experiment. The relevant calculation formulas are as follows:

$$x(CO_2) = \frac{n_{in}(CO_2) - n_{out}(CO_2)}{n_{in}(CO_2)} \quad (3)$$

$$s(\text{CH}_3\text{OH}) = \frac{n_{\text{out}}(\text{CH}_3\text{OH})}{n_{\text{out}}(\text{CO}) + n_{\text{out}}(\text{CH}_3\text{OH})} \quad (4)$$

$$s(\text{CO}) = \frac{n_{\text{out}}(\text{CO})}{n_{\text{out}}(\text{CO}) + n_{\text{out}}(\text{CH}_3\text{OH})} \quad (5)$$

$$Y(\text{CH}_3\text{OH}) = s(\text{CH}_3\text{OH}) \times x(\text{CO}_2) \quad (6)$$

where $n_{\text{in}}(\text{CO}_2)$ and $n_{\text{out}}(\text{CO}_2)$ are the amounts of CO_2 at the inlet and outlet, respectively.

2 Results and discussion

2.1 Structural properties of Cu-based catalysts modified with different metal promoters

Figure 1 presents the X-ray diffraction (XRD) patterns of the calcined Cu-based catalysts modified with different metal promoters. Distinct characteristic diffraction peaks corresponding to the (-111), (111) and (-202) crystal planes of CuO are clearly observed at 2θ of 35.5° , 38.7° and 48.7° , respectively. The diffraction peaks at 28.7° and 47.7° are attributed to CeO_2 , while those at 31.7° , 56.5° , 62.8° and 67.8° correspond to ZnO , and the peak at 35.3° is assigned to ZrO_2 . Notably, no obvious characteristic diffraction peaks of Al_2O_3 are detected in the XRD pattern of the CZA catalyst, indicating that Al_2O_3 is highly dispersed in the catalyst in an amorphous form. The above characteristic peaks match well with the standard cards of CuO and ZnO phases in the target products, confirming the successful preparation of the four catalysts.

Further analysis reveals that after the introduction of metal promoters, the diffraction peak of the CuO (-111) crystal plane in the CZZr and CZC catalysts shifts toward higher 2θ , whereas this peak in the CZA catalyst shifts toward lower 2θ .

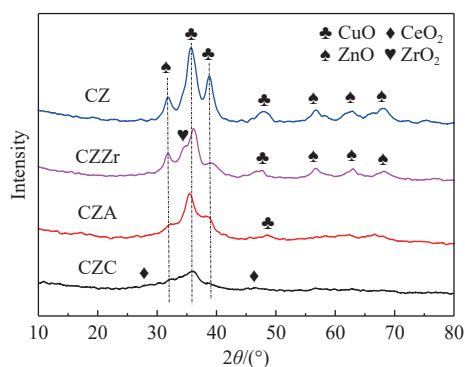


Fig. 1 XRD patterns of the Cu-based catalysts modified by different metal promoters

This change in peak position indicates that lattice substitution occurs between the metal promoters and Cu atoms, forming an oxide solid solution structure, which in turn causes distortion of the catalyst crystal structure. According to the lattice distortion theory, the unit cell volume increases while the unit cell parameters decrease accordingly^[15]. The CuO grain size was calculated using the Scherrer equation (as shown in Table 1). The data demonstrate that the introduction of metal promoters significantly inhibits the growth of Cu particles, leading to a marked reduction in CuO grain size. Among the catalysts, the CZC catalyst exhibits the smallest CuO grain size (only 11.41 nm), demonstrating the optimal grain refinement effect.

A comparison between the CZ catalyst (without promoter) and the modified catalysts shows that the XRD diffraction peaks of the CZ catalyst are sharp, indicating that Cu particles crystallize into large-sized particles with relatively high crystallinity. In contrast, after the addition of metal promoters, the intensity of the CuO characteristic peaks weakens significantly. This phenomenon suggests that metal promoters can effectively promote the dispersion of Cu species on the catalyst surface, significantly increase the exposed area of Cu, and reduce the overall crystallinity of the catalyst—thereby providing more active sites for the adsorption and activation of H_2 and CO_2 molecules. Among the three metal promoters, the CuO characteristic peak of the CZC catalyst is the broadest, while that of the CZA catalyst is the sharpest, with the CZZr catalyst falling between the two. This result fully confirms that Ce is more effective than Al and Zr in inhibiting the agglomeration of CuO particles and refining grains, enabling Cu species to exist in the catalyst system as smaller-sized particles.

There is a close intrinsic relationship between the pore structure characteristics of catalysts, the dispersion of active metals, and the selectivity of catalytic reactions. Table 1 presents the specific surface area, pore size, pore volume, Cu-specific surface area, and Cu dispersion of Cu-based catalysts modified with different metal promoters, as determined by N_2 physical adsorption-desorption and N_2O titration. Figure 2 shows the corresponding N_2 adsorption-desorption curves and pore size distribution profiles of the catalysts.

As can be seen from the data in Table 1, compared with the unmodified CZ catalyst, the introduction of metal promoters leads to a significant increase in both the specific surface area and pore volume of the catalysts. Among them, the catalysts modified with Al_2O_3 and CeO_2 exhibit particularly prominent increases in specific surface area and pore volume.

Table 1 Texture property of the Cu-based catalysts modified by different metal promoters

Sample	$S_{\text{BET}}/(\text{m}^2 \cdot \text{g}^{-1})$	Pore size/nm	$v_{\text{pore}}/(\text{cm}^3 \cdot \text{g}^{-1})$	d_{CuO}/nm	$d_{\text{Cu}}/\%$	$S_{\text{Cu}}/(\text{m}^2 \cdot \text{g}^{-1})$
CZ	53.5	30.36	0.17	31.0	3.21	33.18
CZA	85.1	15.15	0.53	14.9	5.43	63.30
CZC	68.6	13.84	0.42	11.4	7.82	40.36
CZZr	57.5	19.35	0.29	19.3	5.86	38.25

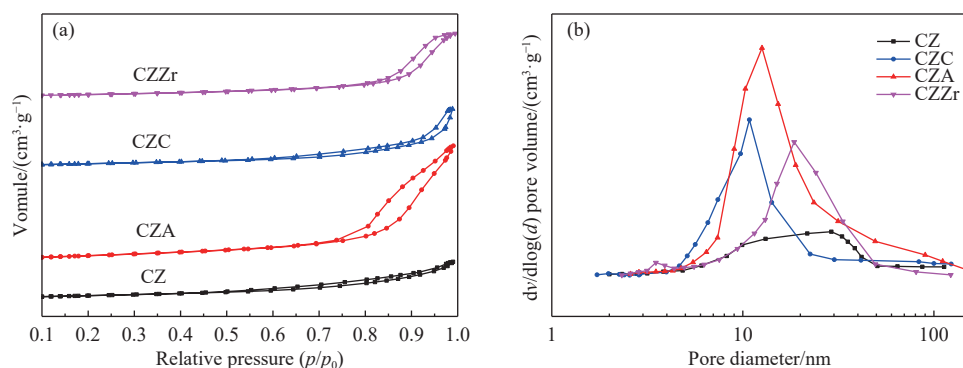


Fig. 2 (a) N_2 adsorption and desorption curves of the Cu-based catalysts with different metals, (b) pore size distribution of the Cu-based catalysts with different metals

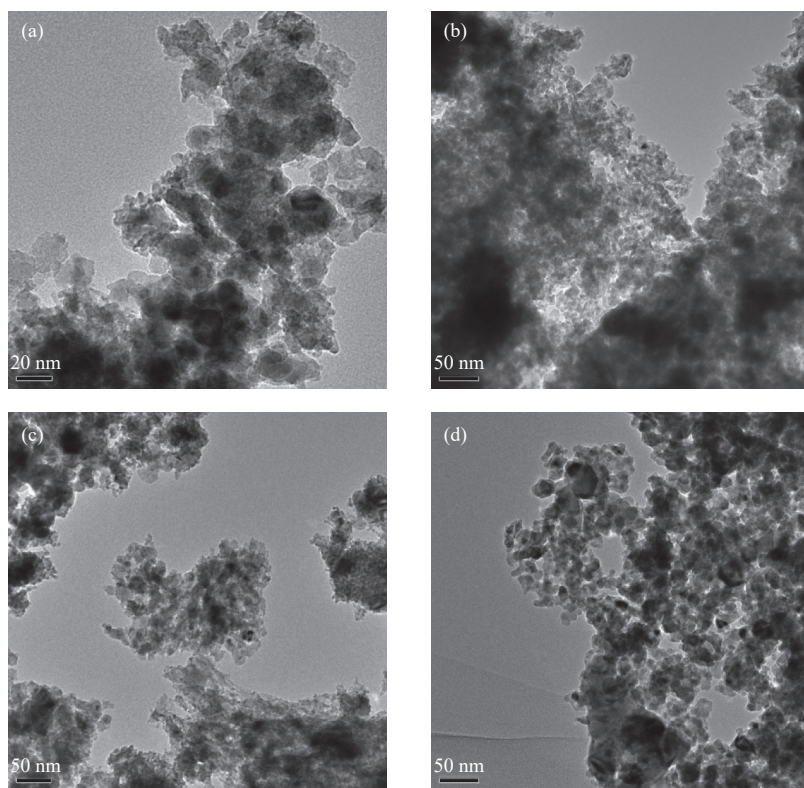
This phenomenon can be attributed to the fact that metal promoters effectively promote the dispersion of Cu species, inhibit the growth of CuO grains, and facilitate the formation of smaller-sized particles, thereby increasing the specific surface area of the catalyst. A large specific surface area can provide more adsorption and reaction active sites for reactant molecules, which plays a positive role in improving CO_2 conversion and methanol selectivity. This conclusion is consistent with the XRD analysis results.

Analysis of the N_2 adsorption-desorption curves in Figure 2 (a) shows that all Cu-based catalysts modified with different metal promoters exhibit type III isotherms with H3-type hysteresis loops—characteristics typical of mesoporous materials with slit-like pore structures. Although the overall morphology of the adsorption-desorption isotherms of the catalysts modified with different metal promoters is similar (indicating that the type of metal has a limited impact on the basic pore structure of the catalyst), the size of the hysteresis loop of the catalysts slightly increases after the introduction of metal promoters. This change intuitively reflects that the addition of metal promoters can effectively increase the number of mesopores in the catalyst, enrich its pore structure, and provide a more favorable spatial environment for the diffusion and adsorption of reactant molecules.

Further observation of the pore size distribution profiles in Figure 2(b) reveals that all four catalysts exhibit a single-peak pore size distribution. The pore size of the CZ catalyst is mainly distributed in the range of 10–42 nm; the pore size distribution range of the Al modified CZA catalyst narrows to 7–23 nm; the pore size of the Zr-modified CZZr catalyst ranges from 9–49 nm; and the pore size distribution range of the Ce modified CZC catalyst is the narrowest, concentrated in the range of 5–22 nm. Notably, the pore size corresponding to the peak of the pore size distribution of the modified catalysts is smaller than that of the CZ catalyst. Among them, the CZC catalyst has the smallest average pore size (only 13.84 nm), which fully confirms that the introduction of metal promoters can effectively refine the pore size of the catalyst grains. However, the change trend of the average pore size of the CZA catalyst is inconsistent with the changes in its specific surface area and pore volume. It is speculated that this is due to the strong

hydrophilicity of Al_2O_3 : the by-product water generated during the catalytic reaction, due to its high surface tension, tends to cause the collapse of small internal pores of the catalyst during subsequent drying and calcination, resulting in an increase in the average pore size. This phenomenon reveals the complexity of pore structure evolution during catalyst preparation.

To gain insight into the surface morphology and active metal distribution of the reduced Cu-based catalysts modified with different metal promoters, transmission electron microscopy (TEM) characterization was performed on the CZ, CZA, CZC and CZZr catalysts, with the results shown in Figure 3. Combined with the XRD analysis results, the fine particles observed in the TEM images can be preliminarily identified as CuO species. Observing the TEM image of the unmodified CZ catalyst (Figure 3(a)) reveals that the reduced catalyst exhibits a spherical particle morphology, with a large number of particles aggregating to form large-sized agglomerates, indicating significant particle agglomeration. This agglomeration behavior is attributed to the extremely small particle size of nano-sized Cu particles and the short distance between particles, which causes the van der Waals force between particles to be much greater than their own gravity. This promotes the spontaneous agglomeration of Cu particles (some even form bulk aggregates), resulting in low dispersion of Cu species. In contrast, the catalysts modified with metal promoters (Figure 3(b)–(d)) exhibit distinctly different microstructures. In the modified catalysts, Cu particles are more uniformly distributed on the support surface. This phenomenon fully confirms that the introduction of metal promoters can effectively improve the dispersion of Cu species and significantly inhibit the agglomeration of Cu-Zn particles^[16]. Among the three metal promoters, the CZC catalyst exhibits the best dispersion effect: the agglomeration of Cu particles on its surface is extremely weak, and the particles are small in size and uniformly distributed, showing regular and homogeneous microstructure characteristics. In addition, there are a large number of interparticle voids between the particles of the CZC catalyst—a feature that is consistent with the results of N_2 physical adsorption-desorption analysis, further confirming the presence of a rich mesoporous structure in this catalyst.



(a): CZ; (b): CZA; (c): CZZr; (d): CZC.

Fig. 3 Representative TEM images of the Cu-based catalysts with different metals

The above results indicate that the Ce promoter performs best in promoting the dispersion of Cu species and optimizing the catalyst microstructure, providing a more favorable structural basis for the exposure of active sites and the diffusion of reactant molecules.

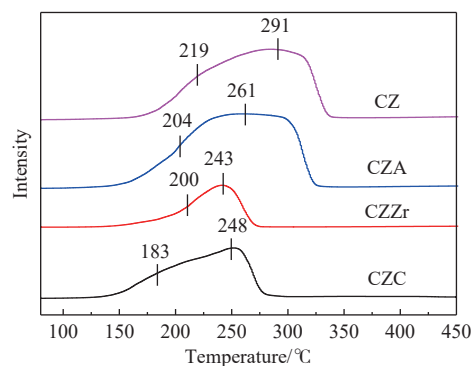
2.2 Effect of metal promoters on catalyst reduction properties

Figure 4 shows the H_2 temperature-programmed reduction (H_2 -TPR) profiles of the CZ, CZA, CZC and CZZr catalysts. The H_2 -TPR profiles of all catalyst samples exhibit two characteristic reduction peaks, corresponding to the stepwise reduction process of CuO species, indicating the presence of two CuO species in different chemical environments within the catalysts. Specifically, the low-temperature reduction peak is attributed to the reduction of highly dispersed CuO species, while the high-temperature reduction peak corresponds to the reduction of bulk CuO^[17].

The peak temperatures of the low-temperature reduction peaks of the catalysts follow the order: CZC < CZZr < CZA < CZ. This result indicates that the introduction of metal promoters significantly reduces the reduction temperature of highly dispersed CuO species. The underlying mechanism is that metal promoters regulate the mesostructure of the catalyst, promoting the dispersion of CuO species. According to the grain size effect, smaller CuO grains, due to their higher surface energy and defect

concentration, are more easily reduced at low temperatures. Combined with the XRD and TEM characterization results, the CZC catalyst has the smallest CuO grain size, so its low-temperature reduction peak temperature is the lowest, demonstrating the strongest low-temperature reduction activity^[18].

The peak temperatures of the high-temperature reduction peaks follow the order: CZZr < CZC < CZA < CZ. This high-temperature reduction peak is mainly associated with the strong metal-support interaction (SMSI) between dispersed CuO and the support. After the introduction of metal promoters, the strong interaction formed between CuO particles, the support, and other metal oxides significantly enhances the reducibility of CuO species, causing the high-temperature reduction peak to shift toward lower temperatures.

Fig. 4 H_2 -TPR patterns of the Cu-based catalysts with different metals

This interaction not only inhibits the growth of CuO particles but also promotes the reduction of bulk CuO through the hydrogen spillover effect—hydrogen atoms can spill over from the surface of highly dispersed CuO or ZnO and migrate to bulk CuO sites, thereby reducing the difficulty of its reduction^[19–20].

2.3 Effect of metal promoters on catalyst adsorption properties

To investigate the effect of catalyst composition on the surface adsorption performance of CO₂, CO₂ temperature-programmed desorption (CO₂-TPD) tests were conducted on Cu-ZnO catalysts modified with different metal promoters, with the results shown in Figure 5. After Gaussian fitting, the CO₂-TPD curves of all catalysts can be decomposed into three characteristic peaks: The α peak corresponds to CO₂ desorption from weakly basic sites, with weak adsorption force. It originates from –OH groups on the surface of metal oxides and reflects the linear adsorption of CO₂ by surface Cu species. The β peak is attributed to moderately basic sites in Lewis acid-base pairs, which are associated with metal-oxygen bonds (e.g., Ce–O, Zr–O, Al–O). It characterizes the bridged activated adsorption of CO₂ by surface Cu species. The γ peak represents CO₂ desorption from strongly basic sites, involving low-coordination oxygen atoms. It reflects the bridged adsorption and activation of CO₂ by surface Cu species under the synergistic effect of ZnO^[21].

The presence of these three peaks indicates significant differences in the basic strength of CO₂ adsorption by the oxides on the catalyst surface.

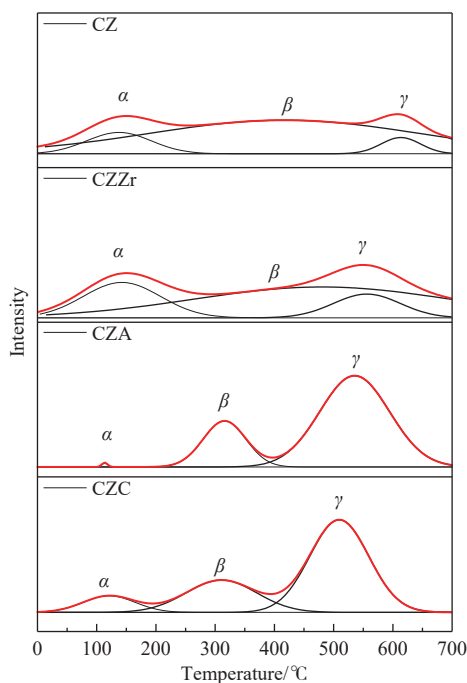


Fig. 5 CO₂-TPD patterns of the Cu-based catalysts with different metals

A comparison of the CO₂-TPD curves of the catalysts before and after modification reveals that after the introduction of metal promoters, the position of the α peak does not shift significantly, indicating that the addition of metal promoters and changes in promoter type do not significantly alter the chemical environment of –OH groups on the catalyst surface. In contrast, both the β peak and γ peak shift toward lower temperatures, and the temperatures of the desorption peaks follow the order: CZC < CZA < CZZr < CZ. This phenomenon indicates that the introduction of metal promoters effectively weakens the adsorption strength of strongly basic sites (and moderately basic sites) for CO₂, reducing the desorption energy barrier of CO₂ molecules. This is more conducive to the activation of CO₂ on the catalyst surface and promotes its hydrogenation with hydrogen to form methanol, thereby improving catalytic activity.

A further comparison of the CO₂ desorption peak areas shows that compared with the unmodified CZ catalyst, the areas of the β peak and γ peak of the catalysts with added metal promoters change significantly. To quantify the CO₂ adsorption characteristics of different catalysts, the CO₂ desorption amount of the CZ catalyst was used as a reference (assigned a value of 1), and the relative desorption amounts of other catalysts were calculated. The results are shown in Table 2. The data indicate that except for the CZA catalyst, the number of weakly basic sites (–OH groups) in the CZC and CZZr catalysts increases. This difference is attributed to the strong hydrophilicity of Al₂O₃: it easily combines with water molecules generated during the reaction, leading to the coverage or consumption of some –OH groups, thereby reducing the number of weakly basic sites.

For moderately basic sites, the Lewis acid-base pairs formed by metal-oxygen bonds can combine with CO₂ to form bidentate carbonate intermediates, enhancing the CO₂ adsorption capacity of the catalyst through bridged adsorption^[22–23]. Among the samples, the CZC and CZA catalysts have significantly more moderately basic sites than the other samples. In particular, the relative desorption amount of the CZC catalyst is 11.51 times that of the CZ catalyst. This phenomenon is attributed to the introduction of CeO₂: its rich oxygen vacancy structure promotes the formation of Ce–O metal-oxygen pairs, providing more active sites for CO₂ adsorption.

The CO₂ desorption behavior of strongly basic sites is closely related to the strong interaction of active centers on the catalyst surface. The data in Table 2 show that after the addition of metal promoters, the metal-support interaction of the catalyst is significantly enhanced, thereby improving its CO₂ adsorption capacity. The CO₂ desorption amounts of the CZC and CZA catalysts at strongly basic sites are significantly higher than that of the CZ catalyst, with the relative desorption amount of the CZC catalyst reaching up to 17.14 times that of the CZ catalyst. This is mainly due to the synergistic effect between Cu, Zn, and Ce in the CZC catalyst and the unique electronic structure of CeO₂: the

$\text{Ce}^{3+}/\text{Ce}^{4+}$ redox cycle in CeO_2 can generate a large number of low-coordination oxygen atoms and oxygen vacancy defects, while significantly increasing the surface basicity of the catalyst. This provides abundant active sites for CO_2 adsorption, thereby enhancing the CO_2 adsorption and activation capacity^[24–25].

2.4 Effect of metal promoters on catalyst electronic structure

To reveal the intrinsic relationships between the valence state and composition of surface elements as well as the

interaction between metals in the catalysts, X-ray photoelectron spectroscopy (XPS) characterization was conducted on the hydrogen-reduced Cu-based catalysts modified with different metal promoters. The results are presented in Figure 6.

Figure 6(a) shows the Cu 2p XPS spectra of the CZA, CZ, CZC and CZZr catalysts. All catalysts exhibit main peaks corresponding to Cu 2p_{3/2} and Cu 2p_{1/2} at 930–935 and 950–955 eV, respectively, indicating that Cu species on the catalyst surface coexist in two valence states: Cu⁰ and Cu⁺. Meanwhile, satellite peaks at 940–945 and 960–965 eV confirm the presence of a small amount of Cu²⁺^[26–28].

Table 2 CO₂ desorption types and distribution of Cu-based catalysts with different metals

Sample	Peak α	Peak β	Peak γ
CZ	1	1	1
CZA	0.30	8.75	14.28
CZC	2.27	11.51	17.14
CZZr	1.40	1.25	2.46

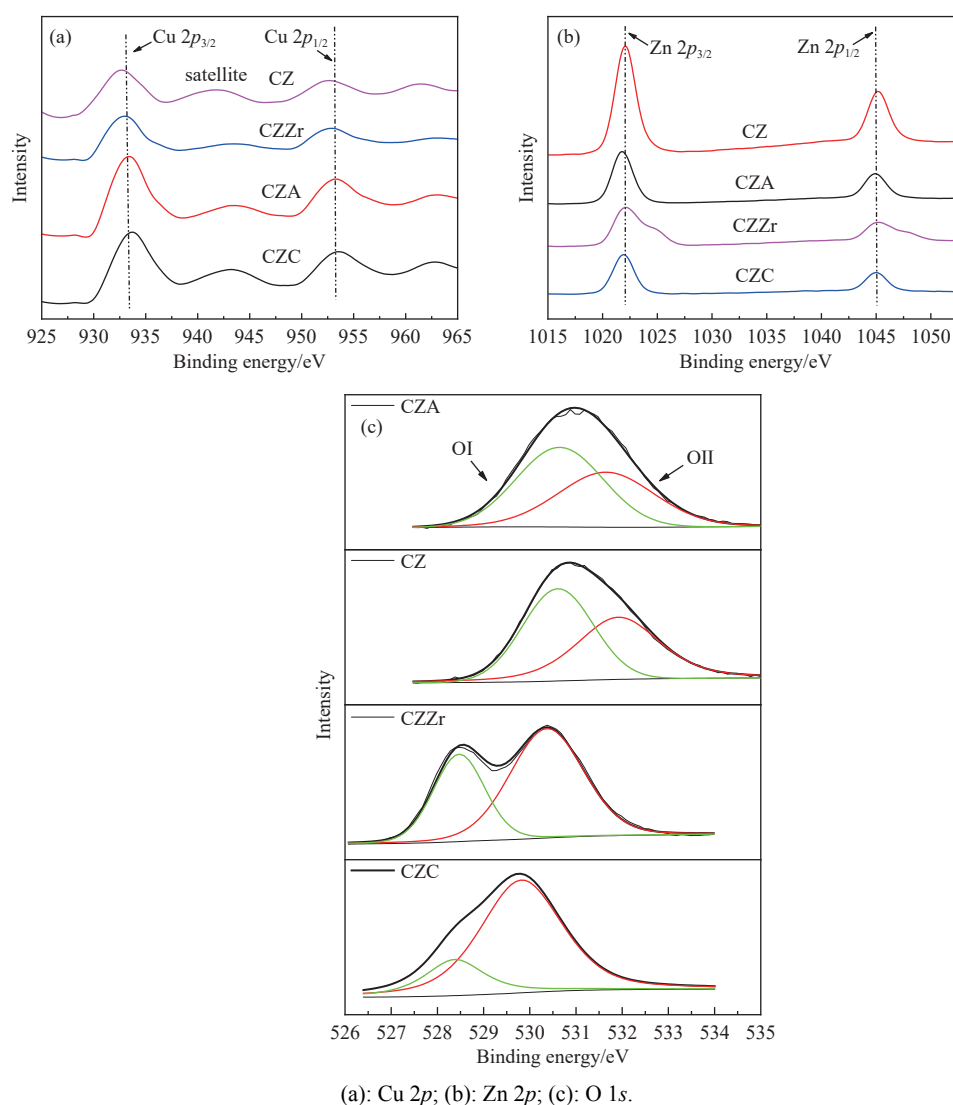


Fig. 6 Deconvolutions of XPS spectra of the Cu-based catalysts with different metals by hydrogen reduction

This phenomenon can be attributed to the trace water generated during the reaction, which causes partial oxidation of Cu species in air. Compared with the unmodified CZ catalyst, the binding energy of Cu species in the catalysts modified with metal promoters shifts to higher values, implying the formation of a more abundant Cu/Zn interface. This shift arises from the enhanced interaction between Cu species and the support by metal promoters, which reduces the electron cloud density of Cu atoms and induces the reconstruction of the electronic structure. Among them, the synergistic effect between CuO, ZnO and CeO₂ in the CZC catalyst is the most significant, laying an electronic structural foundation for its excellent catalytic performance^[29–31].

As observed from the Zn 2p XPS spectra in Figure 6(b), all Zn-containing catalysts, after reduction, exhibit two strong characteristic peaks at 1020–1025 and 1040–1045 eV, corresponding to the Zn 2p_{3/2} and Zn 2p_{1/2} orbitals, respectively. Their binding energies are consistent with the values reported in the literature without obvious shifts, indicating that Zn in the catalysts mainly exists in the stable Zn²⁺ form^[32]. This valence characteristic ensures the structural stability of the ZnO support during the catalytic reaction.

After Gaussian fitting, the O 1s XPS spectrum in Figure 6(c) can be decomposed into two characteristic peaks: peak O_I is assigned to lattice oxygen in the catalyst, and peak O_{II} corresponds to surface-adsorbed oxygen. The ratio of O_{II}/O_I can be used to quantitatively characterize the concentration of oxygen defects on the catalyst surface^[33]. Studies have shown that a higher O_{II}/O_I ratio indicates the formation of more oxygen vacancies, which is beneficial for improving catalytic activity. The data show that the O_{II}/O_I ratio of the CZC catalyst is as high as 3.15, significantly higher than that of other samples. This is attributed to the fact that the incorporation of Ce⁴⁺ into the CuO lattice enhances the interaction between Cu species, ZnO and CeO₂, inducing more defects in the crystal structure and thereby increasing the concentration of surface oxygen vacancies. The abundant oxygen vacancies not only enhance the adsorption capacity of the catalyst for CO₂ molecules but also provide key active sites for their activation, which is also an important reason for the excellent performance of the CZC catalyst.

2.5 Evaluation of catalyst performance

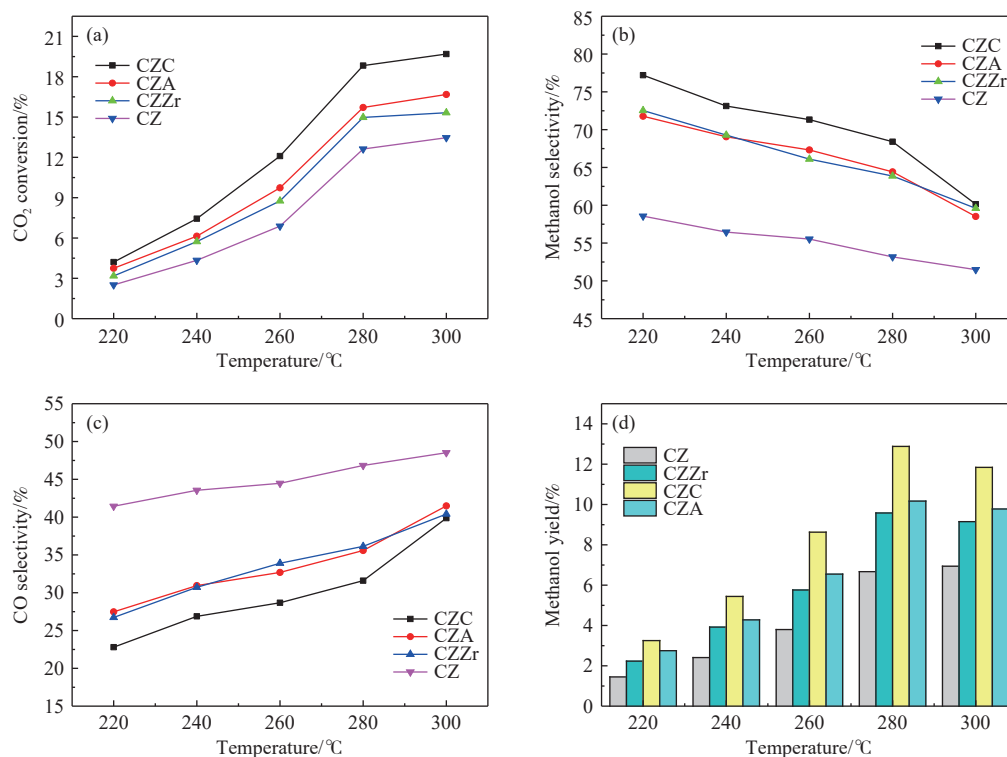
Figure 7(a) shows the variation trend of CO₂ conversion over the four catalysts (CZ, CZZr, CZA and CZC) at different reaction temperatures. The results indicate that the CO₂ conversion of all four catalysts increases with the rise in reaction temperature, following the order: CZ < CZZr < CZA < CZC. Compared with the unmodified CZ catalyst, the three catalysts modified with metal promoters exhibit significantly improved CO₂ conversion, among which the CZC catalyst exhibited the highest. In the reaction

temperature range of 220–300 °C, the CO₂ conversion of the CZC catalyst is 4.21%, 7.44%, 12.10%, 18.83% and 19.69% respectively, with the fastest growth rate observed at 280 °C. This excellent performance is attributed to the unique properties of CeO₂: as a basic oxide, the negative charge characteristics on the CeO₂ surface facilitate electron transfer, stabilize active sites, and provide abundant CO₂ adsorption sites^[34]; meanwhile, the relatively high surface basicity of the CZC catalyst offers more adsorption sites for acidic CO₂ molecules, thereby significantly enhancing the capacity for CO₂ capture and activation.

Figure 7(b) presents the temperature dependence of methanol selectivity over the four catalysts. The experimental data show that the methanol selectivity of all catalysts decreases with increasing reaction temperature, following the same order as CO₂ conversion: CZ < CZZr < CZA < CZC. The CZC catalyst exhibits the highest methanol selectivity at all temperature points. In the range of 220–300 °C (at 220, 240, 260, 280, 300°C), its methanol selectivity is 77.20%, 73.12%, 71.32%, 68.40% and 60.13%, respectively. The introduction of CeO₂ optimizes the adsorption selectivity of the catalyst by increasing the content of dispersed CuO species and enhancing surface basicity: on one hand, the enhanced surface basicity promotes CO adsorption and weakens the adsorption strength of methanol on the catalyst surface, effectively alleviating the inhibitory effect of methanol adsorption on CO₂ adsorption; on the other hand, the high-basicity environment inhibits the side reaction of methanol decomposition into CO, thereby significantly improving the selectivity of the target product.

Figure 7(c) shows the variation of CO selectivity with reaction temperature. The results demonstrate that the CO selectivity of all catalysts is positively correlated with the reaction temperature, with the CZ catalyst showing the highest CO selectivity and the CZC catalyst the lowest. In the temperature range of 220–300 °C, the CO selectivity of the CZC catalyst gradually increases from 22.80% to 39.87%. This phenomenon further confirms the ability of the CZC catalyst to inhibit side reactions, which is mainly because its unique structure and surface properties effectively reduce the occurrence of the reverse water-gas shift (RWGS) reaction, thereby decreasing the formation of CO by-products.

Figure 7(d) shows the evolution trend of methanol yield with temperature. In the range of 220–280 °C, the methanol yield of all catalysts increases with temperature, but decreases at 300 °C. The CZC catalyst also performs outstandingly in this index, achieving the highest methanol yield of 12.88% at 280 °C (the yields at 220–300 °C are 3.25%, 5.44%, 8.63%, 12.88% and 11.84%, respectively). This result indicates that 280 °C is the optimal reaction temperature for the CZC catalyst; although a higher temperature can improve CO₂ conversion, it intensifies methanol decomposition and side reactions, leading to a decrease in methanol yield.



(a): CO₂ conversion; (b): methanol selectivity; (c): CO selectivity; (d): methanol yield.

Fig. 7 Activity of the Cu-based catalysts with different metals

A comprehensive comparison of the performance data of the four catalysts reveals that the introduction of metal promoters significantly improves the overall performance of Cu-based catalysts. The underlying mechanism is mainly reflected in: promoting the dispersion of Cu species, inhibiting particle agglomeration, and forming a small-grain CuO structure with a high specific surface area, thereby exposing more active sites and enhancing the adsorption and activation capacities for CO₂ and H₂. Among them, Ce modification endows the composite catalyst with a synergistic effect: on one hand, Ce reduces the “primary formation” of CO caused by the RWGS reaction by refining Cu grains and regulating the electronic structure; on the other hand, it enhances the surface basicity of the catalyst through the basic properties of CeO₂, inhibiting the decomposition of generated methanol and reducing the “secondary formation” of CO. The combined effect of these two aspects enables the CZC catalyst to achieve excellent performance (CO₂ conversion of 18.83%, methanol selectivity of 68.40% and methanol yield of 12.88%) under the reaction conditions of 2.8 MPa, 8000 h⁻¹ and 280 °C, providing valuable insights for the design of high-efficiency catalysts for CO₂ hydrogenation to methanol.

3 Conclusion

Cu-ZnO catalysts modified with Al, Zr and Ce were successfully prepared via the co-precipitation method. The influence mechanisms of metal promoters on the catalyst structure and performance in CO₂ hydrogenation to

methanol were systematically investigated. The introduction of metal promoters significantly altered the microstructure of the catalysts. Characterization results indicated that the addition of promoters effectively inhibited the agglomeration of Cu particles and refined the CuO grain size. Among them, the Ce-modified CZC catalyst exhibited the smallest grain size, merely 11.41 nm. The promoters increased the specific surface area and pore volume of the catalysts, enhanced the number of mesopores, and optimized the pore structure, providing more favorable conditions for the adsorption and diffusion of reactant molecules. Additionally, the incorporation of promoters strengthened the metal-support interaction, modified the electronic structure of Cu species, and facilitated the formation of surface oxygen vacancies. The CZC catalyst showed the highest surface oxygen vacancy concentration ($O_{II}/O_I = 3.15$), which was conducive to the adsorption and activation of CO₂. The modified catalysts demonstrated superior performance in the CO₂ hydrogenation to methanol reaction. Compared with the unmodified CZ catalyst, the CO₂ conversion, methanol selectivity, and methanol yield of the catalysts with metal promoters were significantly improved. Under the reaction conditions of 2.8 MPa, 8000 h⁻¹ and 280 °C, the CZC catalyst exhibited the optimal catalytic performance, achieving a CO₂ conversion of 18.83%, a methanol selectivity of 68.40%, and a methanol yield of 12.88%. This excellent performance is mainly attributed to the surface basicity of CeO₂ and its synergistic effect with the Cu-ZnO system: it not only increased the number of basic sites on the catalyst surface and enhanced the adsorption of acidic CO₂ molecules but also inhibited

the occurrence of the reverse water-gas shift (RWGS) side reaction, thereby improving the selectivity of the target product.

This study clarifies the structure-activity regulation mechanisms of metal promoters (such as Al, Zr and Ce) on Cu-ZnO catalysts, providing a theoretical basis and practical guidance for the design and development of high-efficiency catalysts for CO₂ hydrogenation to methanol. Future research can further explore the effects of other promoters or promoter combinations on catalyst performance, optimize the catalyst preparation process, and promote the industrial application of CO₂ hydrogenation to methanol technology.

Declaration of Competing Interest

The authors declare no conflict of interest.

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助剂改性 Cu 基催化剂用于 CO_2 加氢制甲醇的构效关联机制研究

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摘 要: 本研究采用共沉淀法制备 Al、Zr、Ce 改性的 Cu-ZnO 催化剂, 探究助剂对催化剂结构-性能的影响机制。通过 XRD、 N_2 物理吸附-脱附、TEM、 H_2 -TPR、 CO_2 -TPD 及 XPS 等表征手段, 结合催化性能评价实验, 深入分析催化剂微观结构与 CO_2 加氢制甲醇反应性能的关联。结果表明, 金属助剂显著改善了催化剂性能, 引入助剂后, 催化剂比表面积和孔容增大, Cu 晶粒尺寸减小, 分散度提高。Ce 改性的 Cu-ZnO 催化剂效果最佳, 其 CuO 晶粒尺寸为 11.41 nm, 表面氧空位浓度 ($\text{O}_{\text{II}}/\text{O}_{\text{I}} = 3.15$) 显著高于其他样品。反应性能测试显示, 在 2.8 MPa、 8000 h^{-1} 、 280°C 条件下, CZC 催化剂的 CO_2 转化率 18.83%, 甲醇选择性为 68.40%, 甲醇收率 12.88%, 均优于其他催化剂。其优异性能归因于 CeO_2 增强了金属-载体相互作用, 提升表面碱度, 促进 CO_2 吸附与活化, 同时抑制逆水煤气变换副反应。本研究明确了助剂改性对 Cu-ZnO 催化剂的构效调控机制, 为高效 CO_2 加氢制甲醇催化剂的开发提供了理论依据与技术参考。

关键词: 二氧化碳; 催化剂; 助剂改性; 加氢; 甲醇

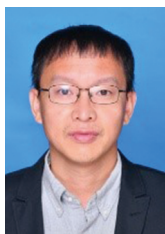
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文献标识码: A

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