

Enhancement of ZnO-ZrO₂ solid solution catalyst via Cu addition for CO₂ hydrogenation to methanol

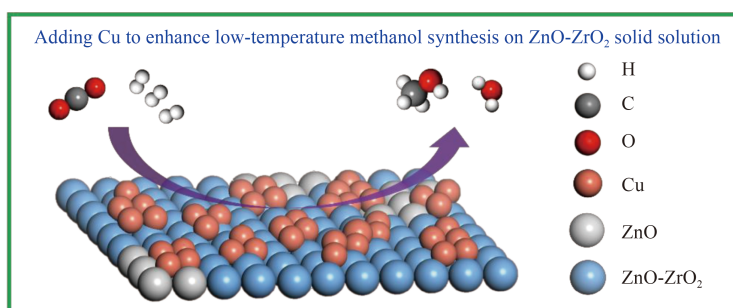
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Abstract: The introduction of an appropriate amount of Cu effectively enhances the catalytic performance of ZnO-ZrO₂ solid solution catalysts in CO₂ hydrogenation to methanol. However, systematic studies on the effect of Cu content in ZnO-ZrO₂ solid solution catalysts remain limited. In this work, a ZnO-ZrO₂ solid solution and a series of Cu/ZnO/ZrO₂-x catalysts (x = 0.3, 0.7 and



0.9, denoting the molar ratio of Cu/(Cu+Zn+Zr)) were prepared by co-precipitation method. Among these catalysts, the Cu/ZnO/ZrO₂-0.7 catalyst exhibited the optimal catalytic performance, with a space-time yield of methanol (162.7 g/(kg·h)) that was 6.6 times higher than that of the ZnO-ZrO₂ solid solution catalyst (24.8 g/(kg·h)) at 250 °C. Structural characterizations reveal that the introduction of an appropriate amount of Cu led to the coexistence of a solid solution and individual metal oxides, and promoted the formation of medium-strength basic sites. *In situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) results further confirm that Cu introduction facilitated the conversion of key reaction intermediates. This work provides a systematic investigation of the influence of Cu content on the methanol synthesis performance of ZnO-ZrO₂ solid solution catalysts and elucidates the promotional mechanism induced by Cu incorporation.

Key words: ZnO-ZrO₂; copper; carbon dioxide; methanol; interface

With the continuous growth of global energy demand, the large-scale consumption of fossil fuels has resulted in severe carbon dioxide (CO₂) emissions, which has exacerbated the greenhouse effect and impacted the global climate system^[1–2]. In this context, the conversion of CO₂ into high-value-added chemicals has emerged as an effective strategy for simultaneously addressing the energy crisis and environmental issues^[3–5]. Among diverse approaches, methanol synthesis *via* the hydrogenation of CO₂ with “green hydrogen” derived from renewable energy sources is regarded as one of the most promising green and low-carbon transformation routes. Methanol can not only serve as a clean fuel to substitute traditional fossil fuels, but also serve as a key platform molecule in C₁ chemistry, presenting broad application prospects in the fields of

chemical feedstocks and energy carriers^[6–8].

Currently, the development of catalysts with both high activity and high selectivity is still one of the major technical challenges in the commercialization of CO₂ hydrogenation to methanol^[9–10]. In recent years, ZnO-ZrO₂ solid solution catalyst first reported by Li's group has garnered significant attention due to its high methanol selectivity and excellent catalytic stability in methanol synthesis^[11–12]. Subsequently, Lee et al.^[13] developed an atomically Pd-promoted ZnO-ZrO₂ solid solution catalyst for methanol synthesis, wherein Pd doping facilitated the formation of oxygen vacancies and enhanced H₂ dissociation. Araújo et al.^[14] synthesized a high-performance ZnO-ZrO₂ solid-solution catalyst *via* a flame spray pyrolysis method, which promoted the generation of

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atomically dispersed Zn²⁺ sites and oxygen vacancies. Zhang et al.^[15] reported that thermal treatment under an H₂/Ar atmosphere induced the formation of abundant asymmetric Zn-O_v-Zr sites in the ZnO-ZrO₂ solid solution, thereby leading to excellent methanol synthesis performance. However, despite their promising potential, current ZnO-ZrO₂ solid-solution catalysts generally require relatively high operating temperatures (>300 °C) and comparatively complex synthesis methods to achieve considerable catalytic activity. Therefore, exploring new strategies to modulate ZnO-ZrO₂ solid solution structure for enhanced catalytic activity is a crucial focus.

Copper (Cu)-based catalysts have been extensively studied for CO₂ hydrogenation to methanol due to their considerable activity and low cost^[16–18]. Recent studies have demonstrated that the introduction of Cu can modulate the structure of ZnO-ZrO₂ solid solution catalysts and thereby enhance their methanol synthesis performance^[19–20]. For instance, Xu et al.^[19] incorporated a small amount of Cu (molar fraction as 0.5%) into ZnO-ZrO₂ solid solution to boost methanol synthesis activity. In this case, the introduction of Cu induced hydrogen spillover on ZnO-ZrO₂ solid solution, thus improving hydrogenation capacity and accelerating the conversion of formate (*HCOO) to methoxy (*CH₃O). Xu et al.^[20] prepared a high-performance ZnO-ZrO₂/Cu inverse catalyst by introducing Cu with molar fraction as 87.0% into ZnO-ZrO₂ solid solution, in which the construction of the inverse structure enhanced the activation ability of CO₂ and increased the hydrogenation rate of key intermediates. Notably, above studies focused on the effect of low or high Cu content on ZnO-ZrO₂ solid solution, while systematic investigation across a wide range of Cu content remains scarce. Consequently, a comprehensive study on how Cu content affects the methanol synthesis performance of ZnO-ZrO₂ solid solution is essential, which will facilitate the further optimization of Cu-based catalyst.

Herein, the ZnO-ZrO₂ solid solution and Cu/ZnO/ZrO₂-*x* catalysts with different Cu contents were prepared by a co-precipitation method for CO₂ hydrogenation to methanol. The effect of Cu content on the catalytic performance of ZnO-ZrO₂ solid solution was systematically evaluated, and the structure-activity relationships of these catalysts were elucidated through various characterizations. Additionally, *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments were conducted to analyze the functional mechanism of Cu in the ZnO-ZrO₂ solid solution catalysts. The present work aims to elucidate the role of Cu content in modulating the methanol synthesis performance of ZnO-ZrO₂ solid solution catalysts, thereby facilitating the development of high-performance methanol synthesis catalysts.

1 Experimental

1.1 Materials

Both Cu(NO₃)₂·3H₂O (99%) and (NH₄)₂CO₃ (analytical

grade) were purchased from Macklin. (CH₃COO)₂Zn·2H₂O (analytical grade) and Zr(NO₃)₄·5H₂O (98%) were obtained from Sinopharm Chemical Reagent and Innochem, respectively. Above reagents were used as received.

1.2 Catalyst preparation

The ZnO-ZrO₂ solid solution and Cu/ZnO/ZrO₂-*x* catalysts were prepared *via* a co-precipitation method. The ZnO-ZrO₂ solid solution catalyst was synthesized according to a procedure reported in the literature, with the Zn/Zr molar ratio being fixed at 1/4^[11]. Cu/ZnO/ZrO₂-*x* catalysts (*x* = 0.3, 0.7 and 0.9, denoting the molar ratio of Cu/(Cu+Zn+Zr)) were prepared using a similar experiment protocol.

Taking the Cu/ZnO/ZrO₂-0.7 catalyst as an illustration, 81.7 mmol Cu(NO₃)₂·3H₂O, 7.0 mmol (CH₃COO)₂Zn·2H₂O and 28.0 mmol Zr(NO₃)₄·5H₂O were dissolved into 300 mL deionized water and then heated to 70 °C in a water bath. Subsequently, 0.15 mol/L (NH₄)₂CO₃ aqueous solution was added into the above solution at a flow rate of 3 mL/min using a peristaltic pump until the pH reached 7. The resultant mixture was then aged at 70 °C for 2 h under vigorous stirring, followed by static aging for an additional 2 h. After aging, the precipitation was collected by centrifugation and washed five times with deionized water. Finally, the product was obtained after drying at 110 °C for 12 h and static calcination at 500 °C for 3 h.

1.3 Catalytic test

The catalytic performance of catalysts for CO₂ hydrogenation to methanol was tested in a high-pressure fixed-bed reactor under 3.0 MPa. Specifically, 1.0 g of catalyst (40–60 mesh) was uniformly mixed with 4.0 g of quartz sand (40–60 mesh) and then loaded into a stainless steel tube (inner diameter: 17 mm). Prior to the reaction, the catalyst was reduced at 320 °C under a 10% H₂/Ar flow (200 mL/min) for 1 h. After the sample was adjusted to target reaction temperature, the reactant gases consisting of H₂/CO₂/Ar with molar ratio of 72:24:4 was introduced at a total flow rate of 200 mL/min. The activity test was respectively conducted at 220, 250 and 320 °C, and the reaction data were obtained after 6.0 h of time-on-stream. The stability test was performed at 250 °C and 3.0 MPa for 30 h. The products were analyzed using an online gas chromatograph (Agilent 8860) equipped with both thermal conductivity detector (TCD) and flame ionized detector (FID).

The CO₂ conversion (*x*_{CO₂}), methanol selectivity (*s*_{MeOH}), and space time yield of methanol (STY_{MeOH}) were calculated according to the following equations:

$$x_{\text{CO}_2} = \frac{f_{\text{CO}}A_{\text{CO}} + f_{\text{MeOH}}A_{\text{MeOH}}}{f_{\text{CO}}A_{\text{CO}} + f_{\text{MeOH}}A_{\text{MeOH}} + f_{\text{CO}_2}A_{\text{CO}_2}} \quad (1)$$

$$s_{\text{MeOH}} = \frac{f_{\text{MeOH}} A_{\text{MeOH}}}{f_{\text{CO}} A_{\text{CO}} + f_{\text{MeOH}} A_{\text{MeOH}}} \quad (2)$$

$$\text{STY}_{\text{MeOH}} = \frac{F_{\text{CO}_2, \text{in}} \times x_{\text{CO}_2} \times s_{\text{MeOH}} \times M_{\text{MeOH}}}{W_{\text{cat}}} \quad (3)$$

where f_i , A_i , $F_{\text{CO}_2, \text{in}}$, M_{MeOH} and W_{cat} represent the correction factor, peak area, molar flow rate of CO₂ inlet, molar mass of methanol, and catalyst mass, respectively.

1.4 Catalyst characterization

X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advance diffractometer with Cu K α radiation at a scanning rate of 5°/min. The crystalline phases were identified by comparing with the Joint Committee on Powder Diffraction Standards (JCPDS).

Transmission electron microscopy (TEM) and high-resolution TEM (HR-TEM) were obtained on a JEM-2100F system (Rigaku) at a working voltage of 200 kV. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energy-dispersive X-ray spectroscopy (EDX) elemental mapping were measured using a JEM-F200 Multi-purpose Electron Microscope instrument with an acceleration voltage of 200 kV. Prior to TEM measurements, the catalyst powder was sonicated in ethanol and then dispersed on a carbon-coated copper grid.

CO₂ temperature-programmed desorption (CO₂-TPD) experiments were carried out on a Micromeritics Autochem II 2920 instrument equipped with a TCD. Specifically, the calcined sample (200 mg) was first reduced by flowing 10% H₂/He (50 mL/min) at 320 °C for 1 h and then purged in flowing He (50 mL/min) at 320 °C for 0.5 h. After being cooled to 50 °C in flowing He (50 mL/min), the catalyst was saturated by a CO₂ stream (50 mL/min) for 1 h and then flushed with flowing He (50 mL/min) for 1 h. Finally, the CO₂-TPD profile was recorded as the sample was heated to 800 °C at a rate of 10 °C/min in flowing He (50 mL/min).

In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) spectra were collected on a spectrometer (Bruker, TENSOR II) equipped with an MCT detector. The catalyst was first reduced at 320 °C for 1 h in flowing 10% H₂/Ar (30 mL/min) and then purged at 250 °C for 1 h in flowing Ar (30 mL/min). Subsequently,

background spectra were recorded under Ar atmosphere. Finally, *in situ* DRIFTS spectra as a function of reaction time were collected after introducing the reactant gases (CO₂/H₂ = 5:15 mL/min) at 250 °C.

2 Results and discussion

2.1 Catalytic performance

Figure 1 displays the catalytic performance of ZnO-ZrO₂ and Cu/ZnO/ZrO₂- x catalysts at diverse reaction temperatures. Generally, the ZnO-ZrO₂ catalyst exhibited low CO₂ conversion but high methanol selectivity, and its performance is similar with that of ZnO-ZrO₂ solid solution catalysts reported in the literature^[11,19,21]. In comparison with the ZnO-ZrO₂ catalyst, the Cu/ZnO/ZrO₂- x catalysts showed significantly increased CO₂ conversion but decreased methanol selectivity. Notably, the STY_{MeOH} of the Cu/ZnO/ZrO₂- x catalyst was significantly higher than that of the ZnO-ZrO₂ catalyst at both 220 and 250 °C, but lower at 320 °C. This result indicates that the introduction of Cu effectively enhances the methanol synthesis performance of the ZnO-ZrO₂ catalyst at lower temperatures. Specifically, the STY_{MeOH} at 250 °C for ZnO-ZrO₂, Cu/ZnO/ZrO₂-0.3, Cu/ZnO/ZrO₂-0.7 and Cu/ZnO/ZrO₂-0.9 catalysts were 24.8, 87.8, 162.7 and 54.6 g/(kg·h), respectively. Among these catalysts, the Cu/ZnO/ZrO₂-0.7 catalyst exhibited the highest methanol formation rate, with its STY_{MeOH} being 6.6 times that of the ZnO-ZrO₂ catalyst. Moreover, the optimal Cu/ZnO/ZrO₂-0.7 catalyst demonstrated superior methanol synthesis activity compared to other reported CuZnZr catalysts (Table 1)^[7,22–26].

2.2 Catalyst characterization

To investigate the promotional effect of Cu introduction on the low-temperature methanol synthesis activity of ZnO-ZrO₂ catalyst, the structures of the ZnO-ZrO₂ and Cu/ZnO/ZrO₂- x catalysts were analyzed using a series of characterization techniques. Figure 2 shows the XRD patterns of the reduced catalysts. For the ZnO-ZrO₂ catalyst, the characteristic peaks of typical tetragonal phase ZrO₂ (t -ZrO₂) were observed.

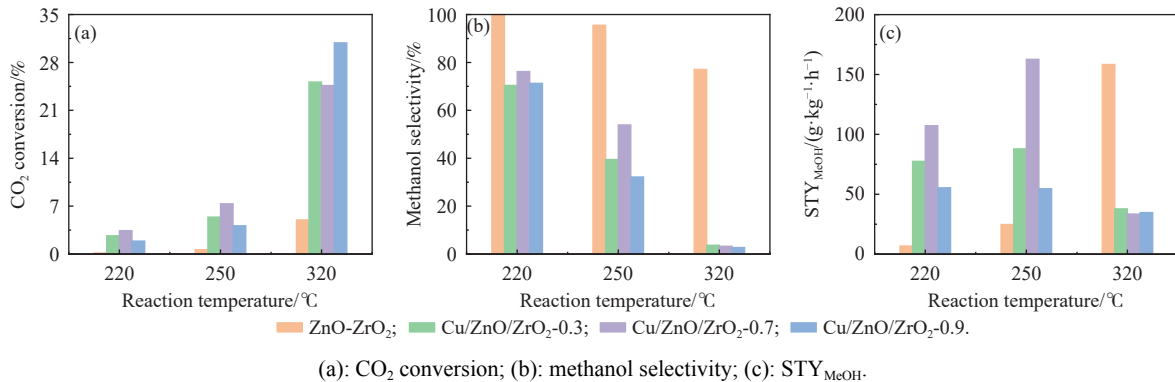
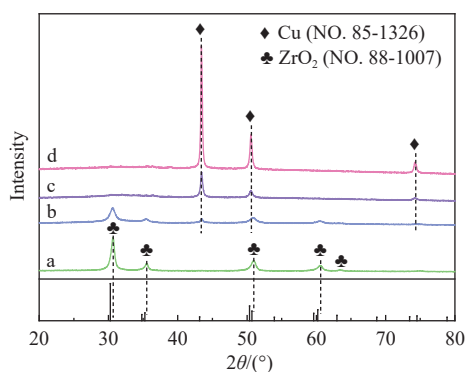


Fig. 1 Methanol synthesis performance over various catalysts under 3.0 MPa

Table 1 Performance comparison of Cu/ZnO/ZrO₂-0.7 catalyst in this work with other CuZnZr catalysts reported in the literatures under comparable reaction conditions

Catalyst	WHSV/(mL·h ⁻¹ ·g ⁻¹)	p/MPa	t/°C	STY _{MeOH} ^a /(g·kg ⁻¹ ·h ⁻¹)	References
Cu/ZnO/ZrO ₂ -0.7	12000	3.0	250	162.7	this work
Cu-Zn-Zr-I(0)	24000	3.0	250	130.0	[22]
Cu-ZnZr	24000	3.0	230	177.0	[23]
CZZ-9	12000	3.0	250	119.7	[7]
CZZ-CP	7200	3.0	240	111.9	[24]
Cu-ZnO-ZrO ₂	6000	3.0	220	128.0	[25]
CZZ-flower	3 600	3.0	250	137.6	[26]

^a: Given the sensitivity of CO₂ conversion and methanol selectivity to WHSV, STY_{MeOH} is used to evaluate methanol synthesis performance under comparable reaction pressure and temperature.



a: ZnO-ZrO₂ solid solution; b: Cu/ZnO/ZrO₂-0.3;
c: Cu/ZnO/ZrO₂-0.7; d: Cu/ZnO/ZrO₂-0.9.

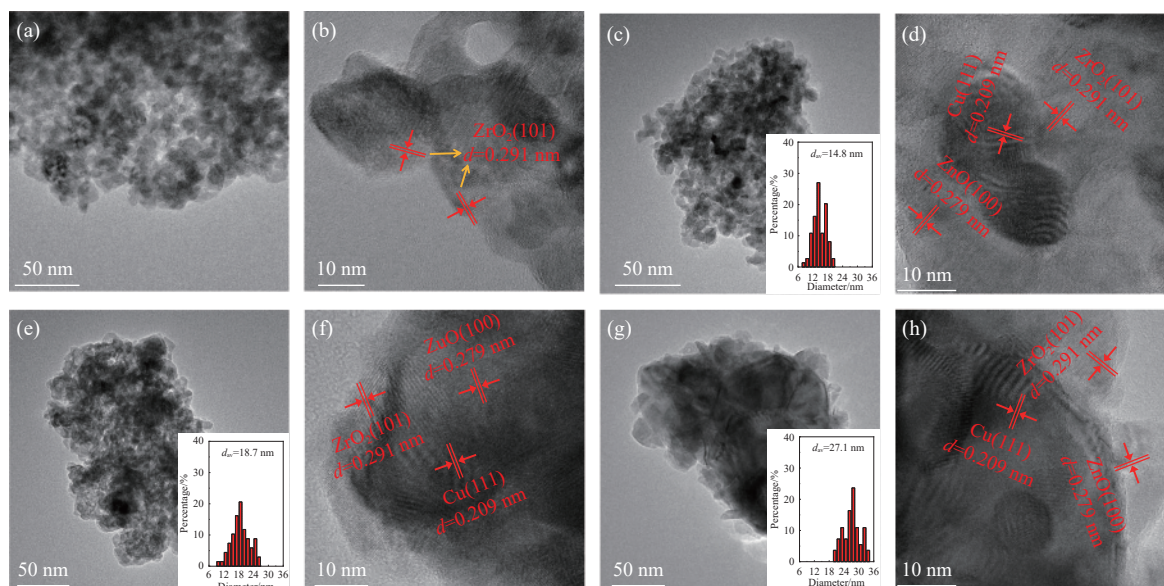
Fig. 2 XRD patterns of reduced catalysts

In comparison with the ZrO₂ in JCPDS standard card, the characteristic peaks of ZnO-ZrO₂ shifted towards higher 2θ values. The shift is attributed to the incorporation of Zn²⁺ with lower ions radius (0.74 Å) into the ZrO₂ lattice (ionic radius of Zr⁴⁺ = 0.82 Å), resulting in a decrease of lattice distance in ZrO₂. This result confirms the formation of a ZnO-ZrO₂ solid solution structure^[11]. For the Cu/ZnO/ZrO₂-*x* catalysts, characteristic peaks corresponding to metallic Cu were detected. Meanwhile, no characteristic peaks associated with ZnO or ZrO₂ were observed in the Cu/ZnO/ZrO₂-0.7 and Cu/ZnO/ZrO₂-0.9 catalysts, which might be due to their high dispersion^[27]. Additionally, the Cu crystallite sizes of the Cu/ZnO/ZrO₂-*x* catalysts were calculated using the Scherrer equation based on the Cu(111) crystal plane, with values of 14.4 nm for Cu/ZnO/ZrO₂-0.3, 18.2 nm for Cu/ZnO/ZrO₂-0.7 and 26.8 nm for Cu/ZnO/ZrO₂-0.9. The absence of a correlation between the catalytic performance and the Cu crystallite size over the Cu/ZnO/ZrO₂-*x* catalysts excludes the latter as a crucial factor influencing methanol synthesis activity.

The morphology of the reduced catalysts was characterized by TEM. As depicted in Figure 3, distinct morphologies were observed between the ZnO-ZrO₂ solid solution and the Cu/ZnO/ZrO₂-*x* catalysts. Uniform nanoparticles were detected on the ZnO-ZrO₂ solid solution (Figure 3(a)). In contrast, aggregates with non-uniform size were found on both the Cu/ZnO/ZrO₂-0.3 (Figure 3(c)) and

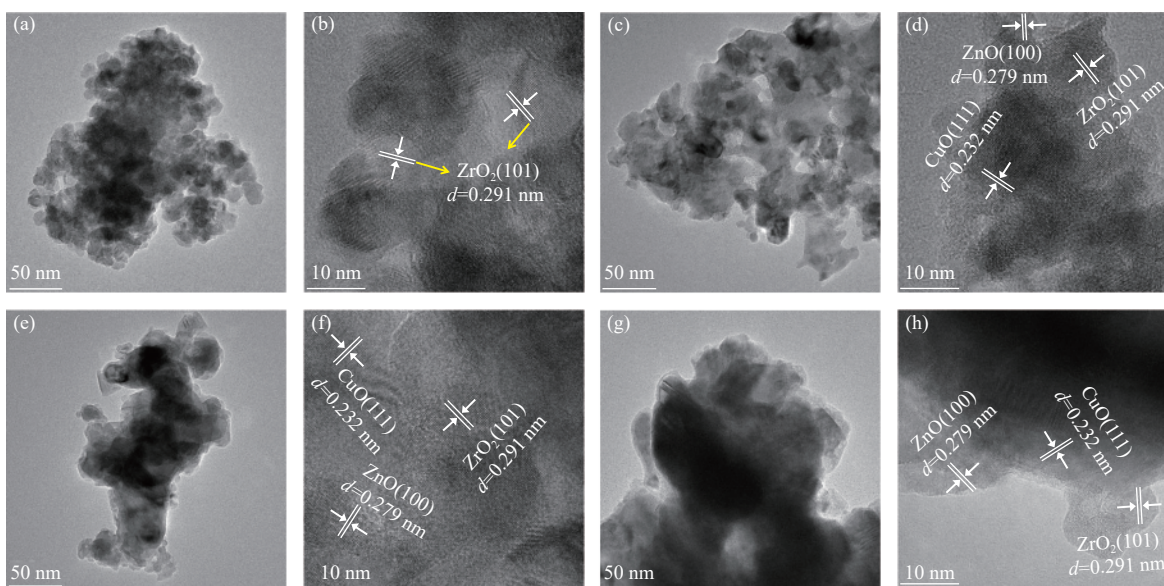
Cu/ZnO/ZrO₂-0.7 (Figure 3(e)) catalysts, and larger aggregates were observed on the Cu/ZnO/ZrO₂-0.9 catalyst (Figure 3(g)). To determine the composition of each particle, HR-TEM images were employed to measure their lattice distance. For the ZnO-ZrO₂ catalyst, the lattice spacing of the nanoparticles (0.291 nm) was smaller than that of *t*-ZrO₂(101) (0.295 nm) (Figure 3(b)), which further demonstrates the formation of a solid solution structure. The lattice spacing corresponding to Cu, ZnO and ZrO₂ were all detected on the Cu/ZnO/ZrO₂-*x* catalysts (Figure 3(d), (f) and (h)). Notably, the lattice spacing of ZrO₂ in Cu/ZnO/ZrO₂-*x* was consistent with that in the ZnO-ZrO₂ solid solution. These results suggest that Cu introduction may partially disrupt the original solid solution structure of ZnO-ZrO₂, resulting in a coexisting structure composed of a solid solution and individual metal oxides. Furthermore, metal-oxide interfaces were observed between Cu and ZnO or ZnO-ZrO₂ solid solution. According to previous studies, such metal-oxide interfaces play a critical role in Cu-based methanol synthesis catalysts^[28–30]. Based on the above findings, it can be concluded that Cu introduction may partially alter the ZnO-ZrO₂ solid solution structure and generate distinct metal-oxide interfaces with both the ZnO-ZrO₂ solid solution and individual metal oxides, thereby enhancing the low-temperature methanol synthesis activity. Additionally, statistical analysis of Cu nanoparticle size reveals that the Cu particle sizes of Cu/ZnO/ZrO₂-0.3, Cu/ZnO/ZrO₂-0.7 and Cu/ZnO/ZrO₂-0.9 were 14.8, 18.7 and 27.1 nm, respectively. Consistent with XRD results, the Cu nanoparticle size is not correlated with the methanol synthesis activity of the Cu/ZnO/ZrO₂-*x* catalysts.

TEM images of the unreduced catalysts were utilized to investigate the morphological changes of all catalysts before and after reduction. Comparative analysis of Figure 3 and Figure 4 reveals that the ZnO-ZrO₂ solid solution exhibited minimal morphological change during the reduction process. In contrast, for the Cu/ZnO/ZrO₂-*x* catalysts, the unreduced Cu/ZnO/ZrO₂-*x* catalysts contained CuO nanoparticles with larger size than the Cu nanoparticles on their reduced counterparts. These results indicate that the reduction treatment mainly affects the structure of the Cu species, while exerting a limited influence upon the overall catalyst morphology.



(a), (b): ZnO-ZrO₂ solid solution; (c), (d): Cu/ZnO/ZrO₂-0.3; (e), (f): Cu/ZnO/ZrO₂-0.7; (g), (h): Cu/ZnO/ZrO₂-0.9.
 Insets in TEM images are the size distribution histogram of Cu nanoparticles.

Fig. 3 TEM (left) and HR-TEM (right) images of the reduced catalysts



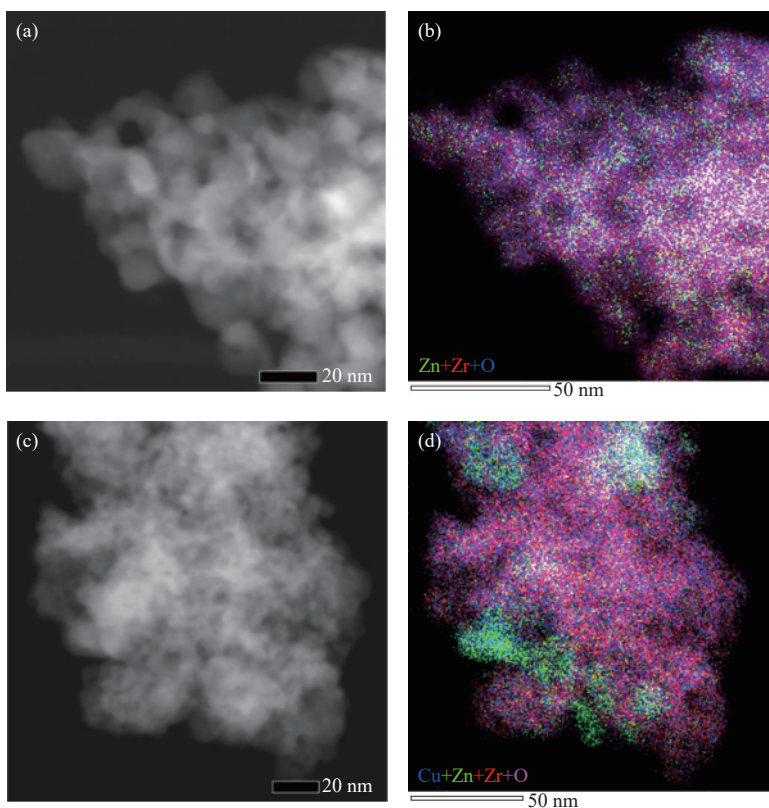
(a), (b) ZnO-ZrO₂ solid solution; (c), (d) Cu/ZnO/ZrO₂-0.3; (e), (f) Cu/ZnO/ZrO₂-0.7; (g), (h) Cu/ZnO/ZrO₂-0.9.

Fig. 4 TEM (left) and HR-TEM (right) images of the unreduced catalysts

To further elucidate the effect of Cu introduction on the microstructure of ZnO-ZrO₂ solid solution, HAADF-STEM images and corresponding EDX elemental mapping were conducted on the ZnO-ZrO₂ solid solution and Cu/ZnO/ZrO₂-0.7 catalysts. As shown in Figure 5(a), (b), the homogeneous distribution of Zn and Zr elements within the ZnO-ZrO₂ catalyst suggests the formation of solid solution structure. In contrast, for the Cu/ZnO/ZrO₂-0.7 catalyst, although the majority of Zn and Zr exhibited uniform dispersion (Figure 5(c), (d)), a small fraction of Zn elements was located in isolated regions. These results provide further evidence that Cu introduction led to the formation of a coexisting structure comprising solid

solution and individual metal oxides.

The surface basicity of catalysts was investigated by CO₂-TPD experiments. As presented in Figure 6, the desorption profiles were deconvoluted into three regions based on desorption temperature, wherein desorption peaks below 150 °C, between 150 and 550 °C, and above 550 °C were attributed to weak, medium, and strong basic sites, respectively^[16,31–32]. Based on previous reports, weak, medium, and strong basic sites originate from surface hydroxyl groups, metal-oxide interfacial sites, and low-coordinated O²⁻ species, respectively. Notably, among these basic sites, medium basic sites are generally recognized as the primary role for CO₂ activation in methanol synthesis^[16,31–33].



(a), (b): ZnO-ZrO₂ solid solution; (c), (d): Cu/ZnO/ZrO₂-0.7.

Fig. 5 HAADF-STEM images and EDX elemental mapping of reduced catalysts

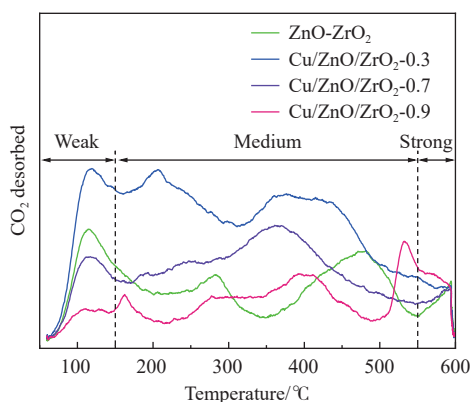


Fig. 6 CO₂-TPD profiles of the reduced catalysts

Quantitative results indicate that the amount of medium basic sites on ZnO-ZrO₂ solid solution, Cu/ZnO/ZrO₂-0.3, Cu/ZnO/ZrO₂-0.7 and Cu/ZnO/ZrO₂-0.9 were quantified at 0.76, 0.78, 0.98 and 0.72 $\mu\text{mol/g}$, respectively. Consequently, introducing Cu with appropriate content can effectively promote the formation of medium basic sites on ZnO-ZrO₂ solid solution, thereby enhancing CO₂ adsorption and activation, and thus improving methanol synthesis activity.

2.3 Mechanism studies

To further elucidate the promotional effect of Cu on the

ZnO-ZrO₂ solid solution, *in situ* DRIFTS experiments were carried out to investigate the reaction mechanism over all catalysts. Figure 7 displays the *in situ* DRIFTS spectra of CO₂ hydrogenation at 250 °C over the different samples. After 1 min of reaction, characteristic bands corresponding to bicarbonate (*HCO₃), carbonate (*CO₃), formate (*HCOO), and methoxy (*CH₃O) were detected on all catalysts. The corresponding band assignments are summarized in Table 2^[17,34–42]. The presence of *HCOO and *CH₃O species indicates that methanol synthesis proceeds via a formate pathway on all catalysts^[13,26,43]. Analysis of the evolution of characteristic band intensities reveals that the intensities of surface intermediates over the ZnO-ZrO₂ solid solution reached a steady after 5 min of reaction. In contrast, for both Cu/ZnO/ZrO₂-0.3 and Cu/ZnO/ZrO₂-0.9, the intensities of the intermediates initially increased and subsequently decreased as the reaction proceeded. Notably, a continuous decrease in the intensity of intermediates was observed over the Cu/ZnO/ZrO₂-0.7 catalyst throughout the reaction, indicating the most efficient conversion of surface intermediates. Similar findings by Liu et al.^[35] demonstrated that the enhanced methanol synthesis activity of inverse ZrO₂/Cu catalysts was closely associated with the accelerated consumption of *HCOO species. Therefore, the optimal conversion of key intermediates on Cu/ZnO/ZrO₂-0.7 contributes to its enhanced methanol synthesis activity.

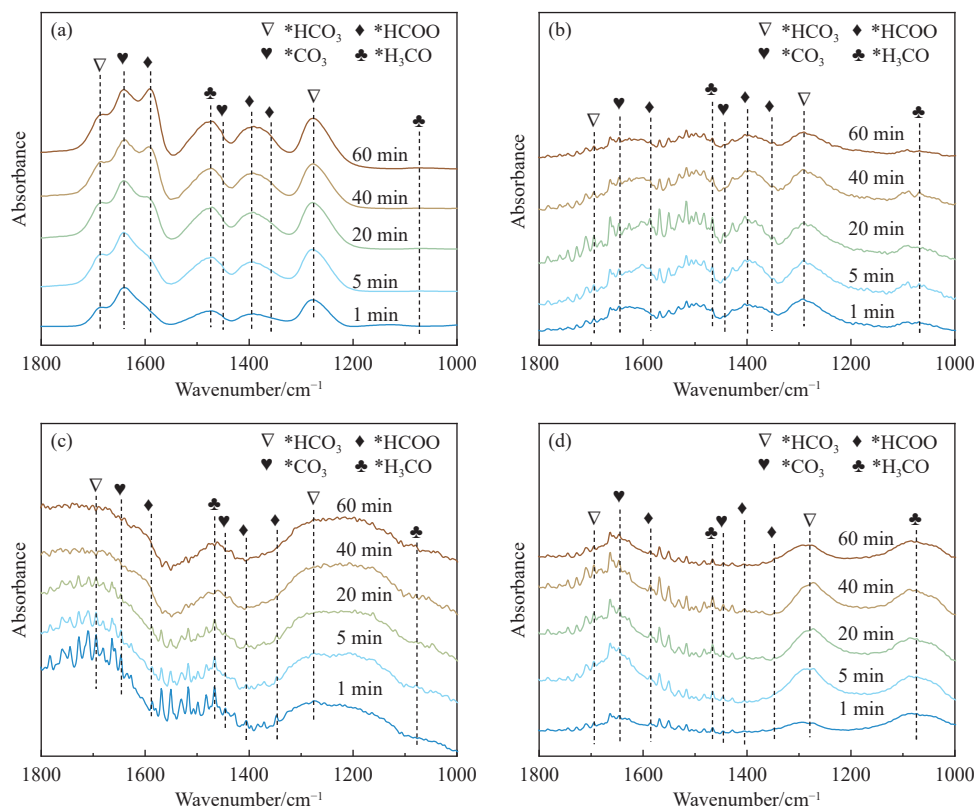


Fig. 7 *In situ* DRIFTS spectra of CO₂ hydrogenation reaction over ZnO-ZrO₂ (a), Cu/ZnO/ZrO₂-0.3 (b), Cu/ZnO/ZrO₂-0.7 (c) and Cu/ZnO/ZrO₂-0.9 (d) under 250 °C

Table 2 The assignment of DRIFTS bands for various reaction intermediate species

Surface specie	Wavenumber/cm	References
Bicarbonate (*HCO ₃)	1690	[34–35]
	1275	
Carbonate (*CO ₃)	1645	[17,36–37]
	1450	
	1398	
Formate (*HCOO)	1585	[38–40]
	1398	
	1350	
Methoxy (*CH ₃ O)	1472	[41–42]
	1073	

2.4 Stability test for Cu/ZnO/ZrO₂-0.7

A 30 h stability test was conducted on the optimal Cu/ZnO/ZrO₂-0.7 catalyst under the reaction conditions of 250 °C and 3.0 MPa. As illustrated in Figure 8, the catalyst exhibited excellent stability, wherein CO₂ conversion, methanol selectivity, and STY_{MeOH} remained stable at 7.4% ± 0.4%, 52.9% ± 1.5%, and 163.2 ± 5.5 g/(kg·h), respectively. Such outstanding stability of the Cu/ZnO/ZrO₂-0.7 catalyst would contribute to its promise for industrial application in CO₂ hydrogenation to methanol.

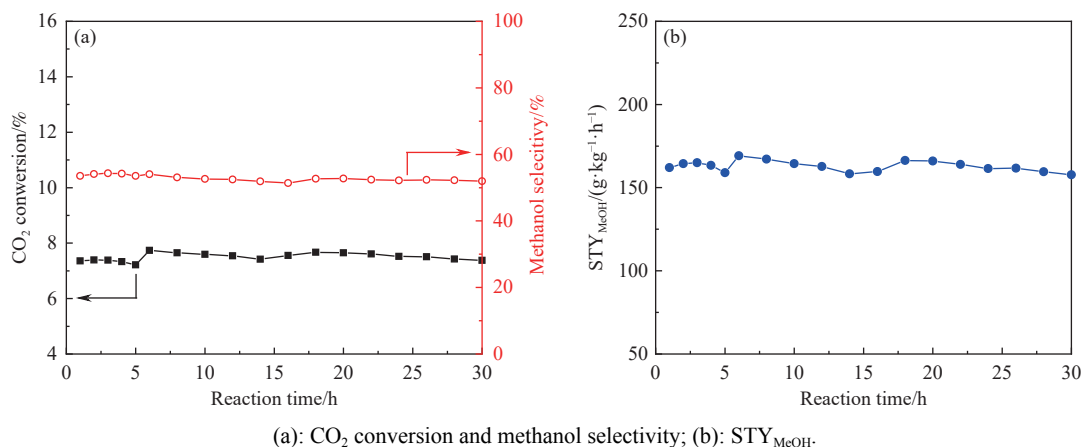


Fig. 8 The stability test of the Cu/ZnO/ZrO₂-0.7 catalyst at 250 °C and 3.0 MPa for 30 h

3 Conclusion

The ZnO-ZrO₂ solid solution and a series of Cu/ZnO/ZrO_{2-x} catalysts with different Cu contents were prepared via a co-precipitation method for CO₂ hydrogenation to methanol. Catalytic evaluations demonstrated that Cu introduction significantly enhanced the methanol synthesis activity of ZnO-ZrO₂ solid solution catalyst at lower temperatures (220 and 250 °C). Specifically, the Cu/ZnO/ZrO₂-0.7 catalyst exhibited the optimal methanol production rate, achieving an STY_{MeOH} of 162.7 g/(kg·h) under conditions of 250 °C and 3.0 MPa, which was 6.6 times higher than that of the ZnO-ZrO₂ solid solution catalyst (24.8 g/(kg·h)). Structural characterizations revealed that the introduction of Cu induced the formation of a coexisting structure composed of a solid solution and individual metal oxides, accompanied by an enrichment of medium basic sites. *In situ* DRIFTS studies further confirmed the facilitated conversion of reaction intermediates on Cu-promoted ZnO-ZrO₂ catalysts. Furthermore, the Cu/ZnO/ZrO₂-0.7 catalyst demonstrated outstanding stability at 250 °C over 30 h of time-on-stream. This work elucidates the promotional effect of Cu content on ZnO-ZrO₂ solid solution catalysts and provides significant guidance for the rational design of high-efficiency solid solution catalysts for low-temperature methanol synthesis.

Declaration of Competing Interest

The authors declare no conflict of interest.

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铜引入对锌锆固溶体催化二氧化碳加氢制甲醇的促进作用研究

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摘 要: 引入适当含量的铜(Cu)可有效提升锌锆(ZnO-ZrO₂)固溶体催化剂的 CO₂ 加氢制甲醇催化性能, 但对 Cu 含量的系统性研究仍相对缺乏。本研究采用共沉淀法制备了 ZnO-ZrO₂ 固溶体和不同 Cu 含量的 Cu/ZnO/ZrO₂-x (x = 0.3、0.7 和 0.9, 表示 Cu/(Cu+Zn+Zr) 物质的量比) 催化剂用于 CO₂ 加氢制甲醇。Cu/ZnO/ZrO₂-0.7 表现出最佳的催化性能, 在 250 °C 下其甲醇时空收率(162.7 g/(kg·h))是 ZnO-ZrO₂ 固溶体(24.8 g/(kg·h))的 6.6 倍。结构表征表明, 适当含量 Cu 的引入使得原有固溶体结构转变为固溶体与其单一金属氧化物共存的结构, 且促进中等强度碱性位点的形成。原位漫反射傅里叶变换红外光谱结果显示, Cu 的引入更有利于反应中间物种的转化。该工作系统研究了 Cu 含量对 ZnO-ZrO₂ 固溶体甲醇合成性能的影响, 阐明了 Cu 的促进作用机制。

关键词: ZnO-ZrO₂; Cu; CO₂; CH₃OH; 界面

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