

The role of copper valence states in CuZnAl catalysts for CO₂-to-methanol conversion

QIU Zhengpu¹, XU Yunzhao², WANG Peng^{2,3,*}, TAO Xiaoxia², ZHANG Huimin¹, CHEN Yang², LIU Yi¹, YANG Hua⁴, CAO Fenghai², FU Yajie², WU Lizhi², TANG Yu², XU Xiaoying^{1,*}, TAN Li^{2,*}

¹ National Institute of Clean-and-Low-Carbon Energy, Beijing 102211, China;

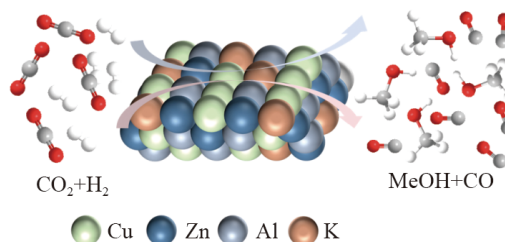
² College of Chemistry, Fuzhou University, Fuzhou 350108, China;

³ School of Future Membrane Technology, Fuzhou University, Fuzhou 350108, China;

⁴ Chongqing Vocational Institute of Safety Technology, Chongqing 404020, China

Abstract: CuZnAl (CZA) is a classic industrial catalyst widely used for the synthesis of methanol from syngas, but its catalytic performance is not optimal for the hydrogenation of CO₂ to methanol. Meanwhile, understanding the catalytic mechanism of Cu species in the CZA catalyst remains a great challenge. In this study, we systematically investigated the valence state change of active Cu species in CZA catalyst and their influence on catalytic performance by modifying the catalysts with varying amounts of electron donor K, thus identifying the catalytic function of Cu species with different valence states. H₂-TPR, XPS and HR-TEM characterizations reveal that the highly dispersed K species supported on CZA catalysts will inhibit the reduction of CuO, resulting in a small amount of Cu₂O active species being produced under reaction conditions thus causing a decrease in catalytic activity. Furthermore, XRD and Cu LMM spectra show that the proportion of Cu⁰ in K-modified CZA catalysts increases with K loading, but a higher proportion of Cu⁰ species on the surface obviously promotes the reverse water gas shift (RWGS) reaction. According to the results of *in situ* infrared spectroscopy, CZA catalyst follows the reaction pathway mediated by HCOO* in the hydrogenation of CO₂ to methanol.

Key words: CO₂ hydrogenation; CuZnAl catalysts; methanol; active species; electronic promoter



The growing carbon dioxide (CO₂) emissions and increasing reliance on fossil fuels highlight critical challenges in today's energy landscape, necessitating a shift toward decarbonization technologies and the development of renewable energy^[1]. The catalytic conversion of CO₂ into methanol represents a cutting-edge sustainable technology with significant implications for reducing carbon emissions^[2]. This catalytic process utilizes catalysts to facilitate the transformation of CO₂ and green hydrogen into methanol. As a crucial chemical building block, methanol serves as a fundamental feedstock for numerous fine chemicals, fuel additives, and chemical raw materials^[3]. Additionally, methanol is regarded as a potential energy carrier due to its high hydrogen storage density and

transportation safety. Therefore, catalytic processes that utilize CO₂ to produce methanol demonstrate the substantial potential in the energy and environmental sectors, offering a viable pathway toward achieving carbon neutrality.

Cu-based catalysts have been extensively studied for methanol synthesis in recent decades^[3–4]. Among the reported non-noble metal catalysts for CO₂ hydrogenation to methanol, they are highly favored by researchers due to their high activity, good selectivity, and low cost^[5–9]. In these catalysts, Cu serves as the main active component, while oxides such as ZnO, ZrO₂, Al₂O₃, CeO₂, SiO₂ and TiO₂ are used as supports to disperse and stabilize the active species^[10–14]. Currently, industrial methanol synthesis primarily employs the classic CuZnAl (CZA) catalyst,

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* Corresponding author. E-mail: p_wang@fzu.edu.cn, xiaoying.xu.d@chnenergy.com.cn, tan@fzu.edu.cn.

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typically composed of 60% Cu, 30% ZnO and 10% Al_2O_3 ^[15]. Although CZA catalysts are used in industrial methanol production from syngas, their catalytic performance in CO_2 hydrogenation to methanol is not satisfactory. Owing to the high stability and chemical inertness of CO_2 , CO_2 conversion remains low at reaction temperatures of 220–280 °C. While increasing the temperature can enhance conversion, it also promotes the reverse water-gas shift (RWGS) side reaction, leading to substantial CO formation and reduced methanol selectivity. Moreover, Cu particles tend to sinter at high temperatures, and the H_2O by-product generated during the reaction can promote the sintering of ZnO and oxidation of active Cu species to CuO, resulting in severe deactivation of the CZA catalyst.

Therefore, considerable research has been devoted to unravel the individual roles of Cu, Zn and Al components and the underlying catalytic mechanisms on CZA catalysts^[16], aiming to design and develop highly efficient Cu-based catalysts with improved performance, including activity, selectivity, water resistance, and stability. Li et al.^[17] prepared Cu-ZnO/ Al_2O_3 catalysts *via* the co-precipitation method, followed by hydrothermal treatment at varying durations and temperatures. They found that hydrothermal treatment caused the agglomeration of Cu and ZnO particles, particularly metallic Cu, leading to a consequent reduction in Cu surface area and catalytic activity. Zhang et al.^[18] synthesized Cu/ZnO/ Al_2O_3 catalysts with different Cu-ZnO interface densities by tuning the chemical composition of zinc-malachite precursors. The results showed that when zinc substitution reached 27.13%, the obtained catalyst exhibited uniformly dispersed Cu and ZnO species with a small Cu crystallite size, which promoted the formation of abundant Cu-ZnO interfaces and significantly enhanced catalytic performance in methanol synthesis. Huang et al.^[19] found that doping Er into the ZnO lattice reduced its particle size, increased the Cu-ZnO interface, and induced strong electronic metal-support interaction between Cu and ZnO. Zhang et al.^[20] synthesized a series of ZnO_{1-x} /Cu catalysts *via* the ball milling method to achieve the strong interfacial interaction between ZnO_{1-x} and Cu, thereby allowing the controllable generation of numerous oxygen vacancies. The ZnO_{1-x} /Cu-100 catalyst prepared under optimal conditions with more oxygen vacancies, exhibited the best performance in CO_2 hydrogenation. Zhang et al.^[21] introduced highly dispersed La species through a one-pot synthesis method, achieving a methanol space-time yield as high as 814.9 g/(kg·h), significantly outperforming the CZA catalyst. The incorporated LaO_x helped disperse and stabilize Cu^+/Cu^0 active sites, strengthened the interaction between Cu active sites and the support, and effectively improved the sintering resistance of Cu nanoparticles. These studies collectively indicate that the active structures of Cu-based catalysts have not yet been fully elucidated.

Herein, we systematically investigate the structure-activity relationship of Cu species with different valence states in CZA catalysts for CO_2 hydrogenation to methanol.

By modifying the catalyst with varying amounts of the alkali metal K, the valence states of Cu species in CZA were effectively tuned. It was revealed that highly dispersed K species on the CZA surface suppress the reducibility of CuO, resulting in fewer Cu^+ active species under reaction conditions and consequently a decline in catalytic activity. Meanwhile, the incorporation of K promotes the dispersion of Cu^0 species, indicating a strengthened interaction between Cu^0 and ZnO. However, the increased abundance of Cu^0 primarily promotes the RWGS side reaction, thereby suppressing methanol formation. *In situ* DRIFTS results further confirm that methanol synthesis proceed *via* a HCOO^* -mediated pathway over CZA catalyst.

1 Experimental

1.1 Chemicals and materials

The chemicals used in this work included: copper(II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, AR), aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, AR), and sodium carbonate anhydrous (Na_2CO_3 , AR), all purchased from Macklin Reagent Co.; zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, AR) and potassium carbonate (K_2CO_3 , AR), which were obtained from Aladdin Reagent Co.

1.2 Catalyst preparation

Synthesis of the CZA catalyst. First, 5.03 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 2.53 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.26 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were weighed and dissolved in 100 mL of deionized water to form an aqueous nitrate solution. Subsequently, 4.77 g of anhydrous sodium carbonate was weighed and dissolved in 100 mL of deionized water to prepare a 0.45 mol/L sodium carbonate solution. Both solutions were simultaneously added dropwise *via* peristaltic pumps with the same flow rate into a beaker containing 100 mL of deionized water. The coprecipitation was carried out at 80 °C under constant stirring in a water bath. Upon completion of the titration, the mixture was aged for 2 h. After cooling to room temperature, the product was subjected to suction filtration, followed by washing with deionized water until the filtrate was neutral. The solid was then dried overnight in an oven at 80 °C, and finally calcined in a muffle furnace at 350 °C for 4 h to obtain the CZA catalyst. ICP-OES analysis of the synthesized CZA sample determined the actual mass percentages of Cu, Zn, and Al to be 70.5%, 28.6% and 0.9%, respectively, closely matching the theoretically calculated values.

A series of K-modified CZA catalysts were synthesized *via* the incipient wetness impregnation method. The synthesis procedure was as follows: first, K_2CO_3 was dissolved in 1.3 mL of deionized water and the resulting solution was then added dropwise using a pipette onto 1 g of the CZA catalyst support under constant stirring with a glass rod. After the addition of the solution, the mixture was

aged at room temperature for 2 h. Subsequently, the sample was dried in an oven at 80 °C, yielding the $x\text{K/CZA}$ ($x = 0.1\%$, 0.5% , 1%) catalysts where x represents the nominal mass percentage of K loaded on the CZA support.

1.3 Catalyst characterization

X-ray diffraction (XRD) measurements were performed on a Rigaku Smart Lab SE diffractometer using Cu $K\alpha$ radiation ($\lambda = 0.15406$ nm). The data were collected in the 2θ range of 5° to 90° with a scanning rate of $5^\circ/\text{min}$, operating at 40 kV and 40 mA.

N_2 physisorption analyses were conducted on a Micromeritics ASAP 2020PLUS HD88 instrument at -196°C to determine the specific surface area and pore volume. Before analysis, the samples were degassed under vacuum at 300°C for 6 h.

Inductively coupled plasma optical emission spectrometry (ICP-OES) was carried out on a Thermo Scientific iCAP 7000 spectrometer to determine the elemental composition.

H_2 temperature-programmed reduction (H_2 -TPR) experiments were performed on a Micromeritics AutoChem II chemisorption analyzer. Approximately 0.1 g of catalyst was pretreated in a He stream at 300°C for 2 h. After cooling to room temperature, the TPR profile was recorded under a $10\% \text{H}_2/\text{Ar}$ flow.

CO_2 temperature-programmed desorption (CO_2 -TPD) was conducted using the same Micromeritics AutoChem II analyzer. About 0.1 g of catalyst was first pretreated in a $10\% \text{H}_2/\text{Ar}$ atmosphere at 230°C for 2 h. Subsequently, the CO_2 -TPD profile was obtained using a $10\% \text{CO}_2/\text{Ar}$ stream.

Transmission electron microscopy (TEM) images were acquired on a Thermo Scientific Talos F200S G2 microscope. A small amount of catalyst was ultrasonically dispersed in ethanol, and a drop of the suspension was deposited onto a copper grid for observation.

In situ diffuse reflectance infrared Fourier transform spectroscopy (*in situ* DRIFTS) studies were performed on a Thermo Scientific Nicolet iS50 spectrometer equipped with an MCT detector and a Harrick reaction cell. The catalyst sample was first pretreated in pure H_2 at 230°C for 2 h. After switching to Ar and cooling to room temperature, a background spectrum was collected. The sample was then exposed to a gas mixture of $5\% \text{CO}_2/15\% \text{H}_2/80\% \text{Ar}$ at 3 MPa and a flow rate of 20 mL/min at 230°C , and the spectra were recorded.

X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo Scientific ESCALAB 250 Xi spectrometer using Al $K\alpha$ monochromatic radiation ($h\nu = 1486.6 \text{ eV}$). All binding energies were calibrated relative to the C 1s peak at 284.8 eV .

1.4 Catalytic performance evaluation

The catalytic performance was evaluated through online

analysis in a fixed-bed reactor coupled with a Shimadzu GC-2014 gas chromatograph. A mixture of 0.2 g of catalyst particles (40–60 mesh) and 0.8 g of quartz sand (30–40 mesh) was loaded into a quartz tube and placed in the isothermal zone of the reactor. The catalyst was first pretreated in pure H_2 at 230°C for 2 h. Subsequently, a feed gas mixture of $24\% \text{CO}_2$, $72\% \text{H}_2$ and $4\% \text{Ar}$ was introduced, and the reaction was carried out at 230°C and 4 MPa.

Product analysis was performed using the gas chromatograph equipped with both a flame ionization detector (FID) and a thermal conductivity detector (TCD). The analysis utilized a combination of four chromatographic columns—MC-1 (PONA $0.25 \text{ mm} \times 50 \text{ m} \times 0.5 \mu\text{m}$), PC-1 (P-N 80/100 mesh $3.2 \times 2.1 \text{ mm} \times 1.0 \text{ m}$), MC-2 (P-N 80/100 mesh $3.2 \times 2.1 \text{ mm} \times 1.0 \text{ m}$), and MC-3 (MS-13X 80/100 mesh $3.2 \times 2.1 \text{ mm} \times 3.0 \text{ m}$)—configured in series and/or parallel.

The catalytic activity was assessed in terms of CO_2 conversion, product selectivity, and methanol space-time yield (STY). The CO_2 conversion was calculated using the following equation:

$$C_{\text{CO}_2} (\%) = \frac{X_{\text{CO}_2, \text{in}} - X_{\text{CO}_2, \text{out}}}{X_{\text{CO}_2, \text{in}}} \times 100\% \quad (1)$$

In the equation, $X_{\text{CO}_2, \text{in}}$ represents the mole fraction of CO_2 in the feed gas, and $X_{\text{CO}_2, \text{out}}$ denotes the mole fraction of CO_2 in the outlet gas mixture.

The product selectivity is calculated as follows:

$$s (\%) = \frac{R_i \times f_{i,m}}{\sum_i R_i \times f_{i,m}} \times 100\% \quad (2)$$

where R_i is the peak area of the product in the chromatogram, and $f_{i,m}$ is the mass correction factor. The formula for calculating the methanol space-time yield (STY) is:

$$\text{STY} (\text{g}_{\text{MeOH}} \cdot \text{kg}_{\text{cat}}^{-1} \cdot \text{h}^{-1}) = \frac{F_{\text{CO}_2, \text{in}} \times C_{\text{CO}_2} \times s_{\text{MeOH}} \times M_{\text{MeOH}}}{W_{\text{cat}}} \quad (3)$$

where $F_{\text{CO}_2, \text{in}}$ is the molar flow rate of CO_2 in the feed gas (mol/h), M_{MeOH} is the molecular weight of methanol (32 g/mol), and W_{cat} is the mass of the catalyst (kg).

2 Results and discussion

2.1 Analysis of the active structure of the catalysts

The XRD patterns of the unmodified and K-modified CZA catalysts before and after reaction are presented in Figure 1. The fresh and K-modified CZA catalysts both exhibit diffraction peaks of CuO at 35.5° and 38.7° , as well as a diffraction peak of the ZnO(100) crystal plane at 31.8° , indicating a mixed oxide phase structure. However, diffraction peaks corresponding to an Al_2O_3 phase were not detected, suggesting that Al_2O_3 is likely present in a highly

dispersed or amorphous state within the synthesized CZA catalysts. Furthermore, after the incorporation of alkali metal K, diffraction peaks that are characteristic of a hydrotalcite structure appear at 11.8° and 23.6° ^[22–24]. This is attributed to localized structural reconstruction during the preparation process induced by the relatively high pH of the solution, where the modified K species exist in the form of hydrotalcite-like particles. As shown in Figure 1(b), the hydrotalcite structure disappears in the spent K-modified CZA catalyst, indicating a transformation of the surface hydrotalcite phase under the reaction conditions at 230°C . Notably, the intensity of the diffraction peak at 38.7° (corresponding to the CuO crystalline phase) in the spent catalysts (both CZA and K-modified CZA), increases with increasing K content. Correspondingly, the spent unmodified CZA catalyst shows the strongest diffraction peaks at 43.3° and 50.3° , which are assigned to the metallic Cu⁰ species formed by the reduction of CuO. Moreover, the intensity of the diffraction peaks corresponding to the Cu⁰ phase in the series of K-modified CZA catalysts gradually decreases as the K loading increases and completely disappears when the K content up to 1%. The crystal sizes of different phases, calculated from the XRD peaks using the Scherrer equation, are listed in Table 1. For the fresh catalysts, the introduction of the K modifier did not significantly alter the crystal sizes of ZnO and CuO. However, for the spent catalysts, the crystal sizes of both ZnO and CuO increased noticeably, suggesting particle agglomeration occurred during the reaction. Concurrently, relatively large Cu⁰ crystallites (approximately 16 nm)

appeared in the spent catalysts. Overall, the crystal sizes in the K-modified CZA catalysts are almost unchanged compared to the parent CZA, indicating that this series of catalysts possesses comparable particle dimensions. This allows for a subsequent comparative analysis of their electronic structures using H₂-TPR and XPS techniques.

The reduction properties of the parent CZA and K-modified CZA catalysts were investigated by H₂-TPR, and the results are shown in Figure 2 and Table 2. The reduction peaks observed in the temperature range of $100\text{--}500^\circ\text{C}$ are attributed to the reduction of CuO species. The CZA catalyst exhibits three main reduction peaks (α , β and γ). They are assigned to the reduction of highly dispersed surface CuO, bulk CuO particles, and bulk-phase CuO, respectively. Notably, these three reduction peaks shift to higher temperatures in the K-modified CZA catalysts, indicating that the introduction of K inhibits the reduction of CuO species. This observation is consistent with the results reported by Xu et al.^[25] for a Cs-modified CuFeZn catalyst. Although the overall reduction degree is similar for all four catalysts as shown in Table 2, the main reduction peak of the 1K/CZA catalyst shifts most significantly to a higher temperature. Considering the reduction temperature and the actual reaction temperature (230°C), it can be inferred that the amount of CuO reduced during the reaction is the lowest for this catalyst. Therefore, the H₂-TPR results indicate that the extent of reduction of CuO species under reaction conditions is lower in the K-modified CZA catalysts compared to the parent CZA catalyst.

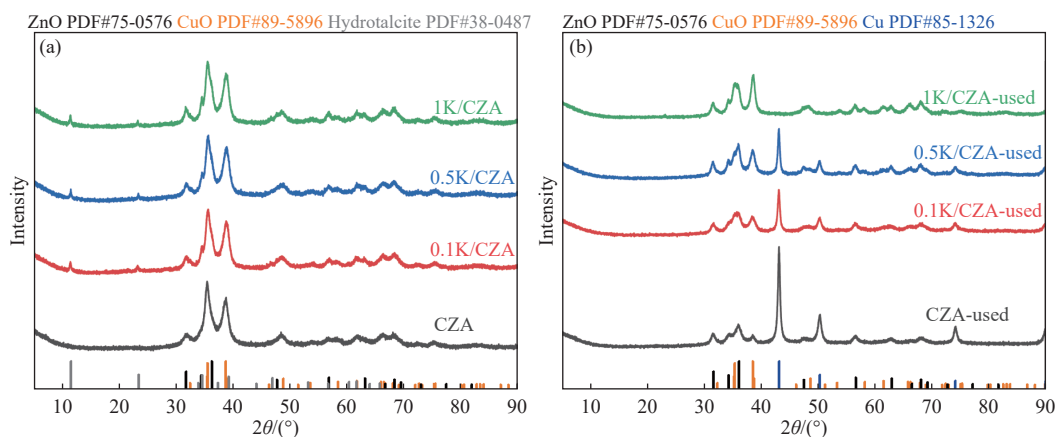


Fig. 1 The XRD patterns of the fresh (a) and used (b) CZA and K-doped CZA catalysts

Table 1 The size estimation of crystal particles on the catalysts before and after reaction derived from XRD patterns according to the Scherrer formula

Sample	Before reaction		After reaction		
	ZnO size/nm	CuO size/nm	ZnO size/nm	CuO size/nm	Cu size/nm
CZA	4.2	6.2	6.6	10.9	16
0.1K/CZA	4.7	6.3	7.7	7.5	16.5
0.5K/CZA	4.7	6.0	8.0	8.4	18.2
1K/CZA	5.8	6.4	7.5	8.9	—

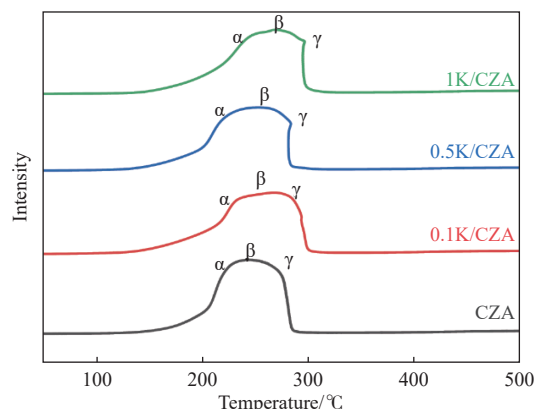


Fig. 2 H₂-TPR profiles of the series xK/CZA catalysts

Table 2 The results of H₂-TPR peak area of samples

Sample	H ₂ consumption/(mmol·g ⁻¹)
CZA	18.66
0.1K/CZA	18.70
0.5K/CZA	18.21
1K/CZA	18.26

The spent catalysts were characterized by XPS to further investigate the electronic states of the surface metal species

with the results shown in Figure 3 and Table 3. Figure 3(a) displays the Cu 2*p* spectra of the spent catalysts. All catalysts exhibit satellite peaks in the ranges of 940–945 and 960–965 eV, which are characteristic of Cu²⁺ species, indicating that a portion of CuO remained unreduced. For the CZA sample, the characteristic peaks of Cu 2*p*_{3/2} and Cu 2*p*_{1/2} appear at 933.1 and 952.9 eV, respectively, which are attributed to Cu⁺/Cu⁰ species^[26], suggesting the coexistence of multiple copper valence states in the catalyst. Compared with CZA, the Cu 2*p* characteristic peaks of the 0.1K/CZA and 1K/CZA catalysts shift toward the lower binding energies, indicating alterations in their electronic structures. Concurrently, the proportion of the fitted peaks corresponding to Cu⁺/Cu⁰ species progressively decreases with increasing K content, implying that the deposited K species reduces the exposure of reduced Cu species. Given the difficulty in distinguishing Cu⁺ from Cu⁰ species based solely on Cu 2*p* spectra, we therefore employed Cu LMM Auger spectra for further analysis (Figure 3(b)). The Auger peaks of the spent CZA sample at kinetic energies of 916.7, 917.5 and 918.8 eV are assigned to Cu⁺, Cu²⁺ and Cu⁰ species, respectively^[27]. Semi-quantitative analysis reveals that the surface Cu species of the spent CZA catalyst consist of 42.4% Cu⁺, 24.9% Cu²⁺ (=100%–42.4%–32.7%) and 32.7% Cu⁰.

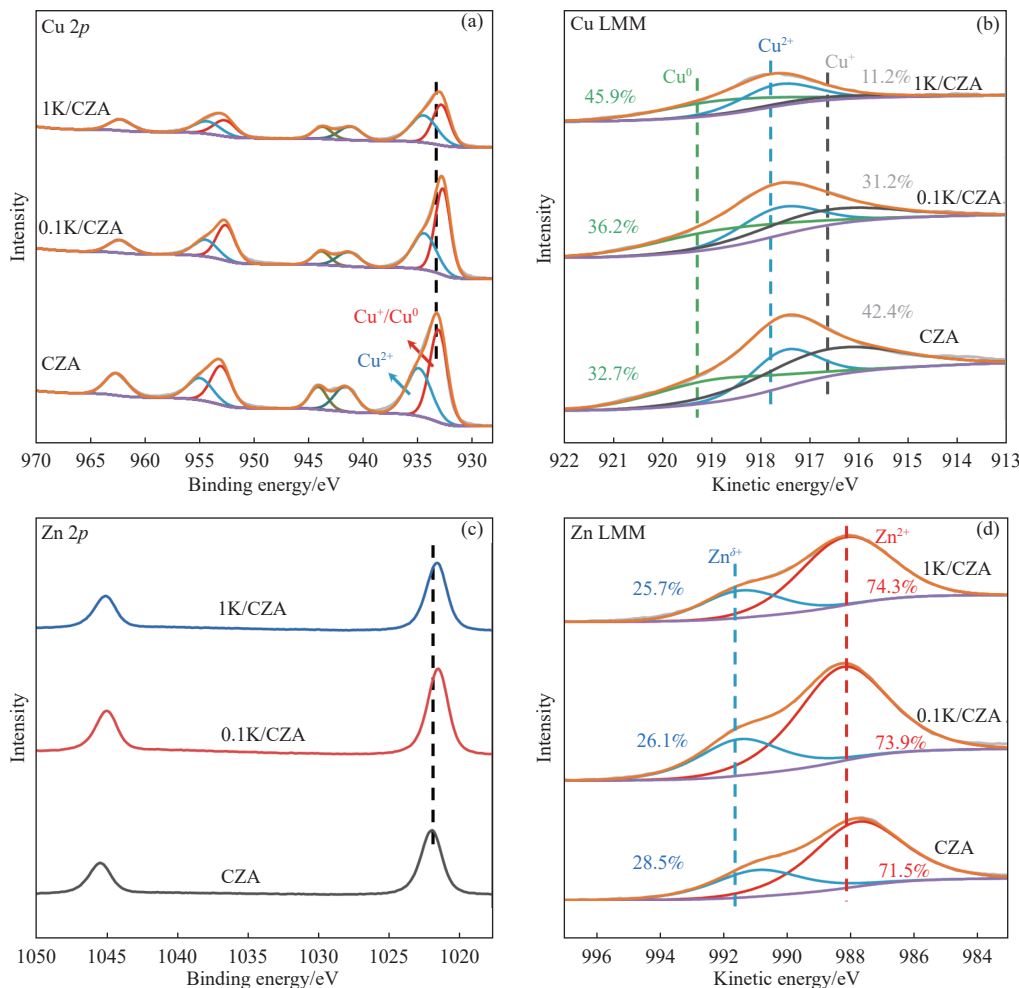


Fig. 3 XPS spectra of (a) Cu 2*p*, (b) Cu LMM, (c) Zn 2*p* and (d) Zn LMM in the series of the used xK/CZA catalysts

Table 3 The semi-quantitative results of the surface elements of the catalysts fitted by XPS

Sample	Binding energy/eV										
	Cu 2p _{3/2}	Cu 2p _{1/2}	Cu ⁺	Cu ²⁺	Cu ⁰	Cu ⁺ /(Cu ⁺ +Cu ⁰)	Zn 2p _{3/2}	Zn 2p _{1/2}	Zn ²⁺	Zn ^{δ+}	Zn ^{δ+} /Zn ²⁺
CZA	933.1/934.9	952.9/954.8	916.7	917.5	918.8	1.30	1022.3	1045.4	987.7	990.9	0.29
0.1K/CZA	932.7/934.4	952.5/954.3	916.7	917.6	918.9	0.86	1021.9	1044.9	988.2	991.4	0.26
1K/CZA	932.8/934.4	952.6/954.2	916.7	917.6	918.8	0.24	1022.0	1045.0	988.1	991.4	0.26

For the 0.1K/CZA catalyst, the surface Cu species also appear in a mixed state, comprising 31.2% Cu⁺, 32.6% Cu²⁺ and 36.2% Cu⁰. When the K content reaches 1%, the surface Cu species of the sample consist of 11.2% Cu⁺, 42.9% Cu²⁺ and 45.9% Cu⁰. Evidently, the proportion of Cu²⁺ species rises with the increase of K content, confirming that K inhibits the reduction of CuO, which is consistent with the H₂-TPR results. Although the incorporation of K helps increase the proportion of Cu⁰ and modulates the Cu⁺/Cu⁰ ratio, it simultaneously reduces the overall content of the reduced Cu species (Cu⁰ and Cu⁺), thereby weakening the hydrogenation capability of the catalyst and ultimately leading to a reduced catalytic activity.

Figure 3(c) shows the Zn 2p spectra of the spent catalysts. The characteristic peaks for Zn 2p_{3/2} and 2p_{1/2} of the CZA catalyst are located at 1022.3 and 1045.4 eV, respectively^[28]. Notably, the Zn 2p peaks of the 0.1K/CZA and 1K/CZA samples shift toward the lower binding energies with K incorporation, following a trend similar to that observed for the Cu 2p peaks. Since the Zn 2p spectra can not distinguish between Zn²⁺ and Zn^{δ+} (0 < δ < 2) species, the Zn LMM Auger spectra were used to identify changes in the zinc valence states. As shown in Figure 3(d), the CZA catalyst exhibits the characteristic peaks at kinetic energies of 987.7 and 990.9 eV that are assigned to Zn²⁺ and Zn^{δ+} species, respectively^[29]. Moreover, the Auger peaks of the K-modified CZA catalysts shift toward the higher kinetic energies. The presence of Zn^{δ+} species indicates a strong interaction between Cu and Zn species, which drives the partial reduction and migration of ZnO, resulting in the formation of defective ZnO_x species^[30]. Consequently, the addition of 1% K decreases the proportion of Zn^{δ+} species from 28.5% to 25.7%, suggesting that the K modifier influences the formation of the active structure.

2.2 Assessment of catalytic performance

The catalytic performance of the CZA catalyst and CZA catalysts with different K loadings was evaluated under identical reaction conditions, with the results presented in Figure 4. The unmodified CZA catalyst exhibits the CO₂ conversion of 16.5% and the methanol selectivity of 61.7%. For the K-modified CZA catalysts, both the CO₂ conversion and methanol selectivity significantly decrease with increasing K contents, accompanied by an enhanced RWGS side reaction. When the K loading reaches 1%, the CO₂ conversion and methanol selectivity drop to 5.6% and 21.4%, respectively. These results demonstrate that the K

modification significantly alters the active structure of the CZA catalyst.

2.3 Analysis of pore structure and electron imaging of the catalysts

Figure 5 shows the N₂ adsorption-desorption isotherms of the catalysts. All catalysts exhibit type IV isotherms, indicating a mesoporous structure. The presence of an H3-type hysteresis loop in the isotherms suggests the existence of slit-like, irregular pores within the catalysts. Furthermore, the introduction of K species leads to a noticeable reduction in the hysteresis loop, which may be attributed to the partial pore blockage caused by the structural changes of the catalysts. The specific surface areas of the CZA, 0.1K/CZA, 0.5K/CZA and 1K/CZA catalysts were estimated to be 54, 48, 47 and 43 m²/g, respectively.

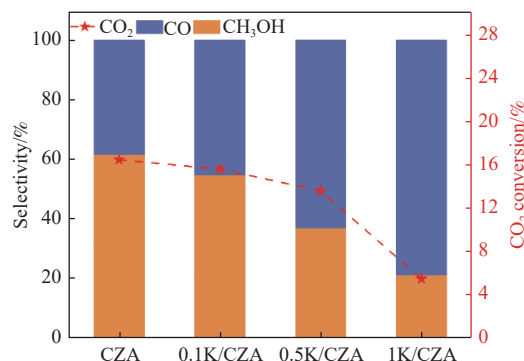


Fig. 4 CO₂ conversion and products selectivity of CZA catalysts with different K loadings

Reaction condition: 0.2 g, 4 MPa, 230 °C, H₂/CO₂=3, WHSV=13500 mL/(g·h).

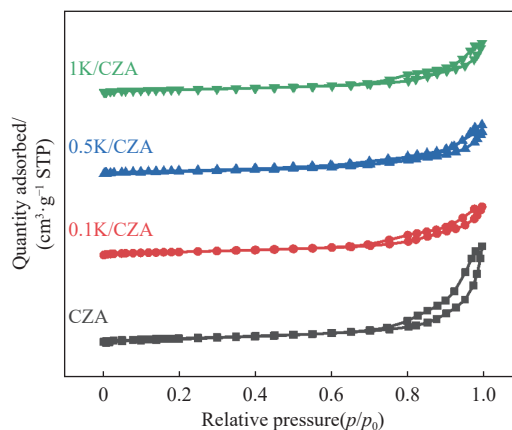


Fig. 5 The N₂ adsorption-desorption isotherms curves of the series of xK/CZA catalysts

These results indicate that the addition of K has only a marginal effect on the specific surface area of the catalysts. Therefore, the primary role of K modifier lies in its influence on the active structure rather than on altering the textural properties.

The morphological structures of the spent catalysts were analyzed by TEM imaging. As shown in Figure 6(a), the spent CZA catalyst exhibits lattice fringes with spacings of 2.5, 2.4, 2.3 and 2.1 Å, corresponding to the (101) plane of ZnO, the (111) plane of Cu₂O, the (200) plane of CuO, and the (111) plane of metallic Cu, respectively. This suggests that the Cu species in the catalyst were reduced by H₂ during the reaction, resulting in the coexistence of multiple valence states. Notably, Cu⁰ species are mainly dispersed adjacent to ZnO, forming Cu-ZnO interfaces^[18]. This, combined with the elemental mapping showing a uniform distribution of Cu, Zn and Al, promotes the formation of the

abundant Cu-ZnO_x structures^[21,30]. This phenomenon can be attributed to the strong interaction between Cu and Zn species. With the incorporation of 0.1% K, distinct Cu species in different valence states and their interfaces with ZnO can still be clearly observed in Figure 6(b). The elemental mapping confirms the highly dispersed distribution of the K species. For the 1K/CZA catalyst, only Cu₂O, CuO and ZnO species are observed on the surface (Figure 6(c)). Combined with the aforementioned XRD, H₂-TPR and XPS analyses, it can be inferred that the surface Cu⁰ species are present in a highly dispersed or amorphous state. Additionally, the relatively high amount of K species likely covers some active sites, leading to the lower catalytic activity. While no distinct Al₂O₃ crystallites are detected in any of the three samples, the uniform distribution of Al in the elemental mapping indicates that Al₂O₃ exists in a highly dispersed or amorphous form.

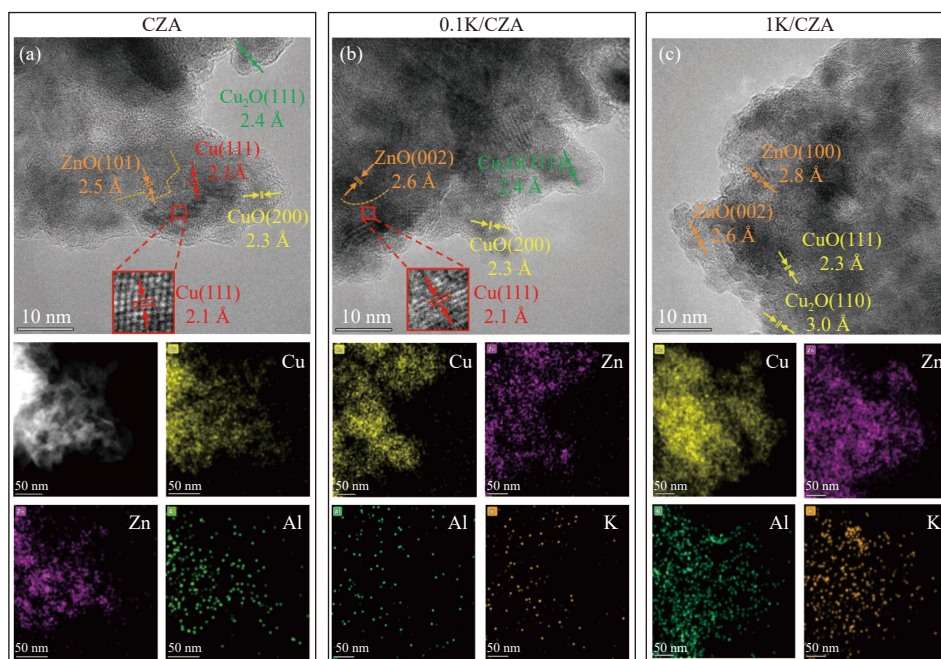


Fig. 6 HR-TEM images, HAADF-STEM images and corresponding elements mapping of the series of used xK/CZA catalysts

2.4 Analysis of catalyst surface adsorption and reactivity

The influence of the modification of K on the CO₂ adsorption behavior of the CZA catalyst was investigated by CO₂-TPD (Figure 7). All catalysts exhibit similar CO₂ desorption peak with a broad desorption peak centered at around 100 °C, corresponding to the weak basic sites^[31]. The intensity of the desorption signal decreases significantly with increasing K content, which indicates that the modification of K species masks the original basic sites of the CZA catalyst, thereby weakening the CO₂ adsorption and inhibiting the catalytic reaction activity.

To elucidate the reaction mechanism of CO₂ hydrogenation to methanol, the formation and evolution of surface species during the reaction were monitored using *in situ* DRIFTS, as shown in Figure 8.

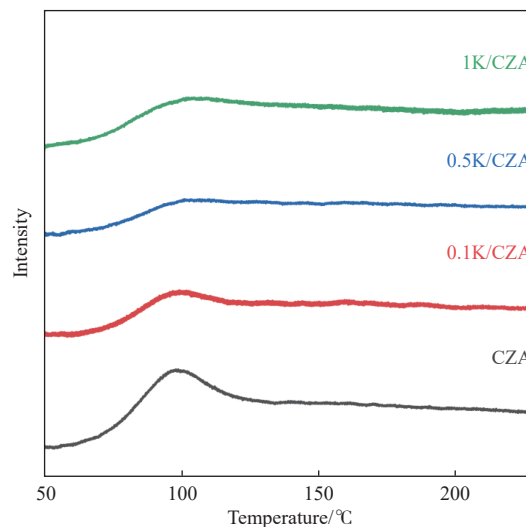


Fig. 7 CO₂-TPD profiles of the series of xK/CZA catalysts

Figure 8 displays the time-dependent evolution of surface-adsorbed species for the CZA and 1K/CZA samples under 3 MPa and 230 °C. The vibrational band appearing at 1617 cm^{-1} is assigned to HCO_3^* species, while the characteristic peaks appearing at approximately 1586, 1390 and 1372 cm^{-1} correspond to HCOO^* species. The intensities of these vibrational bands associated with the active intermediates gradually increase with reaction time^[29,32–34]. It is generally accepted that HCO_3^* transforms into HCOO^* , which is subsequently hydrogenated to CH_3O and finally to methanol^[35–36]. As reflected in Figure 9, the intensity of the HCOO^* species ($\sim 1586 \text{ cm}^{-1}$) increases rapidly during the initial stage of the reaction (0–20 min)

and then approaches a steady-state value in the subsequent stage (20–100 min). This behavior may be attributed to either a reduction in the number of available active sites due to the accumulation of adsorbed intermediates or a balance between the formation and consumption rates of the active intermediates, enabling the reaction to proceed steadily. The variation trends in the formation rate of HCOO^* are similar for the CZA and 1K/CZA catalysts, suggesting that the difference in their catalytic activities likely stems from the subsequent hydrogenation steps rather than the formation of HCOO^* . Based on the above IR results, it can be concluded that both catalysts favor the HCOO^* -mediated reaction pathway.

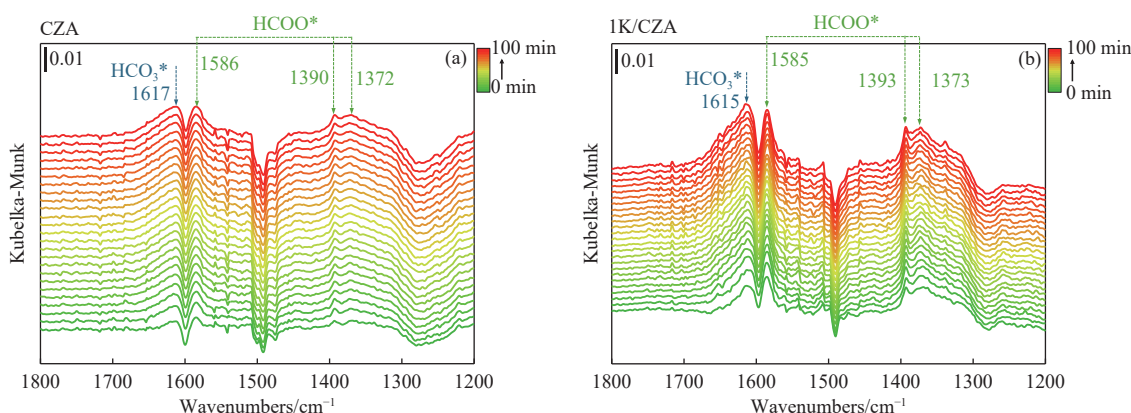


Fig. 8 *In situ* DRIFT spectra on the surface of different catalysts ((a) CZA, (b) 1K/CZA)
Test conditions: 3 MPa, 230 °C, $\text{H}_2/\text{CO}_2=3$, 20 mL/min.

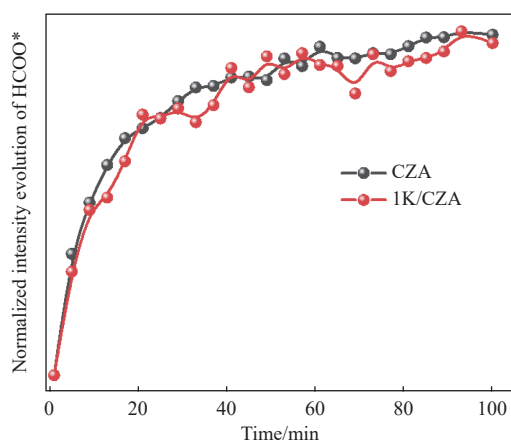


Fig. 9 The time-dependent normalized intensity curves of the active intermediates HCOO^* produced on the two kinds of catalyst surfaces

3 Conclusions

This study systematically investigated how structural modifications affect the catalytic performance of CZA catalysts by incorporating varying amounts of the alkali metal K, in an effort to more accurately identify the catalytic functions associated with different valence states of Cu species. By combining multiple characterization

techniques, we elucidated the influence of the K promoter on the active structure of the catalyst for CO_2 hydrogenation to methanol. CO_2 -TPD results indicate that K modification covers a significant number of basic sites on the catalyst surface, thereby suppressing the CO_2 adsorption capacity. H_2 -TPR, XPS and HR-TEM analyses reveal that highly dispersed K species on the CZA catalyst surface inhibit the reduction of CuO species, consequently fewer Cu_2O active species are generated under reaction conditions in the K-modified CZA catalysts, leading to decreased catalytic activity. However, the K modifier effectively promotes the dispersion of Cu^0 species and strengthen their interaction with ZnO, which facilitates the formation of more Cu^0 -ZnO interfaces. Nevertheless, the increased population of Cu^0 species primarily promotes the RWGS side reaction, thereby suppressing methanol formation. According to *in situ* IR spectroscopy, the CO_2 hydrogenation to methanol over the CZA catalyst follows a HCOO^* -mediated pathway. This study enhances the understanding of the true active sites of Cu species in methanol synthesis and may provide valuable insights for designing more efficient industrial CZA catalysts.

Declaration of Competing Interest

The authors declare no conflict of interest.

References

- [1] YE J, DIMITRATOS N, ROSSI L M, et al. Hydrogenation of CO₂ for sustainable fuel and chemical production[J]. *Science*, 2025, 387(6737): eadn9388.
- [2] AKLILU E G, BOUNAHMIDI T. Machine learning applications in catalytic hydrogenation of carbon dioxide to methanol: A comprehensive review[J]. *Int J Hydrogen Energy*, 2024, 61: 578–602.
- [3] QUILIS C, MOTA N, MILLÁN E, et al. Application of intermetallic compounds as catalysts for the selective hydrogenation of CO₂ to methanol[J]. *ChemCatChem*, 2024, 16(14): e202301496.
- [4] ZHANG P, HUANG X, QU S, et al. Direct conversion of carbon dioxide into liquefied petroleum gas over zeolite capsule catalyst[J]. *Res Chem Intermed*, 2025, 51(2): 675–693.
- [5] LIU Y, WANG X, WANG Z, et al. Hydrogenation of CO₂ to CH₃OH on the Cu-ZnO-SrTiO₃ catalysts: The electronic metal-support interaction induces oxygen vacancy generation[J]. *ACS Catal*, 2024, 14(16): 12610–12622.
- [6] WANG Y, YU M, ZHANG X, et al. Density functional theory study of CO₂ hydrogenation on transition-metal-doped Cu(211) surfaces[J]. *Molecules*, 2023, 28(6): 2852.
- [7] JENSEN S, CHEULA R, HEDEVANG M, et al. Role of Cu Oxide and Cu adatoms in the reactivity of CO₂ on Cu(110)[J]. *Angew Chem Int Ed*, 2024, 63(33): e202405554.
- [8] JIN S, KWON C, BUGAEV A, et al. Atom-by-atom design of Cu/ZrO_x clusters on MgO for CO₂ hydrogenation using liquid-phase atomic layer deposition[J]. *Nat Catal*, 2024, 7(11): 1199–1212.
- [9] CAO F, LIU J, XU K, et al. Optimized active structure configuration of the MOF derived Cu-based catalysts via different atmospheres for selective CO₂ hydrogenation[J]. *Appl Surf Sci*, 2025, 698: 163134.
- [10] YE R, MA L, MAO J, et al. A Ce-CuZn catalyst with abundant Cu/Zn-OV-Ce active sites for CO₂ hydrogenation to methanol[J]. *Nat Commun*, 2024, 15(1): 2159.
- [11] LIU H-X, LI S-Q, WANG W-W, et al. Partially sintered copper-ceria as excellent catalyst for the high-temperature reverse water gas shift reaction[J]. *Nat Commun*, 2022, 13(1): 867.
- [12] LU S, ZHANG J, MENG H, et al. Catalytic direct dehydrogenation of ethyl lactate to produce ethyl pyruvate over a synergetic Cu⁰/Cu⁺ interface[J]. *Appl Catal B: Environ*, 2023, 325: 122329.
- [13] TU W, REN P, LI Y, et al. Gas-dependent active sites on Cu/ZnO clusters for CH₃OH synthesis[J]. *J Am Chem Soc*, 2023, 145(16): 8751–8756.
- [14] CHANG H, GAO F, LUO A, et al. Oxygen vacancy promoted carbon dioxide activation over Cu/ZrO₂ for CO₂-to-methanol conversion[J]. *Chem Commun*, 2023, 59(49): 7647–7650.
- [15] ZHONG J, YANG X, WU Z, et al. State of the art and perspectives in heterogeneous catalysis of CO₂ hydrogenation to methanol[J]. *Chem Soc Rev*, 2020, 49(5): 1385–1413.
- [16] PACCHIONI G. From CO₂ to methanol on Cu/ZnO/Al₂O₃ industrial catalyst. What do we know about the active phase and the reaction mechanism?[J]. *ACS Catal*, 2024, 14(4): 2730–2745.
- [17] LI J, GUO Q, ZHAO X, et al. Effect of hydrothermal environment on Cu-ZnO/Al₂O₃ catalyst for hydrogenation of CO₂ to methanol[J]. *Mol Catal*, 2023, 549: 113494.
- [18] ZHANG H, HAN C, LI C, et al. Design of Cu/ZnO/Al₂O₃ catalysts with a rich Cu-ZnO interface for enhanced CO₂ hydrogenation to methanol using zinc-malachite as the precursor[J]. *New J Chem*, 2023, 47(12): 5885–5893.
- [19] HUANG C, ZHANG S, WANG W, et al. Modulation of electronic metal-support interaction between Cu and ZnO by Er for effective low-temperature CO₂ hydrogenation to methanol[J]. *ACS Catal*, 2024, 14(3): 1324–1335.
- [20] ZHANG F, LI B, QUAN X, et al. Revealing the dynamics of oxygen vacancy in ZnO_{1-x}/Cu during robust methanol synthesis from CO₂[J]. *ACS Catal*, 2024, 14(9): 7136–7148.
- [21] ZHANG P, WANG W, WANG P, et al. Tuning catalytic performance of CuZnO_x catalyst via functional LaO_x for catalyzing CO₂ hydrogenation reaction[J]. *Mol Catal*, 2025, 573: 114818.
- [22] ZHAO F, FAN L, XU K, et al. Hierarchical sheet-like Cu/Zn/Al nanocatalysts derived from LDH/MOF composites for CO₂ hydrogenation to methanol[J]. *J CO₂ Util*, 2019, 33: 222–232.
- [23] ZHANG H, CHEN J, HAN X, et al. High-performance Cu/ZnO/Al₂O₃ catalysts for CO₂ hydrogenation to methanol[J]. *Ind Eng Chem Res*, 2024, 63(14): 6210–6221.
- [24] LIU H, YU Z, HUANG W, et al. Effect of Ce modification on the performance of CuLDH catalyst for CO₂ hydrogenation to methanol[J]. *J Fuel Chem Technol*, 2024, 52(2): 159–170.
- [25] XU D, DING M, HONG X, et al. Selective C2+ alcohol synthesis from direct CO₂ hydrogenation over a Cs-promoted Cu-Fe-Zn catalyst[J]. *ACS Catal*, 2020, 10(9): 5250–5260.
- [26] WANG S, SONG L, QU Z. Cu/ZnAl₂O₄ catalysts prepared by ammonia evaporation method: Improving methanol selectivity in CO₂ hydrogenation via regulation of metal-support interaction[J]. *Chem Eng J*, 2023, 469: 144008.
- [27] ZHANG G, FAN G, ZHENG L, et al. Ga-promoted CuCo-based catalysts for efficient CO₂ hydrogenation to ethanol: The key synergistic role of Cu-CoGaO_x interfacial sites[J]. *ACS Appl Mater Interfaces*, 2022, 14(31): 35569–35580.
- [28] XIE G, BAI X, MAN Y, et al. High-performance Al-doped Cu/ZnO catalysts for CO₂ hydrogenation to methanol: MIL-53(Al) source-enabled oxygen vacancy engineering and related promoting mechanisms[J]. *Chem Eng J*, 2024, 480: 148195.
- [29] WANG X, YAO Z, GUO X, et al. Modulating electronic interaction over Zr-ZnO catalysts to enhance CO₂ hydrogenation to methanol[J]. *ACS Catal*, 2023, 14(1): 508–521.
- [30] ZHENG W, SUN C, DONG Z, et al. Enhanced CO₂ hydrogenation reaction by tuning interfacial Cu/ZnO_x through synergistic interactions in the precursors[J]. *J Catal*, 2024, 440: 115794.
- [31] XU Y, GAO Z, XU Y, et al. Cu-supported nano-ZrZnO₂ as a highly active inverse catalyst for low temperature methanol

- synthesis from CO₂ hydrogenation[J]. Appl Catal B: Environ, 2024, 344: 123656.
- [32] ZHAO H, YU R, MA S, et al. The role of Cu₁-O₃ species in single-atom Cu/ZrO₂ catalyst for CO₂ hydrogenation[J]. Nat Catal, 2022, 5(9): 818–831.
- [33] PINHEIRO ARAÚJO T, GIANNAKAKIS G, MORALES-VIDAL J, et al. Low-nuclearity CuZn ensembles on ZnZrO_x catalyze methanol synthesis from CO₂[J]. Nat Commun, 2024, 15(1): 3101.
- [34] WANG J, LIU H, WANG T, et al. Boosting CO₂ hydrogenation to methanol via Cu-Zn synergy over highly dispersed Cu, Zn-codoped ZrO₂ catalysts[J]. Catal Today, 2023, 410: 205–214.
- [35] WANG Y, GAO W, LI K, et al. Strong evidence of the role of H₂O in affecting methanol selectivity from CO₂ hydrogenation over Cu-ZnO-ZrO₂[J]. Chem, 2020, 6(2): 419–430.
- [36] YANG M, YU J, ZIMINA A, et al. Probing the nature of zinc in copper-zinc-zirconium catalysts by operando spectroscopies for CO₂ hydrogenation to methanol[J]. Angew Chem Int Ed, 2023, 62(7): e202216803.

CuZnAl 催化剂中 Cu 价态对 CO₂ 加氢合成甲醇反应的影响

邱正璞¹, 许运钊², 王 鹏^{2,3,*}, 陶小霞², 张惠民¹, 陈 阳², 刘 意¹, 杨 桦⁴,
曹逢海², 傅亚杰², 吴立志², 汤 禹², 徐晓颖^{1,*}, 谭 理^{2,*}

(1. 北京低碳清洁能源研究院, 北京 102211; 2. 福州大学 化学学院, 福建 福州 350108;

3. 福州大学 未来膜技术学院, 福建 福州 350108; 4. 重庆安全技术职业学院, 重庆 404020)

摘 要: CuZnAl(CZA)是合成气制备甲醇反应中广泛应用的工业催化剂,然而其在 CO₂ 加氢制甲醇反应中的催化性能欠佳。关于 CZA 催化剂中铜物种的催化作用机制仍存在较大探索空间。为此,本研究通过在 CZA 催化剂中引入不同含量的供电子助剂 K,研究了活性 Cu 物种价态的变化及其对催化性能的影响。H₂-TPR、XPS 和 HR-TEM 表征结果表明,CZA 催化剂表面高分散的 K 物种会抑制 CuO 的还原,导致在反应温度下仅生成少量 Cu₂O 活性物种,从而降低催化活性。同时,XRD 和 Cu LMM 谱图分析表明,随着 K 含量的增加,K 修饰 CZA 催化剂中 Cu⁰ 的比例相应上升,而 Cu⁰ 物种显著促进了逆水煤气变换反应(RWGS),对主反应产生不利影响。此外,基于原位红外光谱结果可以推断,CZA 催化剂在 CO₂ 加氢制甲醇反应中遵循 HCOO* 中间体路径。

关键词: CO₂ 加氢; CuZnAl 催化剂; 甲醇; 活性物种; 电子助剂

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作者简介:



邱正璞(1990), 硕士, 高级工程师, 研究方向为 C1 化工与 CO₂ 转化利用, zhengpu.qiu@chnenergy.com.cn。



徐晓颖(1986), 博士, 高级工程师, 致力于绿色化工、C1 化工、CO₂ 资源化利用相关催化剂及成套技术开发, xiaoying.xu.d@chnenergy.com.cn。



王鹏(1993), 博士, 福州大学副研究员, 研究方向为 C1 化学与化工, p_wang@fzu.edu.cn。



谭理(1989), 博士, 福州大学教授, 博士生导师, 研究方向为 C1 化学与化工, tan@fzu.edu.cn。