

Article

Constructing Abundant Cu–ZnO Interfaces via an MOF-on-MOF Precursor for Efficient CO₂ Hydrogenation to Methanol

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Abstract

In this study, a series of Cu_aZn_bO_x catalysts with tunable Cu/Zn molar ratios were fabricated via a MOF-on-MOF precursor strategy for CO₂ hydrogenation to methanol. The optimal catalyst, Cu₆Zn₄O_x, achieved a CO₂ conversion of 14.4%, a methanol selectivity of 81.1%, and a space-time yield of 902.1 g_{MeOH}·kg_{cat}^{−1}·h^{−1} at 280 °C and 3 MPa with a GHSV of 24,000 mL·g_{cat}^{−1}·h^{−1}. Characterization results revealed that this strategy successfully constructed small-sized Cu and ZnO particles as well as abundant Cu–ZnO interfaces, reaching the optimal structural and compositional state when the Cu/Zn molar ratio is tuned to 6:4. The effective Cu–ZnO interface on Cu₆Zn₄O_x promotes the CO₂ adsorption and H₂ dissociation, triggering the formation of carbonate species and resulting in the generation of methanol via a carbonate–formate pathway. This work provides a new insight for the rational design of high-performance CO₂ hydrogenation catalysts through precursor interface engineering.

Keywords: CO₂ hydrogenation; MOF-on-MOF; Cu/ZnO catalyst; methanol

1. Introduction

CO₂ hydrogenation technology holds great promise as a key driver in establishing a carbon-neutral circular economy. This technology enables the conversion of CO₂ into high-value chemicals and fuels, such as methanol, dimethyl ether, and olefins [1,2]. Among these, methanol serves as a versatile liquid fuel, a renewable hydrogen carrier, and a crucial precursor for synthesizing other chemicals [3–5]. Therefore, the development of efficient catalysts for CO₂ hydrogenation to methanol is of great significance for achieving both carbon emission reduction and resource utilization.

Cu-based catalysts are widely employed in the hydrogenation of CO₂ to methanol due to their low cost and excellent activity under mild reaction conditions [6–8]. However, this catalytic system still faces the dual challenges of poor stability and low methanol selectivity. The reverse water–gas shift (RWGS) reaction severely compromises methanol selectivity due to its competitive nature, while concurrently, the substantial water generated during the reaction accelerates Cu nanoparticle sintering and triggers phase transformation in supports (e.g., ZnO), ultimately causing active site deactivation [9–14]. Studies have shown that these issues stem from the limited ability of conventional preparation methods to control the microstructure of the catalyst, particularly the precise construction

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of efficient and stable Cu–ZnO interfaces. Therefore, next-generation catalysts for CO₂ hydrogenation to methanol demand strategies that enable atomic-precision engineering of Cu–ZnO interfaces to overcome selectivity and stability limitations.

In recent years, metal–organic frameworks (MOFs) have emerged as ideal precursors for the preparation of high-performance catalysts, owing to their high specific surface area, high structural tunability, and atomically uniform dispersion of metal sites [15,16]. Based on these advantages, researchers have attempted to construct Cu–ZnO catalysts via MOF-derived strategies for CO₂ hydrogenation to methanol. For instance, Hu et al. [17] synthesized an inverse ZnO/Cu catalyst using Cu@ZIF-8 as a precursor. By decorating the Cu particle size (<5 nm) with ZnO nanoparticles, they successfully enhanced methanol yield. Qi et al. [18] successfully prepared a Cu–ZnO@Al₂O₃ catalyst using bimetallic CuZn-BTC as a precursor for CO₂ hydrogenation to methanol. Han et al. [19] tuned the Cu–ZnO interface structure by thermal treatment of a Cu–Zn bimetallic MOF. Sun et al. [20] constructed an inverse catalyst enriched with ZnO_x/Cu interfacial sites using Zn-doped HKUST-1 as a precursor, thereby enhancing the methanol space-time yield and selectivity. Recently, Ramakrishnan et al. [21] demonstrated that Cu–Zn supported on MOF-808 (a Zr-based MOF) exhibited strong Cu–Zn–Zr interactions and achieved a high methanol STY of 193.3 g_{MeOH}·kg_{cat}^{−1}·h^{−1} at 260 °C and 40 bar. San et al. [22] developed a CuO/ZnO-LM catalyst via layered substrate-confined growth of CuZn-MOF, which generated abundant Cu–ZnO interfaces and oxygen vacancies, achieving 18.3% CO₂ conversion and 73.0% methanol selectivity at 280 °C and 3 MPa. Despite advances in MOF-derived catalysts for CO₂ hydrogenation, the quantity and quality of Cu/ZnO interfacial sites remain critical factors limiting methanol yield and selectivity.

Herein, we report for the first time a sequential MOF-on-MOF assembly strategy using HKUST-1 (Cu-MOF) and MOF-5 (Zn-MOF) to construct Cu–ZnO catalysts for CO₂ hydrogenation to methanol. Unlike conventional one-pot bimetallic MOF precursors (e.g., Cu–Zn-MOF-74), our approach enables spatially controlled growth of Zn-MOF on pre-formed Cu-MOF, generating a unique heterostructure that yields abundant and intimate Cu–ZnO interfaces. A series of Cu_aZn_bO_x catalysts with varying Cu/Zn molar ratios (5:5, 6:4, 7:3) was prepared, and a coprecipitated Cu₆Zn₄O_x-CP catalyst was used as a reference. Through systematic characterizations (XRD, N₂ sorption, TEM, XPS, H₂-TPR, and in situ DRIFTS), we elucidated the structure–performance relationship. The optimal Cu₆Zn₄O_x catalyst exhibits excellent activity and stability, and the DRIFTS results support a carbonate–formate pathway. This work provides a new synthetic paradigm and experimental insights for designing high-performance CO₂ hydrogenation catalysts via MOF-on-MOF interface engineering.

2. Results and Discussion

2.1. Structural Properties of the Catalysts

Figure 1 shows the XRD patterns of the samples after calcination and reduction. As illustrated in Figure 1a, all calcined samples exhibited diffraction peaks at 2θ = 35.5° and 38.7°, corresponding to the (−111) and (111) crystal planes of CuO, respectively; peaks at 2θ = 31.8°, 34.4°, and 36.3° were also observed, corresponding to the (100), (002), and (101) crystal planes of ZnO, respectively. With increasing Cu/Zn molar ratio, the relative intensity of CuO diffraction peaks rose concomitantly with a concomitant suppression of ZnO peak intensities. After reduction (Figure 1b), the CuO phase completely disappeared in all samples, and characteristic diffraction peaks of metallic Cu appeared at 2θ = 43.3° and 50.4°, confirming the successful reduction in Cu²⁺ to Cu⁰. The average crystallite sizes of Cu⁰ and ZnO in the reduced catalysts were calculated using the Scherrer equation (Table 1). The results indicate that both the Cu⁰ and ZnO crystallite sizes of the MOF-derived catalysts were smaller than those of the Cu₆Zn₄O_x-CP sample prepared by the

coprecipitation method. These findings demonstrate that the MOF-on-MOF precursor strategy is beneficial for obtaining Cu/ZnO catalysts with smaller crystallite sizes.

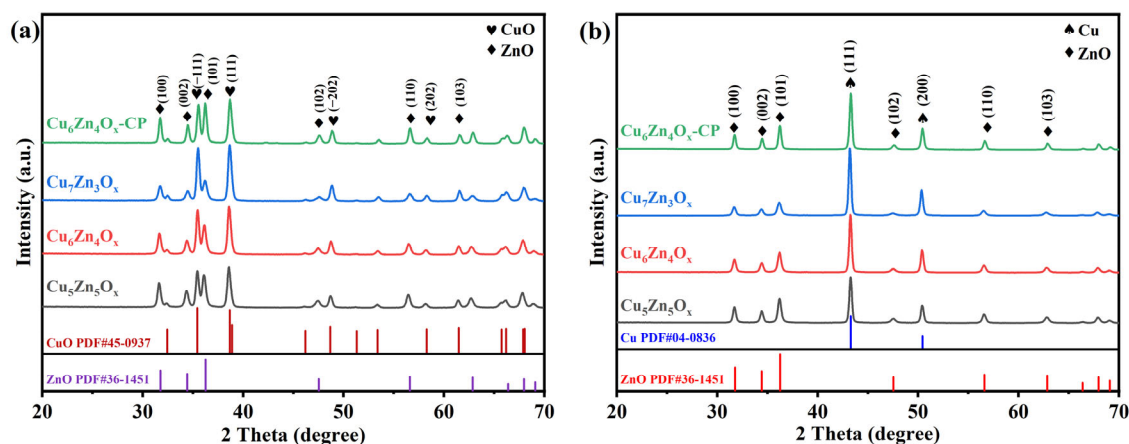


Figure 1. XRD spectra of catalysts after calcination (a) and reduction (b).

Table 1. Physical parameters of catalysts.

Catalyst	S_{BET}^a ($\text{m}^2\cdot\text{g}^{-1}$)	V_{pore}^a ($\text{cm}^3\cdot\text{g}^{-1}$)	D_{pore}^a (nm)	Grain Size of Cu ^b (nm)	Grain Size of ZnO ^b (nm)	S_{Cu}^c ($\text{m}^2\cdot\text{g}^{-1}$)	TOF (h^{-1})
Cu ₅ Zn ₅ O _x	9.1	0.06	24.3	24.8	21.7	2.3	0.13
Cu ₆ Zn ₄ O _x	11.9	0.07	29.6	25.7	19.5	4.1	0.18
Cu ₇ Zn ₃ O _x	7.2	0.05	35.7	26.4	18.3	3.7	0.14
Cu ₆ Zn ₄ O _x -CP	16.6	0.19	47.2	28.5	25.1	3.5	0.11

^a Obtained from BJH desorption average pore volume and pore diameter. ^b The grain size of Cu and ZnO was calculated by the Scherrer formula, where $2\theta = 43.3^\circ$, 50.4° , and 31.8° , 34.4° , 36.3° . ^c Determined from N₂O chemisorption.

Figure 2 shows the N₂ adsorption–desorption isotherms of the catalysts. All catalysts exhibited type IV isotherms with H3-type hysteresis loops. As summarized in Table 1, the BET specific surface areas of the MOF-derived catalysts ranged from 7 to 15 $\text{m}^2\cdot\text{g}^{-1}$, all of which were lower than that of the Cu₆Zn₄O_x-CP catalyst (16.6 $\text{m}^2\cdot\text{g}^{-1}$) prepared by the coprecipitation method. This indicates that grain size does not show a simple inverse correlation with specific surface area. Moreover, among the MOF-derived catalysts, the metallic copper surface area (S_{Cu}) first increased and then decreased with increasing Cu/Zn molar ratio (Table 1). Notably, Cu₆Zn₄O_x exhibited the highest S_{Cu} value (4.1 $\text{m}^2\cdot\text{g}^{-1}$), which was higher than that of the coprecipitated Cu₆Zn₄O_x-CP catalyst (3.5 $\text{m}^2\cdot\text{g}^{-1}$). S_{Cu} is directly correlated with the number of exposed active copper sites; a larger S_{Cu} generally implies a greater abundance of active sites available for H₂ dissociation and CO₂ hydrogenation.

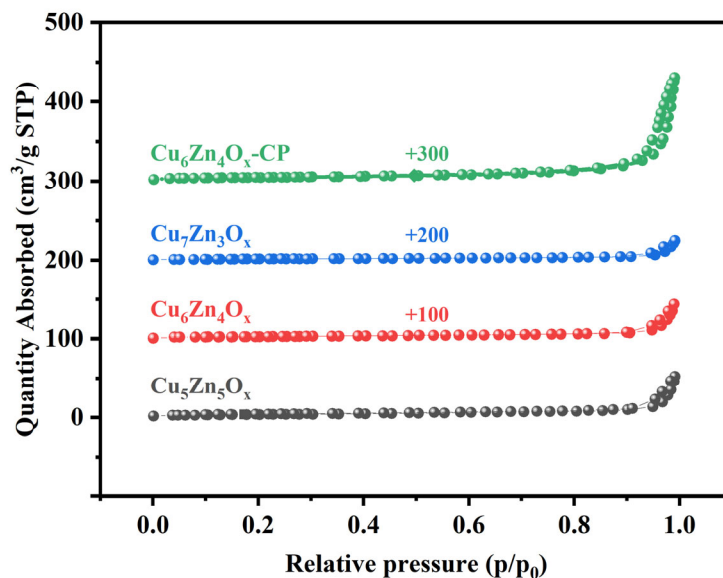


Figure 2. N₂ adsorption–desorption isotherms of catalysts.

The microstructures of the reduced catalysts were analyzed by HR-TEM. Low-magnification images (Figure 3(a1–d1)) reveal that all the samples exhibited a spherical stacking morphology, and the MOF-derived Cu_aZn_bO_x catalysts showed reduced particle sizes compared to the Cu₆Zn₄O_x-CP counterpart. High-resolution images (Figure 3(a2–d2)) reveal the predominant exposure of Cu (111), Cu (200), ZnO (100), and ZnO (101) crystal planes on the surfaces of catalysts, and provide direct evidence of the Cu–ZnO interface. For the MOF-derived samples, the metallic Cu (111) crystal plane ($d \approx 0.20$ nm) was in intimate contact with the adjacent ZnO crystal planes. In contrast, for the Cu₆Zn₄O_x-CP sample, the interface between Cu particles and ZnO appeared indistinct or showed limited contact. Elemental distribution maps (Figure 3(a3–d3)) confirm that the Cu and Zn signals were highly intertwined in the MOF-derived catalysts, indicating a compact nanoscale composite, whereas the distribution of the two elements in the Cu₆Zn₄O_x-CP was relatively separate. Notably, among the MOF-derived series, the Cu₆Zn₄O_x catalyst exhibited the smallest Cu nanoparticle size. These results demonstrate that the MOF precursor strategy enables precise regulation and construction of abundant Cu–ZnO interfaces [19,21], which is the key structural reason for the excellent catalytic activity of the Cu₆Zn₄O_x catalyst.

2.2. Catalytic Performance

As shown in Figure 4a, under the conditions of 280 °C, 3 MPa, H₂/CO₂ = 3, and a gas hourly space velocity (GHSV) of 24,000 mL·g_{cat}^{−1}·h^{−1}, all MOF-derived Cu_aZn_bO_x catalysts exhibited significantly higher CO₂ conversion and methanol selectivity than that of Cu₆Zn₄O_x-CP catalyst prepared by the coprecipitation method. Further analysis revealed that CO₂ conversion followed a volcano-shaped trend with increasing Cu/Zn molar ratio. Cu₆Zn₄O_x exhibited high efficacy for methanol synthesis from CO₂ hydrogenation, achieving a high methanol selectivity of 81.1% with a CO₂ conversion of 14.4%. Meanwhile, the turnover frequency (TOF) of methanol formation, which represents the molecular number of methanol formed per second per metallic copper atom, was calculated from the S_{Cu} for various catalysts. As shown in Table 1, Cu₆Zn₄O_x also showed the highest TOF of 0.18 h^{−1}.

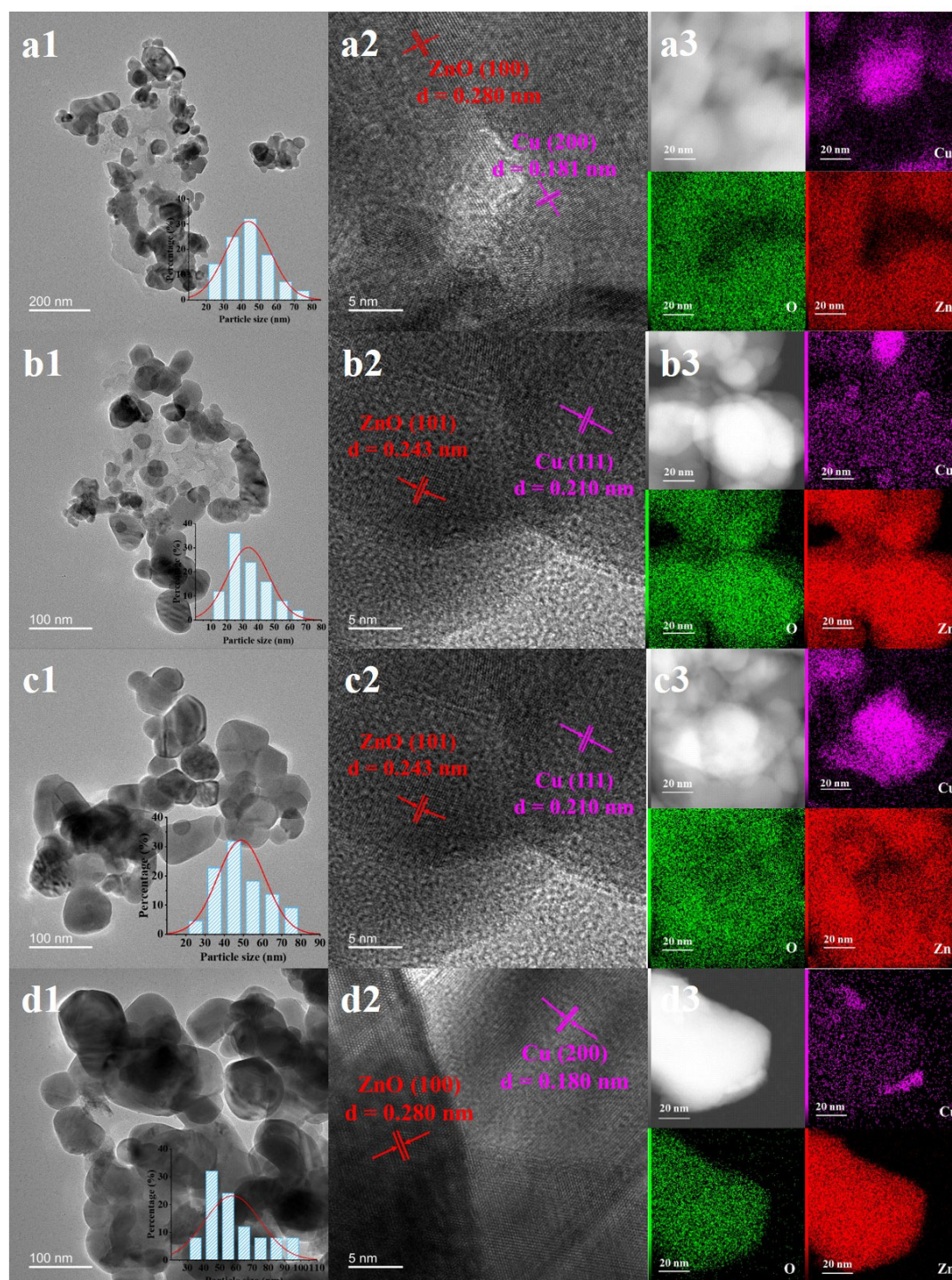


Figure 3. TEM images and EDS Mapping of $\text{Cu}_5\text{Zn}_5\text{O}_x$ (a1–a3), $\text{Cu}_6\text{Zn}_4\text{O}_x$ (b1–b3), $\text{Cu}_7\text{Zn}_3\text{O}_x$ (c1–c3), $\text{Cu}_6\text{Zn}_4\text{O}_x\text{-CP}$ (d1–d3).

Based on these results, $\text{Cu}_6\text{Zn}_4\text{O}_x$ was selected for further investigation of the influence of reaction conditions. As the temperature increased from 220 to 300 °C, CO_2 conversion increased due to enhanced kinetics, while methanol selectivity decreased sharply after 280 °C owing to thermodynamic equilibrium limitations, resulting in a maximum methanol yield of 11.7% at 280 °C (Figure 4b). As shown in Figure 4c, higher space velocity ($>24,000 \text{ mL} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$) resulted in decreased CO_2 conversion, whereas methanol selectivity remained relatively stable. At a GHSV of $24,000 \text{ mL} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$, the optimal balance among CO_2 conversion (14.4%), methanol selectivity (81.1%), and methanol STY ($902.1 \text{ g}_{\text{MeOH}} \cdot \text{kg}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$) was achieved, defining the optimal process window for this system.

Stability test was conducted over the $\text{Cu}_6\text{Zn}_4\text{O}_x$ catalyst under the conditions of H_2/CO_2 molar ratio of 3, reaction temperature of 280 °C, reaction pressure of 3 MPa, and GHSV of 24,000 $\text{mL}\cdot\text{g}_{\text{cat}}^{-1}\cdot\text{h}^{-1}$ (Figure 4d). After 100 h of continuous operation, both CO_2 conversion efficiency and methanol selectivity remained nearly unchanged, which fully demonstrates the excellent long-term catalytic stability of this catalyst. As shown in Table 2, our $\text{Cu}_6\text{Zn}_4\text{O}_x$ catalyst exhibits competitive or superior performance compared to recently reported Cu–ZnO-based catalysts under similar reaction conditions.

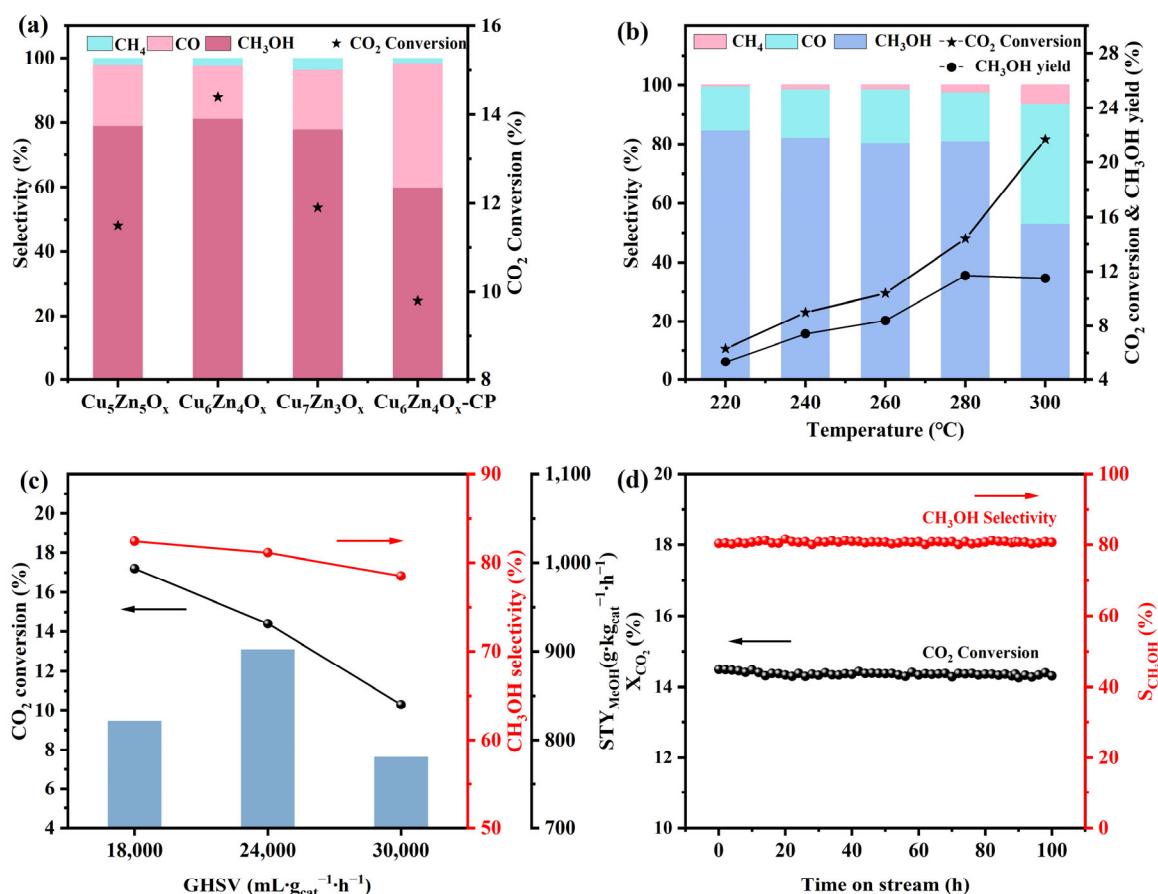


Figure 4. The catalytic activity of $\text{Cu}_a\text{Zn}_b\text{O}_x$ and $\text{Cu}_6\text{Zn}_4\text{O}_x\text{-CP}$ (a), effect of reaction temperature (b) and reaction velocity (c) on the catalytic performance of $\text{Cu}_6\text{Zn}_4\text{O}_x$, the CO_2 conversion and ethanol selectivity vs. time-on-stream for the $\text{Cu}_6\text{Zn}_4\text{O}_x$ operated at 280 °C, $\text{H}_2/\text{CO}_2 = 3$, 24,000 $\text{mL}\cdot\text{g}_{\text{cat}}^{-1}\cdot\text{h}^{-1}$ and 3 MPa (d).

Table 2. Comparison of catalytic performance of $\text{Cu}_6\text{Zn}_4\text{O}_x$ with state-of-the-art Cu–ZnO-based catalysts for CO_2 hydrogenation to methanol under similar reaction conditions.

Catalysts	H_2/CO_2	T (°C)	P (MPa)	Space Velocity	CO_2 Conv. (%)	CH_3OH Sel. (%)	$\text{STY}_{\text{MeOH}} (\text{g}_{\text{MeOH}}\cdot\text{kg}_{\text{cat}}^{-1}\cdot\text{h}^{-1})$	Ref.
CuZnO-MOF-74-350	3	240	4.0	(W) 16,000	14.5	54.0	450.0	[19]
ZnO/Cu-MOF-IM	3	240	3.0	(G) 48,000	4.6	75.6	574.6	[20]
50-CZ MOF	3	260	4.0	(G) 18,000	8.6	43.9	193.3	[21]
CuO/ZnO-LM	3	280	2.0	(G) 12,000	18.3	73.0	511.2	[22]
$\text{Cu}_6\text{Zn}_4\text{O}_x$	3	280	3.0	(G) 24,000	14.4	81.1	902.1	This work

2.3. Surface Chemical State of the Catalysts

Figure 5 shows the H₂-TPR profiles of the different catalysts. The reduction peaks of CuO for all samples were located in the range of 200–350 °C. Among them, the coprecipitated Cu₆Zn₄O_x-CP sample exhibited a broad reduction peak at a relatively higher temperature (approximately 275–350 °C). Generally, larger CuO particle sizes lead to a higher energy barrier for reduction, resulting in an increased reduction temperature, which is consistent with the results of TEM. In contrast, the MOF-derived catalysts, particularly Cu₆Zn₄O_x, exhibited lower reduction peak temperatures, indicating that the smaller CuO particles were more readily reduced by H₂. The easier reducibility of Cu₆Zn₄O_x provides a kinetic basis for the formation of more active sites under reaction conditions, which correlates well with its higher catalytic activity.

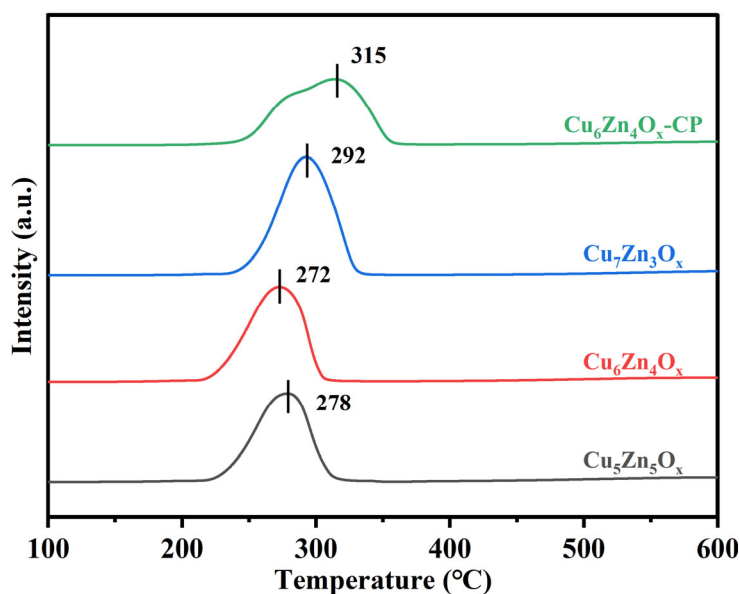


Figure 5. H₂-TPR profiles of catalysts.

To investigate the chemical states of surface elements and their evolution, XPS analysis was performed. As shown in Figure 6a, for all calcined samples, the Cu 2p_{3/2} and Cu 2p_{1/2} main peaks appeared at approximately 933.6 eV and 953.6 eV, respectively, accompanied by prominent satellite peaks in the ranges of 940–945 eV and 960–965 eV, indicating that the Cu species after calcination were predominantly present in the form of CuO [23]. After reduction, the satellite peaks completely disappeared, and the binding energies of the Cu 2p main peaks shifted to lower values (Cu 2p_{3/2} ≈ 932.6 eV, Cu 2p_{1/2} ≈ 952.6 eV) (Figure 6b), demonstrating that Cu²⁺ was completely reduced to Cu⁰ and/or Cu⁺ [24,25].

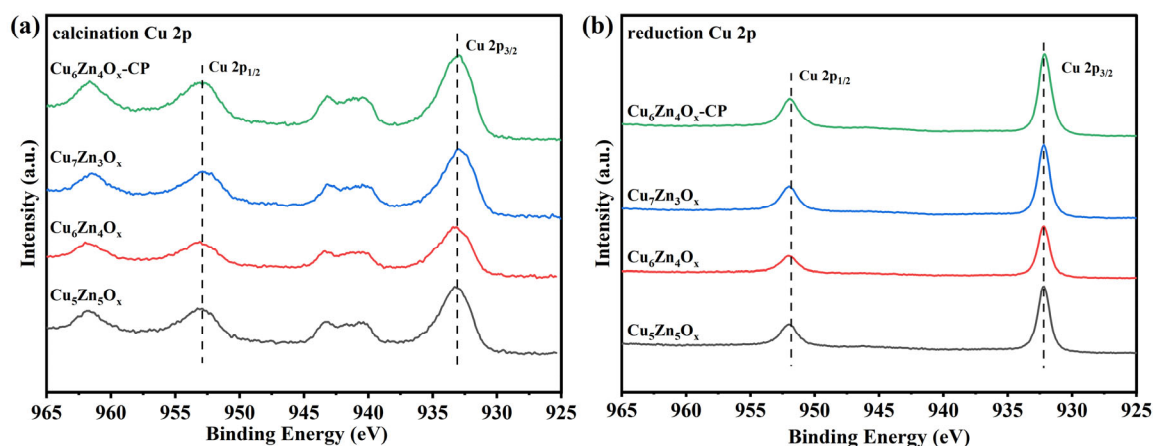


Figure 6. Cu 2p XPS spectra of catalysts after calcination (a) and reduction (b).

As Cu^+ and Cu^0 are not easily distinguishable in XPS spectra, the copper valence states of the reduced catalysts were further precisely analyzed by Cu Auger electron spectroscopy (Cu LMM) (Figure 7). The peaks located at 916.1 eV and 918.4 eV in the spectra are attributed to Cu^+ and Cu^0 species, respectively [26,27]. The relative proportion of Cu^0 on the catalyst surface, expressed as $\text{Cu}^0/(\text{Cu}^0 + \text{Cu}^+)$, was quantitatively calculated by integrating the peak areas. Among the catalysts, the $\text{Cu}_6\text{Zn}_4\text{O}_x$ catalyst exhibited the highest metallic copper (Cu^0) proportion (91.5%), which was significantly higher than that of the $\text{Cu}_6\text{Zn}_4\text{O}_x\text{-CP}$ catalyst (74.1%) prepared via the coprecipitation method with identical composition. We attribute this significant difference to the distinct structural underpinnings resulting from the two disparate preparation methods: the MOF-on-MOF precursor strategy endowed the $\text{Cu}_6\text{Zn}_4\text{O}_x$ catalyst with highly dispersed Cu species and a more abundant Cu–ZnO interface. Cu^0 acts as the active site for the efficient dissociation of H_2 to generate reactive H^* species [28,29]. Therefore, the high abundance of Cu^0 species in the $\text{Cu}_6\text{Zn}_4\text{O}_x$ catalyst is conducive to providing a greater number of active H^* species, thereby facilitating the hydrogenation of CO_2 to methanol.

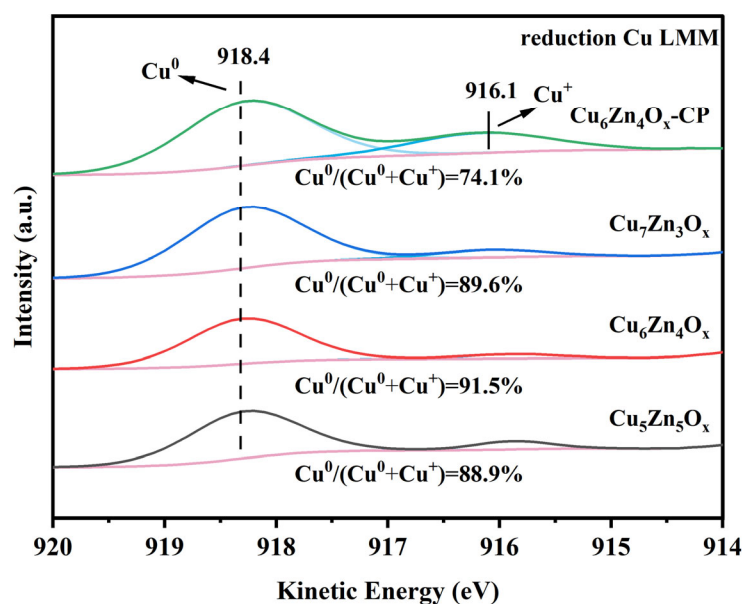


Figure 7. Cu LMM XPS spectra of catalysts after reduction.

Figure 8a and 8b show the Zn 2p XPS spectra of the catalysts after calcination and reduction, respectively. The Zn $2p_{3/2}$ and Zn $2p_{1/2}$ peaks consistently appeared at

approximately 1021.5 eV and 1044.6 eV, respectively, indicating that the Zn species remained in the chemical state of ZnO [30]. Figure 9a and 9b shows the O 1s XPS spectra of the catalysts after calcination and reduction. The O 1s spectrum of the calcined samples (Figure 9a) can be deconvoluted into three components: the γ peak at 529.3 eV assigned to lattice oxygen, the β peak at 530.4 eV belonged to adsorbed oxygen, and the α peak at 532.2 eV attributed to surface hydroxyl groups [31]. After reduction (Figure 9b), the spectrum underwent a significant change. The γ peak completely disappeared, and the spectrum consisted of the β peak (530.5 eV) and the α peak (532.5 eV), indicating that surface lattice oxygen species decreased after reduction, with adsorbed oxygen and hydroxyl species becoming the dominant components.

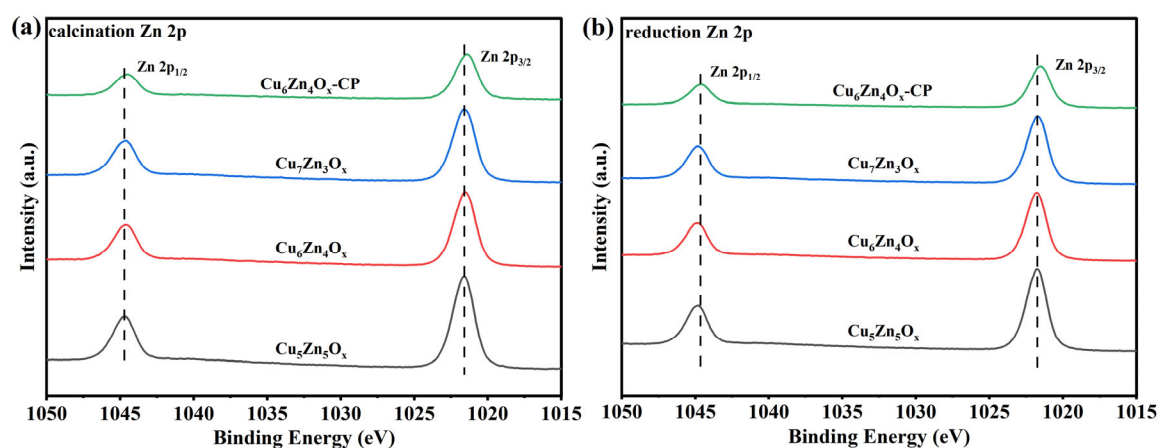


Figure 8. Zn 2p XPS spectra of catalysts after calcination (a) and after reduction (b).

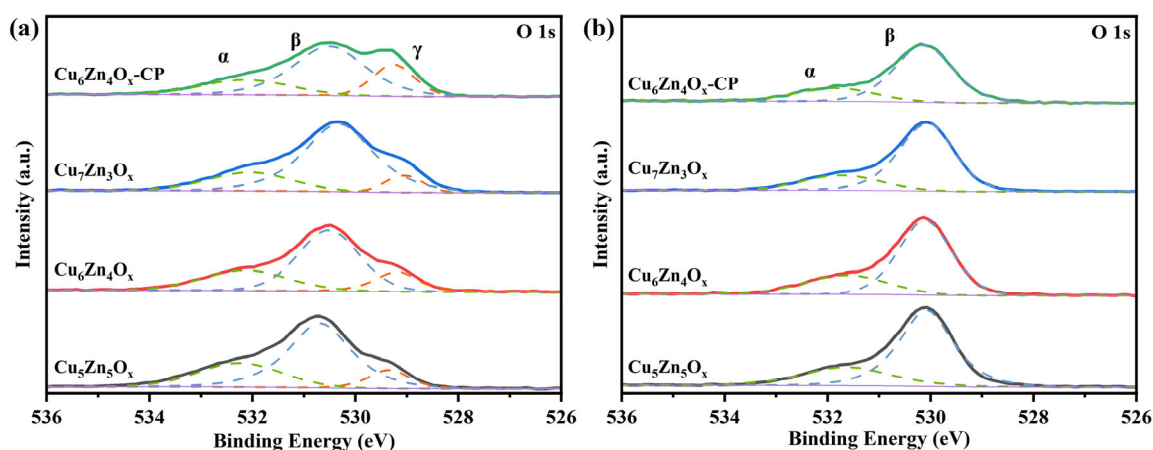


Figure 9. O 1s XPS spectra of catalysts after calcination (a) and after reduction (b).

To investigate the CO_2 adsorption property of the catalysts, CO_2 temperature-programmed desorption (CO_2 -TPD) experiment was performed in a DRIFT cell, with the desorbed species obtained by FT-IR spectrometer (Figure 10a–d). At 30 °C, chemisorbed CO_2 was detected at approximately 2353 cm^{-1} across all catalysts, with the $\text{Cu}_6\text{Zn}_4\text{O}_x$ catalyst exhibiting the strongest intensity. As the temperature increased, the intensity of chemisorbed CO_2 decreased, while characteristic vibrational peaks corresponding to bicarbonate (HCO_3^-) and bidentate carbonate (b-CO_3^{2-}) emerged at approximately 1700 cm^{-1} and 1534 cm^{-1} , respectively [32]. Furthermore, $\text{Cu}_6\text{Zn}_4\text{O}_x$ catalyst also showed the strongest intensities of HCO_3^- and b-CO_3^{2-} species at the reaction temperature (250 °C). It is suggested that the effective Cu–ZnO interface on $\text{Cu}_6\text{Zn}_4\text{O}_x$ promotes the CO_2 adsorption and

H₂ dissociation, triggering the formation of carbonate species and resulting in the generation of methanol via a carbonate–formate pathway [33].

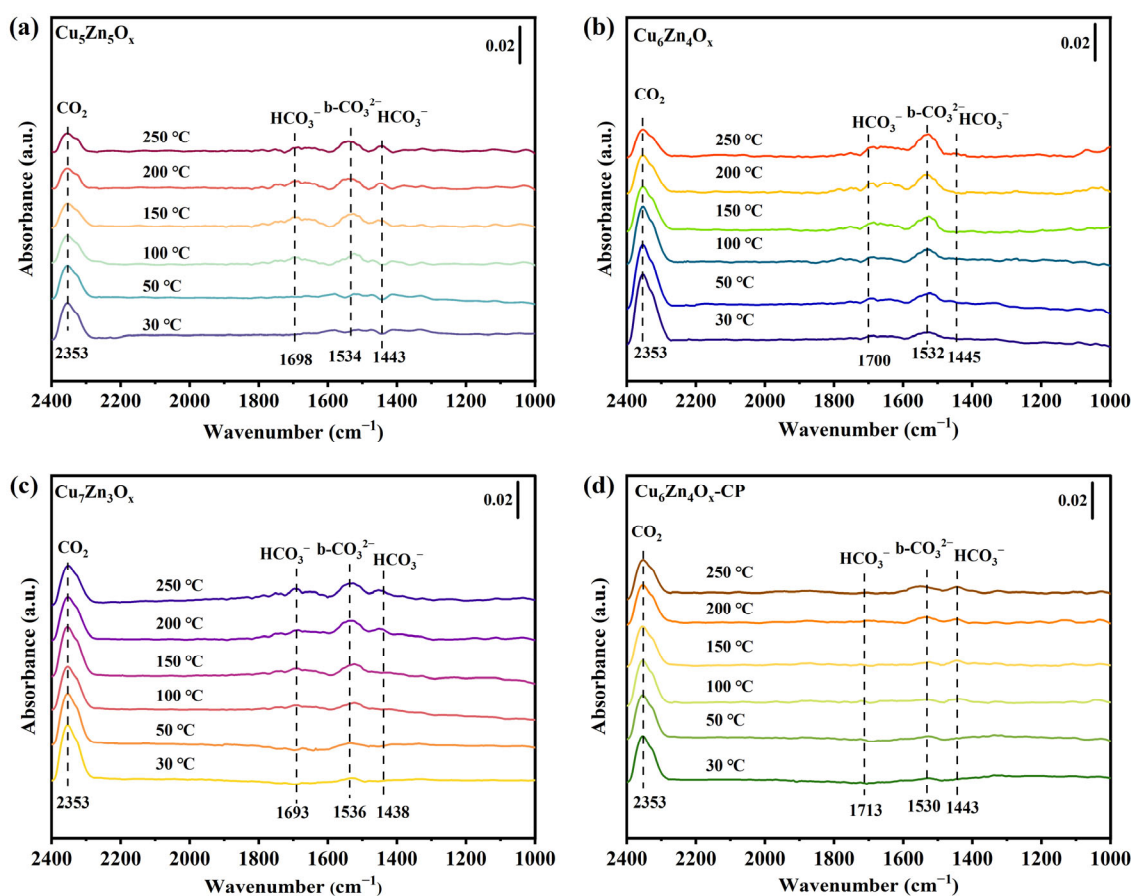


Figure 10. In situ DRIFTS spectra of chemisorbed CO₂ species obtained in the CO₂-TPD process over Cu₅Zn₅O_x (a), Cu₆Zn₄O_x (b), Cu₇Zn₃O_x (c), Cu₆Zn₄O_x-CP (d) catalysts.

3. Materials and Methods

3.1. Chemicals and Materials

Cu(NO₃)₂·3H₂O (AR), 1,3,5-benzenetricarboxylic acid (H₃BTC, ≥98%), N,N-dimethylformamide (DMF, ≥99.5%), Zn(NO₃)₂·6H₂O (AR), 1,4-benzenedicarboxylic acid (H₂BDC, ≥98%), and oxalic acid were purchased from Adamas Reagent Co., Ltd. (Shanghai, China). All reagents were used without further purification.

3.2. Catalyst Preparation

Synthesis of Cu-MOF (HKUST-1). 8.696 g Cu(NO₃)₂·3H₂O and 4.2 g H₃BTC were dissolved in deionized water (120 mL) and DMF (120 mL) to form homogeneous solutions, respectively. The two solutions were then thoroughly mixed under vigorous stirring for 30 min. The mixture was transferred into a Teflon-lined autoclave and kept static at 120 °C in an oven for 12 h. After cooling naturally to room temperature, the supernatant was removed, and the blue crystals were collected. The obtained product was washed several times with ethanol and dried overnight at 80 °C to yield the final product.

Synthesis of HKUST-1@MOF-5. One gram of HKUST-1 powder was dispersed in 30 mL of DMF to form solution A. A specific amount of Zn(NO₃)₂·6H₂O and H₂BDC (corresponding to Cu/Zn molar ratios of 5/5, 6/4, and 7/3) was dissolved in 30 mL of DMF to form solution B. Solution B was then poured into solution A, and the resulting mixture

was transferred into a Teflon-lined autoclave and maintained statically at 120 °C for 24 h. After the system was allowed to cool naturally to room temperature, the product was washed several times with ethanol via centrifugation and dried overnight at 80 °C to obtain the final product.

Synthesis of $\text{Cu}_a\text{Zn}_b\text{O}_x$. The as-synthesized HKUST-1@MOF-5 was calcined in a muffle furnace at 500 °C for 4 h with a heating rate of 5 °C/min. The resulting catalyst was denoted as $\text{Cu}_a\text{Zn}_b\text{O}_x$, where a/b represents the molar ratio of Cu/Zn.

Synthesis of $\text{Cu}_6\text{Zn}_4\text{O}_x$ -CP. The $\text{Cu}_6\text{Zn}_4\text{O}_x$ -CP catalyst was prepared via a co-precipitation method. Specifically, predetermined amounts of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and oxalic acid were used, with a Cu/Zn molar ratio of 6/4 and an oxalic acid/total metal ions molar ratio of 1/1. The weighed $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in deionized water. Under continuous stirring, an oxalic acid solution was added dropwise until complete precipitation was achieved. The precipitate was aged for 3 h, followed by repeated washing with deionized water and centrifugation. The solid was then dried overnight at 80 °C and finally calcined in a muffle furnace at 500 °C for 4 h with a heating rate of 5 °C/min.

3.3. Catalytic Evaluation

The catalytic performance of all catalysts was evaluated in a micro-fixed-bed flow reactor. Prior to the reaction, the catalyst sample (0.15 g, 40–60 mesh) was mixed with quartz sand (0.3 g, 20–40 mesh) and loaded into the central section of the reactor tube to minimize temperature gradients. The temperature was monitored by a thermocouple placed near the catalyst bed. The catalyst was first reduced at 320 °C under atmospheric pressure in a 10 vol% H_2/N_2 flow ($50 \text{ mL} \cdot \text{min}^{-1}$) for 2 h, followed by cooling to the reaction temperature. Subsequently, the gas flow was switched to the reaction gas mixture ($\text{CO}_2/\text{H}_2/\text{N}_2 = 22.5:67.5:10.0$) at a total flow rate of $60 \text{ mL} \cdot \text{min}^{-1}$, and the system pressure was increased to 3 MPa. After initiating the reaction, the effluent was analyzed online using a gas chromatograph (FL GC9720) equipped with an autosampler, a thermal conductivity detector (TCD), and a flame ionization detector (FID). The TCD and FID were connected to a TDX-01 column and an HP-PLOT/Q column (30 m, 0.32 mm inner diameter), respectively. Product identification and quantification were performed using the gas chromatograph. CO_2 conversion, as well as the selectivity to CH_4 , CO, and CH_3OH , and the methanol yield were calculated based on the following Equations (1)–(3).

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

$$S_i(\%) = \frac{A_i \times F_i \times n_i}{\sum (A_i \times F_i \times n_i)} \times 100\% \quad (2)$$

$$\text{STY}_{\text{MeOH}} (\text{g}_{\text{MeOH}} / (\text{kg}_{\text{cat}} \cdot \text{h})) = \frac{n_{\text{CO}_2, \text{in}} \times X_{\text{CO}_2} \times S_{\text{CH}_3\text{OH}} \times M_{\text{CH}_3\text{OH}}}{m_{\text{cat}}} \quad (3)$$

Here, $n_{\text{CO}_2, \text{in}}$ and $n_{\text{CO}_2, \text{out}}$ represent the molar flow rates of CO_2 at the inlet and outlet, respectively, while A_i , F_i , and n_i denote the gas chromatography peak area, calibration factor, and number of carbon atoms for each product i , respectively. $M_{\text{CH}_3\text{OH}}$ represents the molecular weight of methanol (g/mol).

3.4. Catalyst Characterization

X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffractometer (Bruker AXS GmbH, Karlsruhe, Germany) with Cu $K\alpha$ radiation, operating at 40 kV and 35 mA. The XRD patterns were recorded in the 2θ range of 10–80° at a scanning rate

of $2^{\circ}\cdot\text{min}^{-1}$. The average crystallite size of the samples was calculated using the Scherrer equation.

Textural characterization of all samples was performed on a Micromeritics ASAP-2020 HD88 adsorption analyzer (Micromeritics, Norcross, USA) at -196°C . Prior to the measurements, the sample (0.1 g) was degassed under vacuum at 200°C for 10 h.

The copper surface area (S_{Cu}) and copper dispersion (D_{Cu}) were determined by N_2O chemisorption. The measurement consisted of three sequential steps: first H_2 -TPR reduction, N_2O chemisorption, and a second H_2 -TPR experiment. The detailed procedure is as follows: The sample was pretreated in N_2 at 300°C for 30 min. After cooling to room temperature, the gas flow was switched to a mixture of 10 vol% H_2/N_2 , and the temperature was ramped from room temperature to 500°C at $10^{\circ}\text{C}\cdot\text{min}^{-1}$, then held at 500°C for 30 min. Subsequently, the system was purged with N_2 for 10 min and cooled to room temperature. The gas flow was then switched to a mixture of 2 vol% $\text{N}_2\text{O}/\text{He}$ for N_2O chemisorption, which lasted for 60 min. After saturation adsorption, a second H_2 -TPR experiment was conducted under the same conditions as the first TPR. The H_2 consumptions recorded by the TCD during the first and second TPR experiments were denoted as X and Y , respectively.

The metallic copper surface area (S_{Cu}) was calculated using the following Equation (4).

$$S_{\text{Cu}} = \frac{2Y \times N}{X \times M_{\text{Cu}} \times 1.4 \times 10^{19}} = \frac{1353Y}{X} (\text{m}^2 \cdot \text{g}^{-1}) \quad (4)$$

where N is Avogadro's number ($6.023 \times 10^{23} \text{ mol}^{-1}$), 1.4×10^{19} is the number of copper atoms per square meter ($\text{atoms}\cdot\text{m}^{-2}$), M_{Cu} is the atomic weight of copper ($63.46 \text{ g}\cdot\text{mol}^{-1}$).

The turnover frequency of methanol ($\text{TOF}_{\text{methanol}}$) is calculated according to Equation (5).

$$\text{TOF}_{\text{methanol}} (\text{h}^{-1}) = \frac{R_{\text{methanol}} \times N}{S_{\text{Cu}} \times 1.4 \times 10^{19}} \quad (5)$$

where R_{methanol} is the rate of methanol production in ($\text{mol}\cdot\text{g}^{-1}\cdot\text{s}^{-1}$).

TEM images and EDS mapping were acquired using a Tecnai G2 F20 S-Twin transmission electron microscope (FEI, Hillsboro, USA) equipped with an energy-dispersive X-ray spectroscopy (EDS) system (Oxford Instruments, High Wycombe, UK). During the measurement, the high-energy electron beam undergoes scattering, absorption, interference, and diffraction upon penetrating the specimen, generating contrast in the image plane and thus producing the image. Prior to the measurement, the catalyst was adequately dispersed in anhydrous ethanol by ultrasonication and then dropped onto a copper grid for analysis.

X-ray photoelectron spectroscopy (XPS) measurements were conducted on a multi-functional ESCALAB 250Xi photoelectron spectrometer (Thermo Fisher Scientific, Waltham, USA) to determine the chemical composition of the samples. All binding energies were calibrated with reference to the C 1s peak at 284.6 eV .

Temperature-programmed reduction by H_2 (H_2 -TPR) was carried out using a conventional flow apparatus equipped with a thermal conductivity detector (Fuli Instruments, Wen Ling, China). Typically, 0.1 g of the sample was first purged with nitrogen at 300°C for 30 min. After cooling to room temperature, the reduction gas, consisting of 10 vol% H_2 in N_2 ($50 \text{ mL}\cdot\text{min}^{-1}$), was introduced, and the measurement was performed from 50°C to 600°C at a heating rate of $5^{\circ}\text{C}\cdot\text{min}^{-1}$.

In situ diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy was performed in a reaction cell equipped with CaF_2 windows. First, 0.1 g of the sample was loaded into the cell and pretreated under a flow of 10 vol% H_2/Ar ($30 \text{ mL}\cdot\text{min}^{-1}$) at 320°C for 2 h, followed by purging with Ar ($30 \text{ mL}\cdot\text{min}^{-1}$) for 30 min. The background spectrum was then collected after cooling to 250°C . Subsequently, the sample was exposed to 5

vol% CO₂/Ar (30 mL·min^{−1}) at 30 °C for 30 min, after which the gas flow was switched back to Ar for temperature-programmed desorption. Finally, the corresponding infrared spectra of the desorbed species were recorded using a Nicolet 6700 FT-IR spectrometer (Thermo Fisher Scientific, Waltham, USA). Each spectrum was acquired by scanning 64 times at a resolution of 4 cm^{−1}.

4. Conclusions

In this study, a series of Cu_aZn_bO_x catalysts with abundant Cu–ZnO interfaces were successfully constructed via a MOF-on-MOF precursor strategy. At a Cu/Zn molar ratio of 6/4, the Cu₆Zn₄O_x catalyst exhibited optimal performance for CO₂ hydrogenation to methanol, achieving a CO₂ conversion of 14.4%, a methanol selectivity of 81.1%, and a methanol space-time yield of 902.1 g_{MeOH}·kg_{cat}^{−1}·h^{−1} under the conditions of 280 °C, 3 MPa, and a GHSV of 24,000 mL·g_{cat}^{−1}·h^{−1}.

Characterization results confirm that the MOF-on-MOF precursor strategy not only yields ultrasmall Cu and ZnO nanoparticles, but also facilitates the construction of highly intimate Cu–ZnO interfacial architectures. Notably, the Cu_aZn_bO_x catalyst reaches its optimal structural and compositional state when the Cu/Zn molar ratio is tuned to 6:4. The optimized properties of Cu₆Zn₄O_x not only facilitate the simultaneous formation of a high proportion of Cu⁰ active sites after reduction but also promote CO₂ chemisorption and intermediate conversion, thereby synergistically enhancing the efficiency of methanol synthesis. This work elucidates the critical mechanism through which interface engineering modulates the surface/interface properties and reaction kinetics of catalysts, thereby providing novel insights into the rational design of high-performance catalysts for CO₂ hydrogenation.

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