



Article Hydrogen Production via Methanol Steam Reforming over CuO/ZnO/Al₂O₃ Catalysts Prepared via Oxalate-Precursor Synthesis

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Abstract: CuO/ZnO/Al₂O₃ catalysts are commonly used for the methanol steam reforming reaction. The oxalate precursor of CuO/ZnO/Al₂O₃ catalysts were prepared via the co-precipitation method using oxalic acid as the precipitator, deionized water and ethanol as the solvent, and microwave radiation and water baths as aging heating methods, respectively. This suggests that ethanol selects the crystalline phase composition of oxalate precursors and limits their growth. Microwave irradiation prompted the isomorphous substitution between Cu²⁺ of CuC₂O₄ and Zn²⁺ of ZnC₂O₄ in the mother liquid; Zn²⁺ in ZnC₂O₄·xH₂O was substituted with Cu²⁺ in CuC₂O₄, forming the master phase (Cu,Zn)C₂O₄ in the precursor. Moreover, the solid solution Cu-O-Zn formed after calcination, which exhibited nano-fibriform morphology. It has the characteristics of small CuO grains, a large surface area, and strong synergistic effects between CuO and ZnO, which is conducive to improving the catalytic performance of methanol steam reforming. The conversion rate of methanol reached 91.2%, the space time yield of H₂ reached 516.7 mL·g⁻¹·h⁻¹, and the selectivity of CO was only 0.29%.

Keywords: microwave irradiation; CuO/ZnO/Al₂O₃ catalyst; isomorphous substitution; methanol steam reforming

1. Introduction

With exponential growth in global energy consumption and disorderly emissions of greenhouse gases, the production of sustainable and ecofriendly renewable energy is highly urgent [1]. Hydrogen energy is called "the ultimate energy of the 21st century", and hydrogen energy has a huge space for development. Among various hydrogen production methods, hydrogen production via methanol is increasingly favored by researchers, and methanol is easy to store and transport as a raw material [2]. Currently, there are four main ways to produce hydrogen from methanol: methanol decomposition, (MD, Equation (1)), partial oxidative reforming of methanol (POM, Equation (2)) methanol steam reforming (MSR, Equation (3)), and oxidized methanol steam reforming (OSRM, Equation (4)), respectively [3].

$$CH_3OH \rightarrow 2H_2 + CO \quad \Delta H = +128.0 \text{ kJ} \cdot \text{mol}^{-1}$$
(1)

$$CH_3OH + 0.5O_2 \rightarrow 2H_2 + CO_2 \quad \Delta H = -192.2 \text{ kJ} \cdot \text{mol}^{-1}$$
 (2)

$$CH_3OH + H_2O \rightarrow 3H_2 + CO_2 \quad \Delta H = +49.4 \text{ kJ} \cdot \text{mol}^{-1}$$
(3)

$$CH_3OH + (1-n)H_2O + 0.5nO_2 \rightarrow (3-n)H_2 + CO_2 \quad \Delta H = +49(1-n) - 192.2n \text{ kJ} \cdot \text{mol}^{-1}$$
 (4)



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Among the four methods of hydrogen production, MSR is the most widely and deeply studied method. MSR produces the highest amount of hydrogen per mole of methanol, and has the advantages of high hydrogen purity and low CO content [4]. Moreover, MSR technology has a low reaction temperature, low energy consumption, and low investment [5].

Therefore, various transition metal oxides are widely used in MSR. There are two types of catalysts used in MSR for hydrogen production: one type is precious metal catalysts (such as Pd/ZnO, etc.); the other type is non-precious metal catalysts, including non-copperbased catalysts (such as Zn-Cr, etc.) and copper-based catalysts (such as CuO/ZnO/Al₂O₃, etc.). CuO/ZnO, as a promising catalytic material, is widely used and reported on due to its low cost, abundant availability, easy synthesis, low toxicity, and chemical stability [6–8].

Cu-based catalysts can produce H_2 with high selectively at low temperatures and have low CO selectivity; as a result, Cu-based catalysts are widely used. The Cu-based catalysts for MSR have been widely studied, and it was found that the effects of the synergistic effect between CuO and ZnO and the surface structure of CuO/ZnO/Al₂O₃ catalysts on the catalytic activities are critical [9,10].

Co-precipitation is a common method for preparing CuO/ZnO/Al₂O₃ catalysts, and the precipitation process has a profound influence on the structure and properties of the prepared catalysts. Inui et al. [11] studied the effects of pH and temperature on catalyst precursors in the precipitation process. It indicated that the formation of Cu₂(NO₃)(OH)₃ is advantageous when pH \leq 6, whereas (Cu,Zn)₂CO₃(OH)₂ is dominant when pH \geq 7. The effect of temperature on the precursor is mainly to change the reaction rate; it has almost no effect on its phase composition. Spencer et al. [12] studied the phase transition process in the mother liquid; it was indicated that amorphous Cu₂CO₃(OH)₂ was first generated, which gradually transformed into (Cu,Zn)₂CO₃(OH)₂ during the aging process. Fang et al. [13] studied the effects of different feeding methods. Cu₂(NO₃)(OH)₃ mainly formed as a result of the concurrent flow method, which interacts with Zn₅(CO₃)₂(OH)₆ and transforms into (Cu,Zn)₂CO₃(OH)₂ and (Cu,Zn)₅(CO₃)₂(OH)₆, respectively. A CuO-ZnO solid solution formed after decomposition, which is the active phase of the MSR reaction.

The solvents and heating methods are the main factors in the precipitation process. Ma et al. [14] prepared a CuO/ZnO/Al₂O₃ catalyst using ethanol and diethylene glycol as solvents, which possessed a larger superficial area and exhibited higher catalytic performance. Zhang et al. [15,16] synthesized the smaller particle CuO/ZnO/Al₂O₃ catalyst via oxalate co-precipitation using ethanol as a solvent; the catalyst showed better catalytic performance for MSR. Dai et al. [17] investigated the surface property of CuO/ZnO/Al₂O₃ catalysts prepared via oxalate co-precipitation, and explained that isomorphous substitution promoted synergistic effects between CuO and ZnO and increased the superficial content of CuO.

Microwave irradiation heating was rapid, and even in the preparation of catalysts, the active components were well-distributed on the support. Moreover, microwave irradiation could control the micro structure of materials and enhance the selectivity of the target product [18]. It is reported that microwave irradiation had obvious effects on the preparation of ZnO and Al₂O₃ nanoparticles [19]. Zhang et al. [20] treated CuO/ZnO/Al₂O₃ catalysts with microwave irritation (200 W) for 3–10 min; the results showed that the catalyst micro structure was significantly improved, and the catalytic activity of MSR increased by 7%. Fernández et al. [21] synthesized CuO/ZnO precursor mainly containing aurichalcite and CuO/ZnO/Al₂O₃ precursor only containing hydrotalcite, respectively, under microwave irradiation. The aurichalcite was burned into Cu-O-Zn solid solution, which exhibited strong synergistic effects and excellent activity and stability in MSR reactions.

At present, researchers generally believe that the strong synergy between Cu and Zn is conducive to hydrogen production in MSR, providing a lot of direct evidence for the evolution of the structure, morphology, and coordination state of Cu-O-Zn solid solutions, and laying a foundation for the identification of active sites in the catalytic process and the study of interface effects [22–24].

In present work, the synergistic effect between CuO and ZnO was further enhanced using oxalate precursor instead of carbonate precursor, ethanol instead of water as the solvent, and a microwave instead of the conventional heating method. The effects of solvent and heating method on the composition of oxalate precursor, the structure and properties of calcined catalyst, and the final MSR reaction performance were studied from atomic scale to nano scale.

2. Results and Discussion

2.1. XRD Characterization of Precursors

Figure 1 shows the XRD patterns of all catalyst precursors. It is seen that the phases of $CuC_2O_4 \cdot xH_2O$ (2 θ = 18.5°, 23.1°, 31.2°, 36°, 38.5°, JCPDS card No. 48-1054), α -ZnC₂O₄·2H₂O $(2\theta = 18.9^{\circ}, 35.1^{\circ}, \text{JCPDS card No. 25-1029})$, and β -ZnC₂O₄ $(2\theta = 24^{\circ}, 25.1^{\circ}, 29.1^{\circ}, 34.1^{\circ}, 29.1^{\circ}, 34.1^{\circ})$ 36.9°, JCPDS card No. 37-0718) were observed in the precursor of WWP prepared via water solvent and water bath heating. However, only diffraction peaks of $CuC_2O_4 \cdot xH_2O$ $(2\theta = 23.1^{\circ}, 36^{\circ}, 38.5^{\circ}, \text{JCPDS card No. 48-1054})$ and weak peaks of β -ZnC₂O₄ (2 θ = 24°, 36.9°, JCPDS card No. 37-0718) existed in the precursor of EWP prepared using ethanol solvent and water bath heating; no α -ZnC₂O₄·2H₂O phase was observed. It indicated that ethanol solvent restrained the formation of α -ZnC₂O₄·2H₂O, and enhanced the phase selectivity of the product. Microwave irradiation promoted the isomorphous substitution between Cu^{2+} of $CuC_2O_4 \cdot xH_2O$ and Zn^{2+} of ZnC_2O_4 in mother liquid, thus, WMP and EMP mainly contained (Cu,Zn)C₂O₄ and partial CuC₂O₄ failing to be substituted during aging; thus, the diffraction peaks of CuC_2O_4 ·xH₂O ($2\theta = 23.1^\circ$, 36° , JCPDS card No. 48-1054) and β -ZnC₂O₄ (2 θ = 24°, 36.9°, JCPDS card No. 37-0718) overlapped each other and deviated from their original positions. Compared with WWP and EWP, WMP and EMP did not contain diffraction peaks of α -ZnC₂O₄·2H₂O and β -ZnC₂O₄, and the crystal degree failed to be detected due to isomorphous substitution; this indicated that microwave irradiation has strong selectivity on the formation of the crystal phase [25,26].



Figure 1. XRD patterns of the catalyst precursors.

CuC₂O₄·xH₂O, α -ZnC₂O₄·2H₂O, and β -ZnC₂O₄ generated in the mother liquid in coprecipitation, as shown in Equations (5)–(7). The isomorphous substitution mainly occurred in the aging process, it means that the Cu²⁺ of CuC₂O₄ entered into ZnC₂O₄ and the Zn²⁺ of ZnC₂O₄ entered into CuC₂O₄-formed (Cu,Zn)C₂O₄, as shown in Equations (8) and (9). However, the concentration of Cu²⁺ was higher than that of Zn²⁺; it primarily produced CuC₂O₄ as Equation (5) in the mother liquid, and the amount of ZnC₂O₄ was small. In other

$$Cu^{2+} + C_2O_4^{2-} + xH_2O \rightarrow CuC_2O_4 \cdot xH_2O$$
 (5)

$$Zn^{2+} + C_2O_4^{2-} + 2H_2O \to \alpha - ZnC_2O_4 \cdot 2H_2O$$
(6)

$$Zn^{2+} + C_2O_4^{2-} \to \beta - ZnC_2O_4$$
 (7)

$$CuC_{2}O_{4} + xZn^{2+} \to (Cu_{1-x}, Zn_{x})C_{2}O_{4}$$
(8)

$$ZnC_2O_4 + xCu^{2+} \to (Cu_{x}Zn_{1-x})C_2O_4$$
 (9)

2.2. DTG Characterization of Precursors

DTG curves of different catalyst precursors are shown in Figure 2. Three weight loss peaks for WWP were observed at 118 °C, 308 °C, and 343 °C, respectively, as shown in Equations (10)–(13); the peak at 118 °C was due to the desorption of physically absorbed water of α -ZnC₂O₄·2H₂O, whereas the peak around 308 °C was ascribed to the decomposition of CuC₂O₄·xH₂O or (Cu,Zn)C₂O₄, and the peak at about 343 °C was attributed to decomposition of β -ZnC₂O₄ and further decomposition of α -ZnC₂O₄ [15]. The weight loss peak for CuC₂O₄·xH₂O at 307 °C and weak peak for β -ZnC₂O₄ at 343 °C were observed from curve of EWP, which verified the XRD analysis of its precursor.

$$\alpha - ZnC_2O_4 \cdot 2H_2O \rightarrow \alpha - ZnC_2O_4 + 2H_2O \quad t \approx 118 \,^{\circ}C \tag{10}$$

$$CuC_2O_4 \cdot xH_2O \rightarrow CuO + CO_2 + H_2O \quad t \approx 308 \ ^{\circ}C \tag{11}$$

$$\alpha - ZnC_2O_4 \rightarrow ZnO + CO_2 \quad t \approx 343 \ ^{\circ}C \tag{12}$$

$$\beta - ZnC_2O_4 \rightarrow ZnO + CO_2 \quad t \approx 343 \ ^{\circ}C \tag{13}$$

$$(Cu,Zn)C_2O_4 \rightarrow (Cu,Zn)O + CO_2 \quad t \approx 296 \ ^{\circ}C \tag{14}$$



Figure 2. DTG curves of catalyst precursors.

WMP and EMP prepared under microwave irradiation only included the weight loss peak for $(Cu,Zn)C_2O_4$ or $CuC_2O_4 \cdot xH_2O$ at about 300 °C; it can be speculated that microwave irradiation accelerated the isomorphous substitution between Cu^{2+} and Zn^{2+} ; the lesser Zn^{2+} was incorporated into CuC_2O_4 , so there is little content of α -ZnC₂O₄·2H₂O or β -ZnC₂O₄, and there were no corresponding decomposition peaks. In particular, EMP had a large quantity of substitution and produced more $(Cu,Zn)C_2O_4$; the crystal phase trended to uniformity. Therefore, the decomposition peak of EMP became narrower and the decomposition temperature decreased by 12 °C [25]; the peak was mainly ascribed to $(Cu,Zn)C_2O_4$, and partial CuC_2O_4 was unable to be substituted as Equations (11) and (14).

2.3. SEM Images of Precursors and Catalysts

SEM images of different precursors are shown in Figure 3, and SEM images of different catalysts after calcining the corresponding precursors are shown in Figure 4. The appearance of catalysts kept coherence with precursors to some extent by comparing Figures 3 and 4. WWP is a spherical particle with a diameter of about 400 nm. After calcination, it appears as spherical particles and gathers together, and its particle size is reduced to about 300 nm. EWC consists of irregular bars and blocks with a size of 400 nm, indicating that ethanol solvent has an effect on the forming process of precursors in the mother liquor. Compared with EWP, EWC has not changed much in appearance and size; its size is about 300–400 nm, but there are many tiny porous channels in its surface structure.



Figure 3. SEM images of catalyst precursors. (a) WWP; (b) EWP; (c) WMP; (d) EMP.

After microwave irradiation, the morphology of WMP can be observed to be an irregular single wafer, the size of which is between 300 and 500 nm. WMC is an acicular flake, not completely decomposed, with a cross-section diameter of 50–100 nm. When ethanol was further selected as the solvent, EMP mainly contained unidirectional ordered fiber nanoparticles with a cross-section diameter of about 50nm, which were fine, fibrous, or flocculent, and dispersed uniformly after calcination [27].

After combining the SEM photos of the precursor and catalyst, it can be concluded that the precursor forms towards the lower size under the action of bulk heating via microwave. The precursor prepared via water bath was spherical and massive, whereas the precursor prepared via microwave irradiation was single-fiber, and its particle size was smaller than the former. The particle size of EMC is only 50nm, with good dispersion and uniform distribution of surface active sites, which is conducive to improving the catalytic performance of MSR.



Figure 4. SEM images of catalysts. (a) WWC; (b) EWC; (c) WMC; (d) EMC.

2.4. XRD Characterization of Catalysts

XRD patterns of different catalysts can be seen in Figure 5. The average grain size calculated via the Scherrer formula at $2\theta \approx 35.5^{\circ}$, 38.7° and the texture parameters of different catalysts are listed in Table 1. There were no peaks assigned to Al₂O₃ in the four patterns, indicating that Al₂O₃ existed as amorphous or that the content of Al₂O₃ was low. Diffraction peaks of CuO appeared in all the four catalysts at 2θ of 38.7° ; CuO peaks of WWC were very sharp, and the grain size of CuO was comparatively large, up to 18.8 nm as shown in Table 1. The CuO peaks of EWC became smoother when using ethanol as a solvent, in which the ZnO peaks at $2\theta = 34.4^{\circ}$, and 36.3° overlapped with the CuO peak at $2\theta = 35.5^{\circ}$. The CuO grain size of EWC reduced to 12 nm, which indicated that viscous ethanol restricted the growth of the precursor in the mother liquid, resulting in a decrease in CuO grain size after calcination.



Figure 5. XRD patterns of catalysts.

Catalyst	Grain S	Size/nm	Textural Properties		
	$2 hetapprox 35.5^\circ$	$2 hetapprox 38.7^\circ$	Surface Area (m ² /g)	Pore Volume (cm ³ /g)	
WWC	18.8	14.4	43.9	0.27	
EWC	12.0	13.9	56.4	0.31	
WMC	8.9	11.2	59.5	0.29	
EMC	8.4	9.5	77.2	0.36	

Table 1. Grain size values and textural properties of catalysts.

From patterns of WMC and EMC in Figure 5, it can be observed that the CuO peak becomes smoother, after introducing microwaves. Weak peaks of ZnO could still be seen in WMC; however, no peaks assigned to ZnO were detected in EMC. It indicated that isomorphous substitution took place in mother liquid when microwave irradiation was introduced, partial Cu^{2+} of CuC_2O_4 was incorporated into ZnC_2O_4 and almost all Zn^{2+} of ZnC_2O_4 was incorporated into CuC_2O_4 , thereby, the original crystal structure were destroyed and the crystal degree declined after substitution. Cu-O-Zn solid solutions were obtained after calcining WMP and EMP, in which CuO and ZnO coordinate and interact closely with each other in the catalysts. This is because microwave irradiation promotes the substitution of Zn²⁺ in ZnC₂O₄·xH₂O compound with Cu²⁺, and increases the content of the $(Cu_2/Zn)C_2O_4$ phase in precursors during the catalyst preparation process. In the calcined catalysts, Cu and Zn atoms are in close contact, dispersed, and perfectly connected, which, accordingly, enhances the synergistic effect of $Cu/ZnO/Al_2O_3$ catalysts. The CuO crystal was surrounded by the ZnO crystal, which restricted the growth of CuO crystallites; thus, the grain sizes of CuO in WMC and EMC were merely 8.9 nm and 8.4 nm, respectively [26].

As shown in Table 1, catalysts prepared under microwave irradiation possessed larger surface area and bigger pore volume than that prepared in the water bath. The surface area and pore volume of EMC were 77.2 m²/g and 0.36 cm³/g, respectively. This is because the $(Cu,Zn)C_2O_4$ content was higher in precursors prepared under microwave irradiation; the precursor were converted into (Cu,Zn)O (or Cu-O-Zn) solid solution after calcination, in which ZnO and CuO arrayed homogeneously and closely, restricting the agglomeration of CuO. Therefore, the catalysts were very fine and possessed a large surface area. The mother liquid was sol-like after aging when ethanol was selected as a solvent, and the catalyst possessed a large surface area after calcining the corresponding precursor [28]; therefore, the pore volume of EWC and EMC was comparatively large, as shown in Table 1.

2.5. H₂-TPR Characterization of Catalysts

Figure 6 shows H₂-TPR curves of different catalysts. Ethanol restricted the growth of the phase in the precursor and favored the formation of fine catalysts, which made the reduction process easy. It manifested that the reduction temperature of catalysts prepared using ethanol as a solvent was lower than that using water. The catalysts prepared via water bath heating were difficult to reduce; the reduction temperature of WWC and EWC was approximately 240 °C, whereas the reduction temperature of catalysts prepared via microwave irradiation was lower (around 220 °C). It proved again that microwave irradiation selected the phase in the generation process of the precursor; the catalyst was arranged orderly in the micro structure, which decreased the difficulty of reducing CuO with H_2 .

As shown in Figure 6, one low temperature reduction peak and one high emerged in curves of WWC, EWC, and WMC; however, three peaks emerged in the curve of EMC. The first two are low temperature reduction peaks, the third is high temperature reduction peak. Low temperature reduction peaks were assigned to the reduction in scattered phase CuO (Peak I), whereas the other was assigned to the reduction in bulk phase CuO (Peak II). The amount of isomorphous substitution was less when aging mother liquids heated via water bath; thus, its synergistic effect between CuO and ZnO was weak, and bulk phase CuO was mainly found in the corresponding catalyst; thus, Peak II was larger. The amount of substitution between Cu^{2+} and Zn^{2+} was great when aging under microwave irradiation, they mainly generated (Cu,Zn)C₂O₄ in precursors which were calcined into Cu-O-Zn solid solutions. CuO and ZnO coordinate and interact closely with each other in the catalysts; Cu and Zn atoms are in close contact, dispersed and perfectly connected, which accordingly enhances the synergistic effect of Cu/ZnO/Al₂O₃ catalysts. The catalysts were homogeneous and dispersive, and the synergistic effect was strong; thus, Peak I was larger. In particular, the amount of substitution for EMC was great, and the reduction peak assigned to high temperature was much smaller than others [29,30].



Figure 6. H₂-TPR curves of catalysts.

2.6. XPS and AES Characterization of Catalysts

XPS spectra of catalysts are shown in Figure 7. As shown in Figure 7a, all catalysts showed a distinctive BE (binding energy) of Cu $2p_{3/2}$ around 932–933 eV, accompanying a characteristic satellite peak between 940 and 945 eV due to the electron shakeup process, which indicated that Cu species were present as CuO. The BE of Cu $2p_{3/2}$ around 932–933 eV in the spectra of WWC, EWC, WMC, and EMC were 932.0 eV, 932.05 eV, 932.10 eV, and 932.95 eV, respectively, increasing gradually. The BE of $Zn2p_{3/2}$ (Figure 7b) in the corresponding spectra were 1021.45 eV, 1020.6 eV, 1020.35 eV, and 1020.15 eV, decreasing gradually, which were lower than the BE (1022.2 eV) of pure ZnO [31].



Figure 7. XPS spectra of catalysts. (a) Cu $2p_{1/2}$ and Cu $2p_{3/2}$; (b) Zn $2p_{3/2}$.

The results show that homogeneous substitution occurs when microwave is introduced in the aging process. The chemical environment and energy state of copper and zinc in Cu-O-Zn solid solution were changed. Since the electronegativity of zinc is higher than that of copper, the outermost electrons of copper move towards zinc, and the electron density of copper decreased and the binding energy increased, while the electron density of zinc increased and the binding energy decreased [25].

Table 2 lists the data analysis based on XPS and AES spectra and the superficial elements concentration of different catalysts. EMC possessed higher superficial copper content and lower superficial zinc content, its ratio of X_{Cu}/X_{Zn} was up to 8.98, which exceeded all others, it can be verified by the intensity of spectra in Figures 7 and 8. In Table 2, it also could be observed that ethanol solvent help to improve the content of superficial copper atoms. Moreover, microwave irradiation raised the yield of $(Cu,Zn)C_2O_4$ in precursor, leading to lower KE (kinetic energy) of Cu LMM and higher KE of Zn LMM in final catalyst as shown in Figure 8. This was coincident with the results reported in the literature [17].

Table 2. XPS and AES data of different catalysts.

Catalyst —	S	Surface Atom/%		BE(Cu 2p _{3/2})	BE(Zn 2p _{3/2})	KE(Cu LMM)	KE(Zn LMM)
	Cu	Zn	X_{Cu}/X_{Zn}	/eV	/eV	/eV	/eV
WWC	6.56	15.61	0.42	932.00	1021.45	919.10	988.30
EWC	4.96	9.17	0.54	932.05	1020.60	919.05	988.35
WMC	5.49	8.7	0.63	932.10	1020.35	918.95	988.80
EMC	10.77	1.2	8.98	932.95	1020.15	918.20	988.85



Figure 8. AES patterns of catalysts. (a) Cu LMM; (b) Zn LMM.

2.7. Catalytic Performance Test for MSR Reaction

The catalytic performance of different catalysts for MSR is listed in Table 3. When comparing WWC and EWC, it can be concluded that ethanol solvent is conducive to reducing the CO selectivity of the catalyst. As can be seen from the XRD data, ethanol optimized the precursor crystal phase composition, thereby reducing the CO selectivity. When comparing WWC and WMC, it can be concluded that microwave heating can improve the methanol conversion of the catalyst. It can be seen from the BET data and SEM images that microwave radiation increases the specific surface area of the catalyst, improves the dispersion of copper, and increases more active sites, thus increasing the methanol conversion rate. It can be seen from the XRD data that microwave radiation promotes equimolar substitution between copper and zinc oxalate precursors; moreover, Cu-O-Zn solid solution formed after calcination, which possessed strong synergistic effects and benefited the MSR reaction.

Catalyst	Solvent	Heating Manner ^a	X _{MeOH} /%	$STY_{H2}/mL \cdot g^{-1} \cdot h^{-1}$	S _{CO} /% ^b
WWC	Water	WB	53.6	300.0	1.53
EWC	Ethanol	WB	59.1	333.9	0.39
WMC	Water	MI	85.0	479.5	0.82
EMC	Ethanol	MI	91.2	516.7	0.29

Table 3. Catalytic performance of different catalysts for MSR reaction.

^a Evaluation conditions: the molar ratio of water to methanol is 1.5 in the methanol aqueous solution, T = 260 °C, P = 0.5 MPa, WHSV = 1.0 h⁻¹. ^b WB represents water bath, MI represents microwave irradiation. S_{CO}: CO selectivity.

In the aging process of catalyst precipitation mother liquid, microwave irradiation can promote the generation of the $(Cu,Zn)C_2O_4$ phase, and the synergistic effect between CuO and ZnO after the phase roasting is stronger; moreover, the CuO and ZnO grains are smaller, and the surface Cu content is higher, so the active sites are more uniform. The chemical environment and energy state of Cu and Zn components in the catalyst have changed. As the electronegativity of Zn is higher than that of Cu, the outermost electrons of Cu shift to Zn, thus reducing the electron cloud density of Cu and increasing the electron-binding energy, while the electron cloud density of Zn increases and decreasing the electronbinding energy. Thus, it illustrated that both ethanol and microwave irradiation benefited to improve the catalytic performance of MSR, the catalyst EMC prepared via ethanol solvents and microwave heating exhibited optimal catalytic performance; the conversion of methanol was 91.2%, the space time yield (STY) of H₂ reached 516.7 mL·g⁻¹·h⁻¹, and its selectivity of CO was only 0.29%. In stark contrast, the catalyst WWC prepared via water solvent and water bath heating showed the worst catalytic performance. Its conversion of methanol was only 53.6%, and the STY of H₂ was 300.0 mL·g⁻¹·h⁻¹; however, its selectivity of CO was as high as 1.53%.

3. Experimental

3.1. Catalyst Preparation

The Cu-O-Zn/Al₂O₃ catalyst precursors were prepared by dropping 1 mol/L Cu(NO₃)₂-Zn(NO₃)₂-Al(NO₃)₃ (Cu²⁺/Zn²⁺/Al³⁺ = 16/8/1 (molar ratio)) solution and 1 mol/L H₂C₂O₄ solution simultaneously into a beaker while stirring constantly and keeping them in a water bath at 70 °C. Then, the suspension was aged in a microwave oven or a water bath with circulating cooling equipment after co-precipitation; the aging process was conducted at 80 °C for 1 h. The precipitate was filtered and washed with distilled water or ethanol, then the precursor was obtained after drying at 110 °C for 12 h, and the catalyst was obtained after calcining the corresponding precursor at 350 °C for 4 h in the muffle furnace. The precursor was designated as XYP, and the catalyst was designated as XYC; X is W for water, or E for ethanol; Y is W for water bath, or M for microwave irradiation; P is for precursor; C is for calcined catalyst). Table 4 shows the summary of the preparation conditions of the catalysts.

Table 4. Summary of the preparation condition of catalysts.

Catalyst	Precursor	Solvent	Heating Manner
WWC	WWP	Water	Water bath (WB)
EWC	EWP	Ethanol	Water bath (WB)
WMC	WMP	Water	Microwave irradiation (MI)
EMC	EMP	Ethanol	Microwave irradiation (MI)

3.2. Catalyst Characterization

X-ray diffraction (XRD) patterns of solid samples were recorded using a Rigaku D/max 2500 power diffractometer with Cu K α radiation at 40 kV and 100 mA with a scanning rate of 8°/min in the 2 θ ranges from 10° to 40°.

Temperature-programmed reduction (H₂-TPR) was performed in an Autochem II 2920. About 20 mg catalyst sample was set in a U-mode quartz tube, pretreated in helium at 50 °C for 30 min, then heated to 300 °C at a rate of 10 °C /min, under a mixture of 10 vol% H₂/Ar (50 mL/min), the sample was then heated to 600 °C at a rate of 10 °C /min, The consumption of hydrogen was monitored using a thermal conductivity detector.

Differential thermal gravity (DTG) measurement was executed in a STA409C thermal analyzer. 30 mg sample was heated to 600 °C at a rate of 8 °C/min in a gas mixture of 20 vol% O_2/N_2 (50 mL/min).

JSM-6700F cold-field scanning electron microscope (SEM) was used to characterize the size and morphology of the samples.

BET specific surface areas and pore distribution of catalyst was measured with a SORPTMATIC 1990 automatic adsorption instrument employing N_2 as the adsorbent. BET specific surface areas were calculated by applying the Brunauer–Emmett–Teller (BET) method.

X-ray photoelectron spectroscopy (XPS) spectra of the samples were collected on an ESCAL-ab 220i-XL electron spectrometer using Al K α radiation at 300 W. The samples were compressed into the pellets of 2 mm thickness and then mounted on a sample holder. The chamber was maintained at a pressure lower than 10^{-10} Torr. The binding energies were calibrated using C1s as the reference energy (C1s = 284.6 eV).

3.3. Catalytic Performance of MSR

The performance evaluation of MSR was conducted on a continuous flow fixed bed device with a catalyst loading of 2 g, using industrial refined methanol as raw material. Evaluation conditions: raw material methanol aqueous solution (the molar ratio of water to methanol is 1.5), reaction temperature 260 °C, pressure 0.5 MPa, WHSV = 1.0 h^{-1} . After cooling, gas and liquid samples were analyzed using chromatographs equipped with PorpakT columns and TDX-01 columns, respectively, and thermal conductivity cell detectors. The methanol conversion rate and product distribution were calculated.

4. Conclusions

In the process of preparing CuO/ZnO/Al₂O₃ catalyst precursors, ethanol solvent selected the crystal phase composition in precursor and restricted its growth. Microwave irradiation promoted the homogeneous substitution of Cu²⁺ of CuC₂O₄ and Zn²⁺ of ZnC₂O₄ in the mother liquid, Zn²⁺ in ZnC₂O₄·xH₂O was replaced with Cu²⁺ in CuC₂O₄, and the main phase (Cu, Zn) C₂O₄ was formed in the precursor; the solid solution Cu-O-Zn was formed after calcination, which showed a nanofiber shape. It has the characteristics of small CuO grains, large surface area, and a strong synergistic effect between CuO and ZnO, which is helpful for improving the catalytic performance of methanol steam reforming. The methanol conversion rate reached 91.2%, the H₂ spacetime yield reached 516.7mL·g⁻¹·h⁻¹, while the CO selectivity was only 0.29%.

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