Performance Enhancement of CuO/ZnO by Deposition on the Metal-Organic Framework of Cu-BTC for Methanol Steam Reforming Reaction

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Abstract

The commonly used CuO/ZnO catalysts are prone to show unsatisfying performance at higher temperatures for hydrogen generation through methanol steam reforming (MSR) reaction, and thus catalyst modifications are required to enhance the performance of catalysts. In this study, CuO/ZnO was successfully loaded on a metal-organic framework material (Cu-BTC) by the impregnation method, with different masses of Cu-BTC. The catalyst ingredients and microstructure were characterized, and the catalytic performance at the temperature range from 200 to 340 °C was investigated in an MSR test system. The catalytic activity, anti-deactivation ability and stability performance of CuO/ZnO/Cu-BTCs were found to be much better than that of CuO/ZnO. The hydrogen concentration and hydrogen generation rate of CuO/ZnO/Cu-BTCs with 0.5 and 1 g Cu-BTC were increased by about 100% and 1000%, respectively, comparing with the CuO/ZnO catalyst at 300 °C. Although superfluous Cu-BTC caused the evident reduction of catalytic activity at low temperatures, no obvious deactivation happened at higher temperatures. The deposition of CuO/ZnO on Cu-BTC has great potential to enhance the performance at higher temperatures for hydrogen generation through MSR reaction.

Keywords: CuO/ZnO/Cu-BTC; methanol steam reforming; metal-organic framework; thermochemical energy storage; hydrogen

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1. Introduction

During the last decades, global warming and other environmental issues have forced more and more countries to apply stringent regulations about fossil fuel utilization and pay more attention to energy storage technologies.^[1] Thermochemical energy storage technology is a promising way for energy storage with high energy density and long storage time.^[2–4] Among various thermochemical energy storage technologies, the methanol steam reforming (MSR)

reaction is a striking method for its ability to generate massive hydrogen, which also surmounts the transit difficulty and storage problem of hydrogen.^[5–7] What's more, the reacting temperature of MSR typically ranges from 180 to 400 °C, which is much lower than the reacting temperature of methane dry reforming, methane steam reforming and ethanol steam reforming.^[6,8–10] The whole MSR reaction can be described by the following chemical reactions:

Experimental parameters like the structure of reformer^[11–13] and catalyst modification have an impact on the performance of MSR reaction.^[14–17] Recently, the investigation about the

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MSR reaction focuses on the copper-based catalyst for its low cost.^[18,19] Among all the copper-based catalysts, CuO/ZnO is the most common one, due to its wide utilization in methanol steam reforming field. However, CuO/ZnO shows good catalytic activity only at temperature of around 250 °C, and deactivation typically happens at temperatures larger than 250 °C.^[5] To improve the catalytic activity, anti-deactivation ability and stability performance of CuO/ZnO at higher temperatures, CuO/ZnO catalysts were modified in different ways. Mateos-Pedrero *et al.*^[20] changed the surface area and polarity ratio of ZnO in CuO/ZnO catalyst and found that higher polarity ratio contributed to better catalytic performance, but no deactivation analysis of the catalysts was carried out in their study. Pu *et al.*^[21] modified CuO/ZnO catalysts with the addition of Sc, by which the hydrogen production rate of CuO/ZnO/Sc₂O₃ at temperatures higher than 260 °C was increased by three times. Besides, Al₂O₃ was utilized as a promoter of the CuO/ZnO catalysts as well. However, most of the activity tests were carried out at temperatures from 200 to 260 °C, and no deactivation analysis of the CuO/ZnO/Al₂O₃ was performed as well.^[15,22-25] Likewise, Pan *et al.*^[26] and Zhou *et al.*^[27] added Zr to improve the reducibility of copper and achieve higher metal surface area, but the deactivation phenomenon was also ignored. In summary, the modification materials of the CuO/ZnO catalysts in the previous works mainly included aluminum, zirconium and strontium, whose influence on the catalytic activity and anti-deactivation ability at temperatures higher than 260 °C was either unsatisfying or seldomly analyzed. Besides, the supports mentioned above had impacts on the catalyst structure, while, they would not assist copper with the MSR reaction. Thus, it would be better if there is one material with the splendid supporting capability and ability to assist copper with the MSR reaction. Cu-BTC (metal-organic framework material) could serve as the dual-functional supporting material for the MSR reaction due to its unique structure and ability to participate in the MSR reaction.

Cu-BTC (MOF-199, HKUST-1), proposed by Chui *et al.*,^[28] is one kind of metal-organic framework (MOF) materials, most of which have been utilized in various fields.^[29-34] Cu-BTC utilizes copper ion as the connection point with TMA (benzene-1,3,5-tricarboxylate) as ligands. Concerning the structure of Cu-BTC, the polymer with face-centered-cubic crystals contains an intersecting three-dimensional (3D) system of large square-shaped pores (9 Å by 9 Å). Moreover, according to the thermogravimetric analysis characterization, ten H₂O molecules don't function as the structure connection in each Cu-BTC unit, which indicates that there are unsaturation coordination points in Cu-BTC. The unique 3D porous structure and unsaturation coordination points endow Cu-BTC with splendid supporting ability, which have been utilized in many fields. Ökte *et al.*^[35] loaded ZnO along with TiO₂ on the Cu-BTC and tested the

adsorption and photocatalytic performance of the composites. Cu-BTC based composites showed higher dark adsorption abilities and higher degradation efficiencies toward methylene blue. Wee *et al.*^[36] loaded Keggin phosphotungstic acid on Cu-BTC and applied the composites to the esterification reaction of acetic acid and propanol. When the ratio of acetic acid and propanol was 1:40, the best catalytic performance was achieved at the catalyst size of 50 nm. Zhao *et al.*^[37] loaded silver on Cu-BTC and treated the composites at 250 °C to obtain Ag/Cu_xO (x=1.2) nanoparticles. The synergy between Cu_xO and Ag enhanced the catalytic activity for CO oxidation. However, based on the researches mentioned above, it is found that Cu-BTC has not been used in the MSR reaction yet.

Due to that Cu-BTC has a unique structure and copper core, it is of great potential to support the CuO/ZnO catalyst and improve the catalytic activity and anti-deactivation ability at higher temperatures. In this study, CuO/ZnO was loaded on Cu-BTC by the impregnation method. For comparison, a regular CuO/ZnO (CZ) catalyst was also prepared. The catalysts were characterized through various ways to investigate the microstructure and the elemental distribution. Besides, an MSR system with a conventional quartz tubular reactor was built for the catalytic activity tests at the broad temperature range from 200 to 380 °C. By combining the characterization of the catalysts with the catalytic performance and the anti-deactivation ability, the overall performance of the CuO/ZnO/Cu-BTC and the effect of the Cu-BTC as supports were analyzed.

2. Experimental

2.1 Preparation of Cu-BTC supports

Cu-BTC (HKUST-1, MOF-199) samples were prepared by the hydrothermal method.^[28] 4.5 mmol (1.1075 g) copper nitrate trihydrate (AR 99% purity, Aladdin Reagent (Shanghai) Co., Ltd.) was dissolved in 15 mL ultra-pure water, while 2.5 mmol (0.6363 g) benzene-1,3,5-tricarboxylate (98% purity, Aladdin Reagent (Shanghai) Co., Ltd.) was dissolved in 15 mL ethanol (≥99.5% purity, Aladdin Reagent (Shanghai) Co., Ltd.). The two solutions were placed separately in the ultrasonic machine, which run in 50 Hz for 15 min to obtain the fully dissolved solutions, and then they were mixed in a 50 mL para polyphenyl lined stainless autoclave that was kept at 120 °C for 24 h. The autoclave was cooled down to the ambient temperature naturally. Then, the resultant was filtered and washed with ethanol and ultra-pure water by vacuum filtration to get rid of the trace Cu₂O. Eventually, the obtained cyan Cu-BTC was dried at 120 °C for 12 h.

2.2 Preparation of CuO/ZnO/Cu-BTCs

The main preparation procedure of CuO/ZnO/Cu-BTC is illustrated in Fig. 1. CuO/ZnO/Cu-BTC catalysts were prepared by the impregnation method. 36.8 mmol (8.8876 g)

Fig. 1 Main fabrication procedure of CuO/ZnO/Cu-BTCs.

copper nitrate trihydrate (AR 99%, Aladdin Reagent (Shanghai) Co., Ltd.) and 13.2 mmol (3.9309 g) zinc nitrate hexahydrate (AR 99%, Aladdin Reagent (Shanghai) Co., Ltd.) were completely dissolved in 200 mL ultra-pure water, and 51.2 mmol (5.4396 g) sodium carbonate (AR≥99.5%, Shanghai Macklin Biochemical Co., Ltd.) was dissolved in 200 mL ultra-pure water. The nitrate solution was slowly added into the sodium carbonate solution with vigorous stirring, and the resulting $\text{CuCO}_3/\text{ZnCO}_3$ suspensions were continuously agitated for 2 h at the ambient temperature to guarantee total coprecipitation. After 2 hrs continuous agitation, Cu-BTC powders were slowly added into the agitating $\text{CuCO}_3/\text{ZnCO}_3$ suspensions. Different masses (0.5 g, 1 g, 2 g, 4 g) of Cu-BTC powders were added in the experiments to investigate the effect of Cu-BTC content on the catalyst performance. The resulting mixtures were continuously stirred for 12 hrs at the room temperature and washed several times with ultra-pure water. Drying was performed at 120 °C for 12 hrs followed by the calcination at 500 °C for 6 hrs with the protection of argon. Calcined CuO/ZnO/Cu-BTC catalysts were tableted under 5 MPa pressure and then crushed. Particles (1 g) of size 40-60 mesh were sieved and mixed with 1 g quartz sand of size 50-80 mesh (Shanghai Macklin Biochemical Co., Ltd.) for the subsequent catalytic performance tests. The obtained composites were named as CZC-0.5, CZC-1, CZC-2, CZC-4, respectively, corresponding to the different Cu-BTC addition masses of 0.5 g, 1 g, 2 g, and 4 g.

CuO/ZnO was also prepared by the coprecipitation method, comparing the performance of the prepared CuO/ZnO/Cu-BTC with the conventional CuO/ZnO. The production of $\text{CuCO}_3/\text{ZnCO}_3$ suspension used the same procedure as mentioned in the preparation of CuO/ZnO/Cu-BTCs. The obtained $\text{CuCO}_3/\text{ZnCO}_3$ suspensions were filtered and washed several times with ultra-pure water to remove the unreacted nitrates and sodium carbonate. The purified resultant was dried in air at 120 °C for 12 hrs. The obtained dry material

was ground into powders and calcined at 500 °C for 6 hrs, during which argon was utilized for protection. The CuO/ZnO catalyst was tableted under 5 MPa pressure and then crushed. 1 g particles of size 40-60 mesh were sieved and mixed with 1 g quartz sand of size 50-80 mesh (Shanghai Macklin Biochemical Co., Ltd.) for the subsequent catalytic performance tests. Besides, the obtained composite was denoted as CZ.

2.3 Characterization of CuO/ZnO/Cu-BTCs

The X-ray diffraction (XRD) patterns of Cu-BTC were obtained on the Bruker D8 Focus X-ray Diffractometer at 40 kV and 40 mA from 5° to 40° and with a scan speed of 0.05 second/step, while the XRD patterns of CuO/ZnO/Cu-BTCs and CuO/ZnO were obtained at 40 kV and 40 mA from 5° to 80° with a scan speed of 0.05 second/step. The scanning electron microscope (SEM) images of the catalysts were recorded by the JSM-7800F Schottky Field Emission Scanning Electron Microscope. Before scanning, gold sputtering treatment was applied to the materials for better electric conduction.

To investigate the microstructure and morphology of the catalysts, CuO/ZnO/Cu-BTCs and CuO/ZnO were subjected to a Tecnai G2 F30 field Emission Gun Transmission Electron Microscope at 300 kV. The samples were dispersed in ethanol by ultrasonication and a drop of the solution was deposited onto a thin copper film. Meanwhile, the elemental analysis was performed on an energy dispersive X-ray analysis unit fixed in the TEM equipment.

2.4 Catalytic activity tests of CuO/ZnO/Cu-BTCs

A methanol steam reforming reaction system was constructed for the catalytic activity tests. The flow chart is shown in Fig. 2. Four components made up the whole system including a reactant injection part, a heating part, a condensation part and a syngas analysis part. In the reactant injection part, a peristaltic pump was utilized to inject methanol solution. To

Fig. 2 The flow chart of the MSR reaction performance evaluation system.

maintain steady syngas flow, the flow rate of the carrier gas and argon was controlled by a flow meter. As for the heating part, an evaporator with sprayer ensured the complete evaporation of methanol and water. Furthermore, the evaporator also functioned as a preheater to assist the tubular quartz reactor, which was loaded with 2 g composites (1 g catalysts mixed with 1 g quartz sand). In the condensation part, a condenser was placed before the gas-liquid separator to cool the high-temperature syngas down. The unreacted methanol and water were deposited in the separator in the liquid phase. In the syngas analysis part, the syngas from the separator was dried by a drier, while the flow rate was measured by a flow meter and the syngas was eventually analyzed by a gas chromatograph (Shimadzu GC-2014).

The operating processes of the tests are introduced below. First, the argon flow rate was kept at around 15 mL/min for half an hour to get rid of the air in the whole system. Second, when the tubular quartz reactor loaded with 2 g catalyst mixture was heated up to the setting temperature with the rate of 10 °C/min, the evaporator started to be heated to 200 °C. Third, the peristaltic pump which was set at around 0.7 mL/min started to inject the methanol solution, where the

H₂O/CH₃OH (S/C) molar ratio was 1.1/1 and the ratio of weight of catalyst to feed of methanol solution (W/F) was 1.4 (g·min/mL). At last, the gas chromatograph was started to analyze the ingredients of the syngas.

Several parameters were detected and calculated to evaluate the MSR reaction performance of CuO/ZnO/Cu-BTC, including the hydrogen concentration (N_{H₂}), the hydrogen selectivity (S_{H₂}), the CO concentration (N_{CO}), the CO selectivity (S_{CO}) and the hydrogen generation rate (V_{H₂}). The hydrogen concentration and CO concentration were detected by the gas chromatograph, and other parameters mentioned above were calculated by the following equations:

$$\text{Hydrogen selectivity : } S_{H_2} = \frac{N_{H_2}}{N_{H_2} + N_{CO}} \quad (4)$$

$$\text{CO selectivity : } S_{CO} = \frac{N_{CO}}{N_{H_2} + N_{CO}} \quad (5)$$

$$\text{Hydrogen generationrate : } V_{H_2} = V_{\text{syngas}} \times N_{H_2} \times e \quad (6)$$

where V_{syngas} is the syngas flow rate detected by the flow meter before the gas chromatograph and e is the modification coefficient of the syngas flow rate given by the manufacturer HORIBA.

$$e = \frac{0.3106 \times (N_{H_2} + 1 \times N_{CO} + 1.01 \times (1 - N_{H_2} - N_{CO}))}{\rho_{H_2} \times C_{PH_2} \times N_{H_2} + \rho_{CO} \times C_{PCO} \times N_{CO} + \rho_{Ar} \times C_{PAr} \times (1 - N_{H_2} - N_{CO})} \div 1.415 \quad (7)$$

where ρ_{H_2} , ρ_{CO} and ρ_{Ar} represent the density of hydrogen, carbon monoxide and argon, while C_{PH_2} , C_{PCO} and C_{PAr} are the corresponding constant-pressure specific heats.

3. Results and discussion

3.1 Properties and characterization of CuO/ZnO/Cu-BTCs, CuO/ZnO and Cu-BTC

The XRD patterns of CZ, CZC-0.5, CZC-1, CZC-2, CZC-4 are shown in Fig. 3. The catalysts showed diffractions of d 100, d 002, d 101, d 102, d 110 and d 103 at 31.7°, 34.4°, 36.2°, 47.5°, 56.5° and 62.8°, respectively, which demonstrates the existence of zinc oxide, while diffraction peaks of d 110, d 111, d 020 and d 211 at 32.5°, 38.7°, 53.4° and 66.1°

demonstrate the successful synthesis of copper oxide. However, copper peaks of d 111, d 200 and d 220 at 43.3°, 50.4° and 74.1°, respectively, appeared in the patterns of CZC-1, CZC-2, CZC-4, indicating the added Cu-BTC might be superfluous. In this case, it is proved that the superfluous Cu-BTC will be calcined into copper at 500 °C, which could assist the copper from the coprecipitation with the catalytic activity.

In the desiccation process of the Cu-BTC fabrication, the existence of air had a significant impact on the color of Cu-BTC. When the Cu-BTC was dried in the air, the resulting material demonstrated aquamarine. However, the Cu-BTC was dark blue when dried in vacuum circumstance. The Cu-BTC dried in vacuum turned to aquamarine as well when exposed in the air for a long time. In case that the structure of Cu-BTC

was affected during the desiccation, the XRD patterns of the Cu-BTC under different dry conditions were obtained and are shown in Fig. 4. The calculated XRD curve was derived from Chui *et al.*^[28] Whatever the dry condition was, the fabricated Cu-BTC's XRD patterns correspond to the patterns in the literature well at 5.8°, 6.7°, 9.5°, 11.6°, 13.4°, 14.7°, 16.5° and 19°. Therefore, the property of Cu-BTC has nothing to do with the dry condition. What's more, it is known that the Cu-BTC trihydrate is aquamarine and will be dehydrated at 120 °C into anhydrous Cu-BTC which is dark blue and cannot decompose until 240 °C. The anhydrous Cu-BTC exposed in the air will adsorb water and turn into Cu-BTC trihydrate sooner or later. In summary, the resulting material dried in the air was Cu-BTC trihydrate due to the presence of water in the air, while the resulting material dried in vacuum was anhydrous Cu-BTC.

The SEM images of Cu-BTC are shown in Fig. 5. In the micrometer scale, the fabricated Cu-BTC shows a faceted octahedral structure, which is consistent with Ref. [28] and suggests that the Cu-BTC is of splendid support capability.

The SEM images of CZ, CZC-0.5, CZC-1, CZC-2, CZC-4 are presented in Fig. 6. Each catalyst was scanned at both 3,000x and 10,000x magnifications to observe the overall structure and small particles on the surface. It is clear that nanoparticles were observed on the surface of the catalysts, and small distinctions existed for different addition masses of Cu-BTC. Besides, CZ showed the smallest particle size among the catalysts, while the particle size of CZC-0.5 was slightly

Fig. 3 The X-ray diffractograms of CZ, CZC-0.5, CZC-1, CZC-2 and CZC-4.

Fig. 4 The X-ray diffractograms of Cu-BTC under different dry conditions.

Fig. 5 The faceted octahedral structure of Cu-BTC in the SEM images.

Fig. 6 The SEM images of CZ (a), (b), CZC-0.5 (c), (d), CZC-1 (e), (f), CZC-2 (g), (h), CZC-4 (i), (j) at 5 μm (×3,000 magnification) and 2 μm (×10,000 magnification) scales.

bigger than that of CZ but similar to that of CZC-1, CZC-2 and CZC-4. On the other hand, the nanoparticles on the CZC-1 and CZC-0.5 surfaces were more well-distributed than that of CZC-2 and CZC-4. Meanwhile, massive catalyst pieces were commonly found in CZC-4, where nanoparticles on the surface were relatively rare. The differences in the surface structure will influence the MSR reaction performance, which will be discussed later.

The catalysts were further analyzed by the TEM and EDS-mapping to verify that copper oxide and zinc oxide were loaded on the Cu-BTC successfully and investigate the nanoparticles on the surface. The TEM images and EDS-mapping of CZ, CZC-0.5, CZC-1, CZC-2, CZC-4 are given in Fig. 7 and Fig. 8, respectively. According to Fig. 8(b) and (c), zinc was well dispersed on copper. According to Fig. 7(c), a

conclusion can be drawn that the bigger particles of 60 nm size were copper oxide and the particles of 30 nm that were connected to copper oxide were zinc oxide. Besides, in Fig. 7(f) and (i), bigger particles of about 100 nm were observed. According to their EDS-mapping, these particles can be validated as the calcined Cu-BTC. According to the 100 nm TEM images of the CZCs, smaller copper oxide particles and zinc oxide particles were connected to the bigger particles, which demonstrates the successful support of the calcined Cu-BTC. In Fig. 7(j) and (m), the CZC-2 and CZC-4 suffered severer agglomeration than the CZC-1 and the CZC-0.5. Besides, in Fig. 8(n) and (o), the superfluous Cu-BTC resulted in the uneven distribution of zinc on the copper in CZC-4, where little zinc was observed in several copper particles.

In a word, the XRD patterns of the catalysts indicate the

Fig. 7 The TEM images of CZ (a, b, c), CZC-0.5 (d, e, f), CZC-1 (g, h, i), CZC-2 (j, k, l) and CZC-4 (m, n, o) at different magnifications.

Fig. 8 The element distributions of CZ (a, b, c), CZC-0.5 (d, e, f), CZC-1 (g, h, i), CZC-2 (j, k, l) and CZC-4 (m, n, o) by the EDS-mapping.

successful synthesis of CuO/ZnO and CuO/ZnO/Cu-BTCs. The discovery of copper peaks demonstrates the unique property of the Cu-BTC calcined at 500 °C. Moreover, the SEM images, TEM images and EDS-mapping denote that copper oxide and zinc oxide have been successfully loaded on

the Cu-BTC and the agglomeration appeared with the superfluous Cu-BTC.

3.2 Catalytic activity of CuO/ZnO/Cu-BTCs and CuO/ZnO

The catalysts reacted with methanol and steam at 250 °C first

to reduce the CuO to Cu referring to Ref. [38]. The methanol steam reforming reaction on the composite catalysts were carried out at 1.2 atm, $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ (S/C) molar ratio of 1.1/1 and weight of catalysts to feed of methanol solution (W/F) ratio of 1.4 g-min/mL, and various reaction temperatures were tested in the range of 200–340 °C. Catalyst mixture (1 g catalyst mixed with 1 g quartz sand) was continuously tested at each temperature condition, where quartz sand aimed to increase the aspect ratio of the catalyst bed and prevent the catalyst particle from overheating. Each test took about eight hours to stabilize the syngas ingredient concentration. When the hydrogen concentration of the syngas remained unchanged, the flow rate of the syngas would be recorded. Then the reacting temperature would be raised by 20 °C and a new test begun. The hydrogen concentration and the carbon monoxide concentration were constantly detected by the gas chromatograph (GC-2014). Eight data around the peak concentration were recorded, and the mean values of the eight data were defined as the exact hydrogen and carbon monoxide concentrations at each temperature.

The values of hydrogen concentration and hydrogen selectivity at different reaction temperatures for the different catalysts are shown in Fig. 9 and the mass fractions of carbon monoxide and hydrogen are shown in Table 1. According to Fig. 9(a) and Table 1, at the low temperature zone from 200 °C to 240 °C, the CZ showed better catalytic performance. According to Roselin *et al.*^[39], the catalytic performance of the

catalysts fluctuated greatly with the change of the weight ratio of copper at relative low temperature, which might have led to the worse catalytic performance of CZCs. When the temperature went higher, the hydrogen concentration of CZ decreased from 33.52% at 260 °C to 30.05% at 280 °C and 19.26% at 300 °C, indicating that CZ suffered severe catalytic deterioration when the reaction temperature was above 260 °C. Whereas, no obvious catalytic deterioration happened for CZC-0.5 and CZC-1 until 300 °C. The hydrogen concentrations of CZC-0.5 and CZC-1 at 260 °C were increased by 13% and 9%, respectively, compared with that of CZ at 260 °C. While at 300 °C, the hydrogen concentrations of CZC-0.5 and CZC-1 were increased by 115% and 126%, respectively, compared with that of CZ. Concerning CZC-2, the performance was close to that of CZ before 280 °C. Notably, the hydrogen concentration of CZC-2 kept 28.52% at 300 °C and 24.12% at 320 °C, which were much higher than that of CZ. Therefore, the overall hydrogen concentration of CZC-2 was still better than that of CZ. As for CZC-4, despite of the relatively lower hydrogen concentrations at relatively low temperatures, the increase of the hydrogen concentration with the reaction temperature was steady and no catalytic deterioration was found. The catalytic performance of CZC-4 even surpassed CZ and CZC-2 at 320 °C.

In summary, the above results show that the addition of Cu-BTC contributed to the improvement of catalytic activity and anti-deactivation ability at the temperature higher than

Fig. 9 The values of hydrogen concentration (a) and hydrogen selectivity (b) at different reaction temperatures for the CuO/ZnO/Cu-BTCs and CuO/ZnO (S/C=1.1, W/F=1.4).

Table 1. Outlet gas component and mass fraction at different temperatures

	CZ (%)		CZC-0.5 (%)		CZC-1 (%)		CZC-2 (%)		CZC-4 (%)	
	H_2	CO	H_2	CO	H_2	CO	H_2	CO	H_2	CO
200	92.5	7.5	84.1	15.9	78.3	21.7	91.9	8.1	89.4	10.6
220	90.5	9.5	83.2	16.8	73.8	26.2	86.1	13.9	88.8	11.2
240	86.5	13.5	81.7	18.3	73.4	26.6	78.7	21.3	85.3	14.7
260	81.4	18.6	78.9	21.1	81.4	18.6	70.7	29.3	83.6	16.4
280	71.5	28.5	75.1	24.9	77.3	22.7	67.2	32.8	85.3	14.7
300	66.8	33.2	70.0	30.0	74.8	25.2	69.7	30.3	88.0	12.0
320	86.7	13.3	60.8	39.2	67.4	32.6	84.4	15.6	89.8	10.2
340	90.6	9.4	88.0	12.0	85.7	14.3	86.7	13.3	90.0	10.0

260 °C. However, the performance of the CZCs was influenced by the quality of Cu-BTC added and the microstructure of the catalysts. For CZC-0.5 and CZC-1, due to the well-dispersed nanoparticles on the surface of the catalysts, they possessed the best catalytic activity and delayed its decay temperature to 320 °C. As for CZC-2, the overloaded Cu-BTC resulted in slightly agglomeration as seen in the microstructure characterization, which caused the lower hydrogen concentration at temperatures higher than 260 °C. Concerning CZC-4, the superfluous Cu-BTC caused severe agglomeration according to the SEM images (Fig. 6(h) and (j)) and TEM images (Fig. 7(j) and (m)), where uneven distribution of nanoparticles on the surface was also observed. The unsatisfying microstructure of CZC-4 resulted in the worst catalytic activity at low temperatures while the overloaded Cu-BTC ensured no decline of hydrogen concentration at higher temperatures.

In Fig. 9(b), the hydrogen selectivity of CZ showed the highest values in the temperature range from 200 °C to 260 °C. Due to the significant decline of hydrogen concentration at the higher temperatures, the hydrogen selectivity of CZ decreased from 98.39% at 260 °C to 97.24% at 280 °C and 96.57% at 300 °C. For CZC-0.5, CZC-1 and CZC-2, the hydrogen selectivity tended to decrease with the reaction temperature at the temperature range between 200 °C and 300 °C from the overall perspective. For CZ and CZC-2 at 320 °C, the hydrogen selectivity experienced a sudden increase and the same condition could be found for CZC-0.5 and CZC-1 at 340 °C as well, whose hydrogen selectivity increased to 99.04% and 98.82% respectively.

Combining with the three reactions mentioned in the introduction, we believe that the catalytic performance of the catalysts should be separated into two parts including the ability to generate hydrogen (reaction (2) and reaction (3)) and the ability to generate carbon monoxide (reaction (2)). When the ability for CZ and CZC-2 to generate hydrogen by reaction (3) which is exothermic declined at the temperatures higher than 260 °C, the ability to generate carbon monoxide by reaction (2) didn't decline until 300 °C for CZ and 280 °C for CZC-2, which resulted in the continuously decrease of hydrogen selectivity. When the temperature was higher than 300 °C for CZ and CZC-2, the reaction (2) was receded, which led to the decrease of the CO generated and hence the sudden increase of the hydrogen selectivity. The hydrogen generation rate shown in Fig. 10 which decreased at the temperature higher than 300 °C proves the recession of the reaction (2). For CZC-0.5 and CZC-1, the sudden increase of the hydrogen selectivity at 320 °C could be explained by the same way as the CZC-2, while the turning points of CZC-0.5 and CZC-1 were delayed to 320 °C because of appropriate Cu-BTC added. However, the hydrogen selectivity of CZC-1 was relatively low at temperature below 260 °C, which could be attributed to that a small part of CZC-1 unreduced consumed a

Fig. 10 The values of hydrogen generation rate at different reaction temperatures for the CuO/ZnO/Cu-BTCs and CuO/ZnO (S/C=1.1, W/F=1.4).

part of generated hydrogen. When the temperature was increased to 260 °C, the reduction was fully completed, leading to the regular hydrogen selectivity. Meanwhile, the overall hydrogen selectivity of CZC-4 was the best, and even the lowest hydrogen selectivity was higher than 98.5%. According to the higher hydrogen selectivity of CZC-4, where the majority of the copper came from Cu-BTC, it was suspected that the copper calcined from Cu-BTC might possess a unique structure to depress the yield of carbon monoxide. Overall, the hydrogen selectivity of CZCs was still kept at a relatively high level (higher than 95%).

The hydrogen generation rates of the catalysts at different reaction temperatures are shown in Fig. 10. In the temperature range from 200 °C to 240 °C, little difference existed for CZ, CZC-0.5 and CZC-1. However, the hydrogen generation rate of CZC-0.5 was increased by 95% at 260 °C, 199% at 280 °C, 857% at 300 °C and 759% at 320 °C respectively, compared with the hydrogen generation rate of CZ, while the hydrogen generation rate of CZC-1 was increased by 59% at 260 °C, 165% at 280 °C, 1155% at 300 °C and 1196% at 320 °C, respectively. With respect to CZC-2, the hydrogen generation rate was similar to that of CZ until 280 °C. Whereas, the hydrogen generation rate of CZC-2 was increased by 119% at 300 °C and 328% at 320 °C compared with that of CZ. CZC-4 showed the lowest rates at the temperature range from 200 °C to 280 °C, but surpassed CZ at 300 °C and 320 °C. Likewise, the drop of hydrogen generation rate started at 280 °C for CZ, 300 °C for CZC-0.5, 320 °C for CZC-1 and 300 °C for CZC-2, while no decline happened for CZC-4. Generally, the trend of CZCs in the hydrogen generation rate was consistent with that in the hydrogen concentration shown in Fig. 9(a). Whereas, taking 300 °C as example, compared with only about 100% growth in the hydrogen concentration, the hydrogen generation rates of CZC-0.5 and CZC-1 were increased by about ten times. This could be caused by the fact that the contact area between catalysts and reactants was increased benefiting from the well-distributed nanoparticles on the surface of CZC-0.5 and CZC-1

(as shown in Fig. 6(d) and (f)), and further confirmed the positive effect of Cu-BTC on the catalytic activity.

The values of carbon monoxide concentration and carbon monoxide selectivity at different reaction temperatures of the different catalysts are presented in Fig. 11. Combining with Fig. 9, Fig. 11(a) and (b) further verifies that the temperature where the ability to generate hydrogen decayed was lower than the temperature where the ability to generate carbon monoxide

decayed. Besides, CZ, CZC-0.5, CZC-1 and CZC-2 showed little distinction in the ability of carbon monoxide depression according to Fig. 11(a). Whereas, the CO selectivity and concentration of CZC-4 were kept at a low level during the whole tests. This indicates the copper calcined from Cu-BTC as the majority catalytic matter might have positive effects on the carbon monoxide depression, which was consistent with the discussion in Fig. 9(b).

Fig. 11 The values of CO concentration (a) and CO selectivity (b) at different reaction temperatures for the CuO/ZnO/Cu-BTCs and CuO/ZnO (S/C=1.1, W/F=1.4).

3.3 Deactivation of CuO/ZnO/Cu-BTCs and CuO/ZnO

The SEM images of the catalysts after long-time reaction were illustrated in Fig. 12. As is illustrated, it is obvious that the particle size of the CZCs expanded with the increase of the Cu-BTC addition, where the particle of CZC-4 was too big to find a separated unit. The bigger small stings could be observed in CZC-0.5, CZC-1 and CZC-4 while the stings in CZC-2 were long enough to be called as branches. Combining with the catalytic activity in section 3.2, the small stings could be viewed as the effective structure that delayed the decay of the catalytic performance to the higher temperature. Whereas, the branches in CZC-2 was so giant (micrometer scale) compared with the small stings (nanometer scale) that the reaction dynamic might be disturbed, which made the catalytic performance of CZC-2 decay ahead at 280 °C.

Taking CZC-1 as the example, the mechanism of the catalytic deterioration was analyzed by Fig. 13. Fig. 13(a) and (b) show the SEM images of CZC-1 before and after the whole reaction tests. It could be seen that the size of the particles on the surface after the reaction tests (around 500 nm) was much bigger than that before the reaction tests (around 150 nm), which indicates the agglomeration was formed during the sintering of copper particles. The agglomeration of the particles caused the deactivation of the catalysts. On the other hand, based on Xu *et al.*^[5] and Li *et al.*,^[40] zinc oxide can inhibit the sintering of copper during the reaction. Considering the agglomeration and the inhibition of zinc oxide mentioned above, the catalyst deactivating process can be illustrated as seen in Fig. 13(c). After long-time reaction, several copper particles that were closed to each other sintered into one bigger

Fig. 12 The SEM images of CZ (a), CZC-0.5 (b), CZC-1 (c), CZC-2 (d) and CZC-4 (e) after long-time reaction.

Fig. 13 (a) The SEM image of CZC-1 before the MSR reaction, (b) the SEM image of CZC-1 after the MSR reaction, and (c) the illustration of copper sintering process.

copper particle, while the copper particles separated by ZnO particles did not sinter together into giant particles.

3.4 Stability of CuO/ZnO/Cu-BTCs and CuO/ZnO

To study the stability performance of the catalysts, a 24-hour stability test was applied at 260 °C. To begin with, the rank of the hydrogen generation rate was consistent with that in Fig. 10. The average values of eight data around the peak rate in the beginning and eight data at the end were recorded in Table 1, where the mean decay rates of the catalysts during the 24 hours were demonstrated as well. According to Fig. 14 and Table 2, the stability performance of CZ was the worst, whose decline rate was nearly as twice as that of CZCs. In this case, the addition of Cu-BTC was of great beneficial to the stability performance. Integrating with the catalytic activity mentioned in section 3.2, CZC-1 possessed the best catalytic performance from the overall perspective, whose stability performance,

Fig. 14 The values of the hydrogen generation rate during the 24-hour stability test at 260 °C for the catalysts.

Table 2. Catalytic performance decline of the catalysts

	Starting rate (mL·min ⁻¹)	End rate (mL·min ⁻¹)	Difference (mL·min ⁻¹)	Decline rate (mL·min ⁻¹ /h)
CZ	52.00	31.34	20.65	0.86
CZC-0.5	56.35	48.43	7.91	0.33
CZC-1	55.24	43.89	11.35	0.47
CZC-2	47.17	40.02	7.15	0.30
CZC-4	22.76	15.25	7.51	0.31

though, was unsatisfying. CZC-2 standing out in the stability test showed inferior catalytic activity. Whereas, the catalytic activity of CZC-0.5 was close to that of CZC-1, and CZC-0.5 also demonstrated fine stability performance. In conclusion, from the aspect of both catalytic activity and stability performance, CZC-0.5 was the best. However, it is also predicted that there would be an optimal loading mass between 0.5 g and 1 g, which endows the catalyst with both high catalytic activity and superior stability performance.

4. Conclusion

In this paper, CuO/ZnO was loaded on different masses of Cu-BTC to improve the catalytic activity, anti-deactivation ability and stability performance of the catalysts for methanol steam reforming reaction. The CuO/ZnO/Cu-BTCs and the Cu-BTC were characterized by XRD, SEM, TEM and EDS-mapping, which confirmed the successful synthesis of the materials. Meanwhile, an MSR system with a conventional fixed bed tubular-quartz reactor was developed to study the catalytic activity, anti-deactivation ability and stability performance of CuO/ZnO/Cu-BTCs at the temperature from 200 °C to 340 °C. The results showed that proper addition of Cu-BTC (e.g., 0.5 g

and 1 g) endowed the catalysts with splendid microstructures, where nanoparticles were uniformly distributed on the surface. Benefiting from the excellent microstructures, the hydrogen concentration and hydrogen generation rate of CZC-0.5 and CZC-1 were increased by about 100% and 1000%, respectively, compared with the regular CuO/ZnO catalyst at 300 °C. Moreover, the unique stings formed on the surface of the reacted particles delayed the deterioration temperature of CZC-0.5 and CZC-1 to 320 °C compared with the deactivation of CuO/ZnO at 280 °C. For CZC-2, the overloaded Cu-BTC resulted in the uneven distribution of nanoparticles on the catalysts surface and the micrometer-scale branches formed on the surface during the reaction, which made CZC-2 to deactivate in advance at 280 °C. However, CZC-2 still showed higher hydrogen concentration and hydrogen generation rate at the temperatures higher than 260 °C compared with the CuO/ZnO. As for CZC-4, the superfluous Cu-BTC caused severe agglomeration, which led to lower hydrogen concentration and lower hydrogen generation rate at the temperatures below 300 °C. Whereas, CZC-4 showed no deterioration during the whole test, which suggests that the copper calcined from the Cu-BTC could be of a unique structure with excellent anti-deactivation ability. Meanwhile, the stability test confirmed that Cu-BTC could improve the stability performance of the catalysts. In summary, CuO/ZnO/Cu-BTCs showed better catalytic activity, anti-deactivation ability and stability performance at the temperatures higher than 260 °C due to the dual-functional ability of Cu-BTC, and thus show great potential as excellent catalysts for hydrogen generation through methanol steam reforming reaction.

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Supporting information

Not applicable

Conflict of interest

There are no conflicts to declare.

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