The influence of composition on the functionality of hybrid CuO–ZnO–Al₂O₃/HZSM-5 for the synthesis of DME from CO₂ hydrogenation

Yubing Hu, Yajing Zhang, Jie Du, Chunyan Li, Kangjun Wang, Lidong Liu, Xinrui Yu, Kai Wang and Nan Liu

A series of CuO–ZnO–Al₂O₃/HZSM-5 hybrid catalysts with different Cu/Zn ratios and disparate Al₂O₃ doping were prepared and characterized by XRD, BET, H₂-TPR, NH₃-TPD and XPS techniques. The optimal Cu/Zn ratio is 7 : 3, and the introduction of a suitable amount of Al₂O₃ to form hybrid catalysts increased the BET specific area and micropore volume, facilitated the CuO dispersion, decreased the CuO crystallite size, increased the interaction between CuO and ZnO, enhanced the number of weak acid sites, altered the copper chemical state and improved the catalytic performance consequently. The highest CO₂ conversion, DME selectivity and DME yield of 27.3%, 67.1% and 18.3%, respectively, were observed over the CZA7H catalyst. The suitable temperature of 260 °C and the appropriate space velocity of 1500 h⁻¹ for one-step synthesis of dimethyl ether (DME) from carbon dioxide (CO₂) hydrogenation were also investigated. The 50 h stability of the CZA7H catalyst was also tested.

1. Introduction

CO₂ emission is increasing at an unparalleled rate due to fossil fuel combustion in recent years. As a consequence, excessive CO₂ release leads to a series of problems such as global warming and environmental pollution. Therefore, CO₂ recycling and utilization are very imperative. CO₂ hydrogenation to dimethyl ether (DME) is an excellent option. DME is attracting more and more interest as a green fuel because it produces less CO₂ emission than petrol diesel. Meanwhile, DME, as a vital chemical intermediate, can also be used to prepare diversified valuable chemical products such as esters and lower olefins. Furthermore, it can be utilized in several fields, for example, in fuel additives of diesel, home heating and cooking gas, and pro-environmental refrigerants.

The hydrogenation of CO₂ to DME over a hybrid catalyst for DME synthesis is principally composed of three independent reactions, methanol synthesis from CO₂ hydrogenation (CO₂ + 3H₂ ↔ CH₃OH + H₂O reaction 1), methanol dehydration to form DME (2CH₃OH ↔ CH₃OCH₃ + H₂O reaction 2), and a reverse water gas shift reaction (RWGS) (CO₂ + H₂ ↔ CO + H₂O reaction 3). DME can be produced via a two-step process including reaction 1 on a copper based catalyst and subsequent reaction 2 over a solid acid catalyst. Furthermore, one-step process (performing the two steps simultaneously over a hybrid catalyst) has a better performance as a thermodynamically favorable course because the equilibrium limitation of reaction 1 can be readily overcome by reaction 2.

Currently, hybrid catalysts of methanol synthesis component and methanol dehydration component are applied to the one-step direct DME synthesis from CO₂. The methanol dehydration components are generally solid acid catalyst such as γ-Al₂O₃, but the active sites of the γ-Al₂O₃ is Lewis acid sites which are favored for water adsorption, resulting in a significant reduction of the amount of acid sites and then a decrease of catalytic activity. Another intriguing solid acid catalyst is WO₃/ZrO₂, but the catalytic activity of WO₃/ZrO₂ is lower due to its weaker acid strength present. Besides, SAPO-18 has been used as acid function owing to its uniform microporous structure and a high stability, but SAPO-18 possesses a large number of moderate strength acid sites, which cause catalyst deactivation as well as undesired products by coke deposition. By contrast, HZSM-5 is the most suitable acidic component due to its more hydrophobic character and advantage of Brønsted acidity, which significantly reduces the impact of water on HZSM-5. Furthermore, HZSM-5 possesses weak acid sites which are in favor of methanol dehydration to DME at low temperatures and exhibits high catalytic activity. However, the methanol synthesis components of the hybrid catalysts are various, and the Cu–Zn based catalyst is regarded as the most promising binary catalyst among them. Xiao et al. reported the deposition of Zn on the surface of copper can increase surface area and can form a unique site at the Cu–ZnO interface to improve the
adsorption of CO₂ and catalytically active Cu–Zn bimetallic compound catalyst, adding an amphoteric metal oxide species as additive to Cu–Zn-based catalysts is an efficient method. Al₂O₃ is a prospective cocatalyst of sufficient attraction due to its mechanical and thermal stability, its excellent dispersion feature of copper and zinc. Nevertheless, only a few literature has reported Al₂O₃ as a single additive of the Cu–Zn-based catalyst for one-step direct DME synthesis from CO₂ hydrogenation at present. Lei et al. studied hydrogenation of CO₂ to CH₃OH over CuO–ZnO–Al₂O₃ catalysts prepared via a solvent-free route, they found that the combination processes and physicochemical properties of catalysts depend strongly on the type and amount of fuel. Allahyari et al. reported CuO–ZnO–Al₂O₃/HZSM-5 nanocatalyst for direct synthesis DME as a green fuel from syngas, the catalysts were prepared by ultrasound-assisted co-precipitation method at different irradiation times, and the result revealed the relationship between irradiation time and catalytic performance. Bowker et al. studied the mechanism of methanol synthesis on copper/zinc oxide/aluminum catalyst, and found that the energetics of formate hydrogenation/hydrogenolysis on the copper component of the catalyst was unaffected by the intimate mixing of copper and zinc oxide in the catalyst. Liu reported preparation of HZSM-5 membrane packed CuO–ZnO–Al₂O₃ nanoparticles for catalysing carbon dioxide hydrogenation to DME, they found zeolite capsule catalysts exhibited an excellent DME selectivity compared with the conventional hybrid catalyst because the further dehydration of DME was restrained. Unfortunately, those above mentioned literature of CO₂ hydrogenation over CuO–ZnO–Al₂O₃ catalyst were mainly related to the influence of catalyst preparation methods to the catalyst activity as well as the mechanism of CO₂ hydrogenation. On the contrary, the effect of the amount of the additive Al₂O₃ of CuO–ZnO–Al₂O₃ catalyst on catalytic activity was rarely investigated. Meanwhile, the Cu/Zn ratio of the CuO–ZnO–Al₂O₃ catalyst currently still derived from methanol synthesis from CO₂ hydrogenation or from syngas hydrogenation. Here, we prepared a series of CuO–ZnO–Al₂O₃/HZSM-5 hybrid catalysts of different Al₂O₃ contents by the oxalate co-precipitation method, on the basis of optimizing Cu:Zn ratio of catalyst for DME synthesis from CO₂ hydrogenation. The effect of Al₂O₃ content on catalytic properties especially CO₂ conversion and DME selectivity of the hybrid catalysts was investigated. Moreover, the influence of reaction temperature and velocity on the catalyst activity of the hybrid catalyst with optimum Al₂O₃ content was also investigated.

2. Experimental

2.1 Preparation of CuO–ZnO/HZSM-5 catalysts

A series of CuO–ZnO/HZSM-5 catalysts of diverse Cu/Zn molar ratio were prepared, aiming at confirming optimum composition. Cu(NO₃)₂·3H₂O, Zn(NO₃)₂·6H₂O (Cu/Zn molar ratio ranging from 2 : 8 to 8 : 2) were dissolved in ethanol to gain the metal nitrates solution and coprecipitated by oxalate under vigorous stirring at 60 °C in a solution containing the HZSM-5 finely dispersed, with a final CuO–ZnO : HZSM-5 weight ratio of 2 : 1, for convenience of comparison with previous work. The HZSM-5 with a SiO₂/Al₂O₃ ratio of 38 was purchased from Catalyst Plant of Nankai University (China). The slurry was heated to 80 °C and was aged for 2 h under stirring. Subsequently, the slurry was evaporated at the same temperature. Then the obtained product was dried in muffler furnace at 120 °C for 12 h and calcined in air at 400 °C for 4 h. The final product was hybrid catalyst named as CₓZₙ₋ₓ–H (the x represents the molar ratio of CuO : CuO–ZnO) and was pressed, crushed and griddled to get the granules (20–40 mesh).

2.2 Preparation of CuO–ZnO–Al₂O₃/HZSM-5 hybrid catalysts

Thereafter, a series of CuO–ZnO–Al₂O₃/HZSM-5 hybrid catalysts of different Al₂O₃ contents were prepared. Cu(NO₃)₂·3H₂O, Zn(NO₃)₂·6H₂O were weighed according to the optimal Cu/Zn mole ratio which was determined in the preliminary experiments. The mixture was dissolved in ethanol followed by the addition of Al(NO₃)₃·9H₂O. The amount of the Al(NO₃)₃·9H₂O used depended on the required Al₂O₃ contents of 0, 1.0, 3.0, 5.0, 7.0, 10.0 wt% in CuO–ZnO–Al₂O₃. Then, the solution of precursors was added to a vigorously stirred ethanol solution containing the oxalic acid and the powdered HZSM-5 in a constant and slow manner at 60 °C. The weight ratio of the final oxide of CuO–ZnO–Al₂O₃ to HZSM-5 is 2 : 1. The slurry was dealt with the same procedure as the CₓZₙ₋ₓ–H and the final product was abbreviated as CZₓAᵧ, where the y represents theoretical Al₂O₃ : CuO–ZnO–Al₂O₃ wt%.

2.3 Catalyst testing

The hybrid catalyst activity was measured in a continuous-flow fixed-bed reactor made of stainless steel (10 mm inner diameter). 1 mL of the hybrid catalyst was diluted with 0.5 mL of the quartz sand (both in 20–40 mesh). Prior to the test, the catalyst was reduced in situ in a stream of 10% H₂/N₂ at 300 °C for 3 h under atmospheric pressure. After the reduction, the reactor was cooled to room temperature under flowing N₂ and reactant gas flow (H₂/CO₂/N₂ = 3/9/1, molar) was introduced, subsequently raising the pressure to 3.0 MPa and the reaction temperature was raised to 260 °C. Analysis of the products were performed applied a gas chromatograph (SP2100A) equipped with both a TCD (for N₂, CO and CO₂, GDX-101 connected with Porapak T column) and a FID (for CH₄, CH₃OH and DME, Porapak Q column). The CO₂ conversion as well as the selectivity toward CO, CH₂OH and DME were calculated by internal standard method.

\[ X_{CO_2} = \frac{CO_2_{in}/N_2_{in} - CO_2_{out}/N_2_{out}}{CO_2_{in}/N_2_{in}} \]  

\[ S_P = \frac{P_C}{1 - CO_2_{out}} \]
where $P_i$ stands for the concentration of a specific product (DME, MeOH, CO).

\[ Y_{DME} = S_{DME}X_{CO2} \]  

### 2.4 Catalyst characterization

X-ray powder diffraction (XRD) patterns of all samples were performed on a Rigaku D/max 2500 pc X-ray diffractometer with Cu-Kα radiation ($\lambda = 1.54156 \text{ Å}$) at a scan rate of 4° min⁻¹ at 50 kV and 250 mA.

The BET surface area of the samples was conducted by N₂ adsorption at −196 °C using a Quantachrome Autosorb 1C. Before the absorption–desorption measurements, samples were degassed under vacuum at 300 °C for 3 h. The specific BET ($S_{BET}$) was estimated from the linear part of the Brunauer–Emmet–Teller (BET) plot.

The X-ray photoelectron spectroscopy (XPS) and X-ray-induced Auger electron spectroscopy were recorded on an ESCALA 250 X-ray spectrometer, using a standard Al-Kα X-ray source (1486.6 eV). The binding energy (BE) values were referenced to the adventitious C 1s peak (284.6 eV). Quantification of the surface atomic concentrations was carried out using the sensitivity factors supplied for the XPS instrument.

H₂-TPR of catalysts were performed on chemisorptions (ChemBET 3000). Before reduction, 0.02 g of sample was preheated with flowing He at 400 °C for 60 min, then cooled down room temperature. Subsequently, the temperature was raised in 10% H₂/Ar (50 mL min⁻¹) at a ramp rate of 10 °C min⁻¹ to 400 °C. H₂ consumption was detected by TCD.

NH₃-TPD of the samples were measured on the same apparatus for H₂-TPR measurements. 0.1 g sample was preheated to 400 °C and maintained for 30 min, then the temperature was cooled to 100 °C. After that, a 6 vol% NH₃/Ar mixture stream was introduced to the sample for 60 min. Then, the examined sample was flushed with helium stream (30 mL min⁻¹) for 60 min to remove the weak adsorbed NH₃. The temperature was raised from 100 °C to 800 °C at a rate of 10 °C min⁻¹.

## 3. Results and discussion

### 3.1 The effect of the Cu/Zn molar ratio on the catalytic performance of C₂Z₁₀⁻xH hybrid catalysts

In order to investigate the optimal Cu/Zn molar ratio of the hybrid catalysts, a series of C₂Z₁₀⁻xH catalysts were prepared. The catalytic performances of catalysts with different Cu/Zn molar ratio were summarized in Table 1. The CO₂ conversion, DME selectivity and the yield of DME increased with the Cu/Zn increased from 2 : 8 to 7 : 3, and decreased if continue raising the Cu/Zn to 8 : 2. The C₂Z₂H exhibited the maximum CO₂ conversion, DME selectivity and DME yield values of 19.2%, 47.8% and 9.2%, respectively. The result revealed the Cu/Zn molar ratio can affect the catalytic performance and the optimal Cu/Zn molar ratio of the hybrid catalysts was 7 : 3.

### 3.2 Catalytic performance of the CZAₙH catalysts

The catalytic performances of the CZAₙH catalysts with different Al₂O₃ contents were listed in Table 2. DME was the major product and the by products included CO and methanol under the reaction temperature of 260 °C, pressure of 3.0 MPa and GHSV of 1500 h⁻¹. Moreover, several hydrocarbons such as CH₄ were also detected. The catalytic performances of the Al₂O₃-modified hybrid catalysts were enhanced remarkably compared with the Al₂O₃-free hybrid catalyst. With the Al₂O₃ contents increase in the catalysts (range from CZA₃H to CZA₇H), the CO₂ conversion, DME selectivity and the DME yield increased significantly. Further increasing the contents of Al₂O₃ (CZA₁₀H) decreased the catalysts activity. The CZA₇H catalyst exhibited the highest catalyst performance and a maximum CO₂ conversion of 27.3% with a DME selectivity of 67.1% and a yield of DME of 18.3%, as shown in Table 2. The DME yield and the DME selectivity of CZA₉-H catalyst were appreciable in comparison of nearly 13.5% and 63.4%, respectively, obtained over CuO–ZnO–ZrO₂/HZSM-5 catalyst reported by Li et al. Meanwhile, the DME selectivity of 67.1% for CZA₇-H catalyst was significantly higher than 49.2% observed over CuO–ZnO–Al₂O₃/HZSM-5 catalyst studied by Zhang et al. These results indicated suitable Al₂O₃ additive can improve the catalytic performance significantly.

Fig. 1 shows the effect of reaction temperature on the catalytic performance of CZA₇-H catalyst. It can be found that volcanic shape change trends of the CO₂ conversion, DME selectivity and the yield of DME versus the variation of the reaction temperature.

### Table 1 Catalytic performance of the C₉Z₁₀⁻xH Hybrid catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion of CO₂/%</th>
<th>Selectivity%</th>
<th>Hydrocarbons</th>
<th>Yield/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂Z₁₀H</td>
<td>16.66</td>
<td>25.41</td>
<td>53.4</td>
<td>1.90</td>
</tr>
<tr>
<td>C₂Z₁₁H</td>
<td>16.44</td>
<td>27.04</td>
<td>80.3</td>
<td>1.79</td>
</tr>
<tr>
<td>C₂Z₁₂H</td>
<td>17.71</td>
<td>36.71</td>
<td>52.3</td>
<td>1.90</td>
</tr>
<tr>
<td>C₂Z₁₃H</td>
<td>17.46</td>
<td>37.73</td>
<td>52.2</td>
<td>1.83</td>
</tr>
<tr>
<td>C₂Z₁₄H</td>
<td>18.06</td>
<td>38.42</td>
<td>60.1</td>
<td>1.87</td>
</tr>
<tr>
<td>C₂Z₁₅H</td>
<td>19.20</td>
<td>47.80</td>
<td>1.70</td>
<td>2.70</td>
</tr>
<tr>
<td>C₂Z₁₆H</td>
<td>18.36</td>
<td>39.53</td>
<td>5.15</td>
<td>2.01</td>
</tr>
</tbody>
</table>

a Reaction conditions: $T = 260 \text{ °C}; P = 3.0 \text{ MPa}; \text{CO}_2 : \text{H}_2 : \text{N}_2 = 3 : 9 : 1$; GHSV = 1500 h⁻¹.

### Table 2 Catalytic performance of the CZAₙH hybrid catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion of CO₂/%</th>
<th>Selectivity%</th>
<th>Hydrocarbons</th>
<th>Yield/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZA₁H</td>
<td>19.2</td>
<td>47.8</td>
<td>1.7</td>
<td>2.7</td>
</tr>
<tr>
<td>CZA₂H</td>
<td>23.6</td>
<td>60.6</td>
<td>2.0</td>
<td>2.8</td>
</tr>
<tr>
<td>CZA₃H</td>
<td>22.9</td>
<td>61.6</td>
<td>2.6</td>
<td>2.7</td>
</tr>
<tr>
<td>CZA₄H</td>
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<td>64.3</td>
<td>5.5</td>
<td>3.7</td>
</tr>
<tr>
<td>CZA₅H</td>
<td>27.3</td>
<td>67.1</td>
<td>3.9</td>
<td>3.5</td>
</tr>
<tr>
<td>CZA₆H</td>
<td>22.6</td>
<td>60.9</td>
<td>3.6</td>
<td>2.8</td>
</tr>
</tbody>
</table>

a Reaction conditions: $T = 260 \text{ °C}; P = 3.0 \text{ MPa}; \text{CO}_2 : \text{H}_2 : \text{N}_2 = 3 : 9 : 1$; GHSV = 1500 h⁻¹.
temperature. With the temperature rising from 220 °C to 260 °C, the conversion of CO$_2$, the selectivity of the DME and the DME yield increased obviously 12.7%, 2.7% and 8.9%, respectively, and then reduced sharply when the reaction temperature reached 280 °C. Comparing the catalytic performance data at several reaction temperatures, the optimal catalytic performance for the CZA$_7$H catalyst were obtained at 260 °C. These results can be explained by the hydrogenation of CO$_2$ for synthesis of DME was a reversible exothermic reaction, the reverse reaction favored with an excessive temperature. Meanwhile, the main side reaction RWGS was an endothermic reaction thus the CO selectivity increased and the selectivity and yield of DME decreased with the reaction temperature higher than 260°C.\[\text{eq:2}\] In addition, the CZA$_7$H catalyst activity may also decrease due to the Cu sintered and crystallized gradually with the reaction temperature increased.\[\text{eq:3}\]

Fig. 1 illustrates the effect of temperature on catalytic CO$_2$ hydrogenation to DME for CZA$_7$H hybrid catalysts.

Fig. 2 illustrates the influence of the space velocity of on the catalytic performance of the CZA$_7$H catalyst. It can be found that the CO$_2$ conversion, the DME selectivity and the DME yield decreased continuously from 27.3% to 20.5%, 67.1% to 52.3% and 18.3% to 10.7%, respectively, as the space velocity increased from 1500 to 3000 h$^{-1}$. With the space velocity increasing, the contact time between reactants and the catalyst becomes short, consequently both the CO$_2$ hydrogenation to methanol and methanol dehydration to DME reactions could not proceed sufficiently.\[\text{eq:4}\] Therefore, the conversion of CO$_2$ and the selectivity of the DME reduced distinctly indicating the efficient effect the space velocity on the catalytic performance.

3.3 Stability of the CZA$_7$H catalyst

The stability of CZA$_7$H catalyst was studied for the reaction of DME synthesis via CO$_2$ hydrogenation at 260 °C and 3.0 MPa with GHSV = 1500 h$^{-1}$. The stability results were recorded every 2 h, as shown in Fig. 3. It can be found that the CO$_2$ conversion of and the DME selectivity decrease slightly from 27.3% and 67.1% to 25.3% and 62.1% during the continuous 50 h reaction process, respectively. The result indicated that the CZA$_7$H catalyst possessed better catalytic performance and stability.

3.4 The structure of the catalysts

Fig. 4 illustrates the XRD patterns of a series of CZA$_x$H catalysts, with different Al$_2$O$_3$ contents before H$_2$ reduction. For all catalysts, the diffraction peaks at 2$\theta$ = 35.5°, 38.7°, 48.7°, 53.4°, 58.2°, 61.5°, 66.2°, 72.3° and 74.9° can be ascribed to CuO phase (JCPDS no. 48-1548), the peaks at 2$\theta$ = 31.7°, 34.3°, 36.1°, 47.4°, 56.5°, 62.8° and 67.8° can be attributed to ZnO phase (JCPDS no. 65-3411), and the peaks appear in the 2$\theta$ range of 21–25° can be matched to HZSM-5 (JCPDS no. 44-0003). The peaks corresponding to Al$_2$O$_3$ phase cannot be observed, indicating that the presence of Al$_2$O$_3$ were amorphous phase or highly dispersed in the catalyst body phase. Compared with the peaks of catalyst CZA$_7$H, the peaks of catalysts with Al$_2$O$_3$ become weaker, indicating the CuO–ZnO oxides possess less intensive crystallinity. The diffraction peaks of CuO and ZnO weakened and broadened gradually with the increasing of Al$_2$O$_3$ contents, even some diffraction peaks of CuO and ZnO phase disappeared, suggesting the decrease of grain size. The grain sizes of CuO ($d_{\text{CuO}}$) and ZnO ($d_{\text{ZnO}}$) for CZA$_x$H catalysts calculated by Scherrer’s equation are listed in Table 3. These results indicated obviously that the additive of Al$_2$O$_3$ can improve the CuO dispersion and
can decrease the grain size of CuO. For all catalysts, the grain size of ZnO phase is greater than that of CuO phase, indicating ZnO phase closely relates to CuO phase. Shimokawabe et al. considered the grain size of ZnO is larger than CuO due to CuO can be well dissolved on the ZnO particles. As a consequence, the active interface increased with the improving the dispersion of CuO. As shown in Table 3, the grain sizes of Cu for reduced CZA7H catalyst decrease significantly, compared to the corresponding peaks for CZA0H catalyst. Furthermore, the grain size of Cu decreased significantly for CZA-H catalyst. As shown in Table 3, and the grain sizes of Cu (d_{Cu}) which calculated by Scherrer’s equation for reduced CZA0H and CZA-H catalysts are 21.4 nm and 9.7 nm, respectively. These results suggest that the addition of Al2O3 can effectively inhibit the Cu crystals growth.

The BET Surface areas (S_{BET}) and the calculated average pore diameter of the catalysts are also listed in Table 3. The S_{BET} of the catalysts approximately increases from 131.7 m² g⁻¹ to 161.2 m² g⁻¹ with the increasing of Al2O3 contents (from CZA0H to CZA7H), then sharply decreases to 143.5 m² g⁻¹ when the Al2O3 contents continuing increasing (CZA10H). The variation trend of the micropore volumes is the same as the S_{BET} while the trend of average pore diameter of the catalysts is contrary to the S_{BET} generally. These results illustrate that the pore structure of the hybrid catalysts can be changed by the introduction of Al2O3. Meanwhile, a maximum S_{BET} of 161.2 m² g⁻¹ and a minimum average pore diameter of 6.8 nm are detected for the CZA7H catalyst which possesses the smallest grain sizes of Cu (d_{Cu}), as determined from XRD. The result revealed that why the catalyst of CZA-H exhibited the maximum of the CO2 conversion, the DME selectivity and the DME yield simultaneously.

### 3.5 The reducibility of the catalysts

TPR measurements were carried out in order to evaluate the reduction behavior of all the catalysts. Fig. 6 shows the H2-TPR profiles of the CZA-H catalysts with different Al2O3 contents. It can be found only a single reduction peak with any satellite peaks for all the catalysts. The result illustrate the opinion the copper oxides on the CZA-H catalysts are easy to be reduced. Since ZnO and Al2O3 cannot be reduced under the experimental condition, the single high temperature reduction peak can be ascribed to the reduction of CuO species with strongly interaction with ZnO and Al2O3. The reduction peak maximum firstly shifted towards higher temperature from CZA0H to CZA7H catalysts, and then shifted towards lower temperature for CZA10H, as shown in Fig. 6. The CZA7H catalyst possessed the highest reduction temperature at 373 °C, which indicated the strongest interaction between the

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**Table 3** Physicochemical properties of the CZA-H hybrid catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>S_{BET}(m² g⁻¹)</th>
<th>V₁ (Micropore volume)/(cm³ g⁻¹)</th>
<th>D (Average pore diameter)/nm</th>
<th>d_{CuO}/nm</th>
<th>d_{Cu}/nm</th>
<th>d_{ZnO}/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>CZA0H</td>
<td>131.7</td>
<td>0.032</td>
<td>8.0</td>
<td>20.4</td>
<td>21.4</td>
<td>29.1</td>
</tr>
<tr>
<td>CZA1H</td>
<td>132.1</td>
<td>0.024</td>
<td>8.7</td>
<td>15.4</td>
<td>—</td>
<td>17.6</td>
</tr>
<tr>
<td>CZA3H</td>
<td>133.4</td>
<td>0.028</td>
<td>7.7</td>
<td>14.4</td>
<td>—</td>
<td>16.5</td>
</tr>
<tr>
<td>CZA5H</td>
<td>134.1</td>
<td>0.031</td>
<td>7.6</td>
<td>11.4</td>
<td>—</td>
<td>14.1</td>
</tr>
<tr>
<td>CZA7H</td>
<td>161.2</td>
<td>0.037</td>
<td>6.8</td>
<td>10.9</td>
<td>9.7</td>
<td>13.4</td>
</tr>
<tr>
<td>CZA10H</td>
<td>143.5</td>
<td>0.030</td>
<td>7.6</td>
<td>10.6</td>
<td>—</td>
<td>12.3</td>
</tr>
</tbody>
</table>

* Determined by Scherrer’s equation.
heterogeneous CuO particles with metal oxides. The CZA-H catalyst exhibited the best catalytic performance which might be explained by strongly interaction between CuO and oxides was beneficial to CO$_2$ hydrogenation to DME. Meanwhile, the CZA-H catalyst possessed the largest area among the reducing peaks, which revealed that the hydrogen consumption of the catalyst was enhanced significantly, as shown in Table 4. The result implied the largest amount of easily reducible well-dispersed copper oxide existed, which might also be ascribed to the improving dispersion of the CuO particles. This may be one reason why when increase Al$_2$O$_3$ contents in the catalysts from CZA$_{0H}$ to CZA$_{7H}$, the conversion and selectivity significantly increased and a further increase in Al$_2$O$_3$ contents adversely influenced conversion and selectivity simultaneously.

3.6 Surface acidity of the CuO–ZnO–Al$_2$O$_3$/HZSM-5 catalysts

Fig. 7 shows NH$_3$-TPD profiles of the CZA-H hybrid catalysts with different Al$_2$O$_3$ contents. It can be found three NH$_3$ desorption peaks which located in the range of 50–200 °C (denoted as peak $\alpha$), 200–350 °C (denoted as peak $\beta$), and 350–600 °C (denoted as peak $\gamma$), respectively. The $\alpha$, $\beta$ and $\gamma$ peaks were attributed to weak, medium and strong acid sites, respectively, indicating the presence of three strength acid sites on the hybrid catalysts.

The intensity of the low-temperature peak $\alpha$ of weak acid sites firstly increased with increasing Al$_2$O$_3$ contents (from CZA$_{0H}$ to CZA$_{7H}$) and then declined with further increasing Al$_2$O$_3$ additive, which was agreement with the trend of $S_{BET}$ and H$_2$-TPR. The CZA-H catalyst of the highest peak intensity possessed the largest amount of weak acid sites which were beneficial for methanol dehydration to DME at low temperatures. This might be ascribed to the fact Al$_2$O$_3$ owned weak acidic character.

In addition, the intensity and the position of the peaks $\beta$ exhibited unconspicuous changes with doping different Al$_2$O$_3$ contents, implying that the strength and amount of medium acid sites cannot be influenced by Al$_2$O$_3$ additive substantially. The position of peaks $\gamma$ shifted towards higher temperature gradually, indicating the intensity of strong acid sites increased with increasing Al$_2$O$_3$ doping, leading to the increase of hydrocarbons in the products. This might be attributed to the fact that the HZSM-5 with possessed strong acid sites could be modified by more oxalic acid with the addition of the more Al$_2$O$_3$ contents, during the preparation of hybrid catalysts by the co-precipitation method. From the above, the amount of weak acid sites enhanced with optimal Al$_2$O$_3$ modified, which was in favor of obtaining the highest catalytic performance for one-step DME synthesis reaction.

3.7 XPS analysis

The XPS spectra of reduced catalysts are shown in Fig. 8. Both of the spectra contained two peaks at about 1022 and 1045 eV (Fig. 8a), which were assigned to Zn 2p$_{3/2}$ and Zn 2p$_{1/2}$ peaks of ZnO, respectively, with a spin energy separation of 23 eV. This illustrates that the Zn atoms are in a completely oxidized state and were not reduced. It can be observed a single peak centered near 74.2 eV in Fig. 8b, which was ascribed to Al 2p$_{3/2}$ of Al$_2$O$_3$, therefore, the form of Al was Al$_2$O$_3$. Fig. 8c showed the XPS spectra of the Cu 2p for the reduced CZA$_{7H}$ and CZA$_{10H}$ catalysts. Two reduced catalysts displayed Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$ main characteristics peaks with binding energy (BE) values of approximately 932.6 eV and 952.6 eV, respectively, with a Cu 2p core level split spin–orbit components ($\Delta$Cu 2p) of 20.0 eV. The shake-up satellite peaks between 940 eV and 945 eV were not detected, which illustrates the absence of Cu$^{3+}$ species in both CZA$_{7H}$ and CZA$_{10H}$ catalysts can be reduced to Cu$^+$ and/or Cu$^0$ species completely. Meanwhile, the binding energy (BE) of Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$ for reduced CZA-H can be observed slightly shifted towards lower BE values, which revealed an enhancement on the interaction between Cu and ZnO with the increasing Al$_2$O$_3$ contents. The result indicated an influence on Cu chemical combination state due to the increase of the outer-shell electron density of Cu as a consequence of the introduction of additive Al$_2$O$_3$. Liu et al. thought that the
The work discussed the effect of the amount of \( \text{Al}_2\text{O}_3 \) additive of the \( \text{CuO–ZnO–Al}_2\text{O}_3/\text{HZSM-5} \) catalysts on the physicochemical properties and catalytic performance of the hybrid catalysts based on the optimizing \( \text{Cu}/\text{Zn} \) ratio. The hybrid catalysts for the reaction of \( \text{CO}_2 \) directly hydrogenation to \( \text{DME} \) improved the \( \text{CuO} \) dispersion, reduced the \( \text{CuO} \) crystallite size, decreased the grain size of the \( \text{Cu} \), enhanced the BET surface areas, increased the interaction between the \( \text{CuO} \) and \( \text{ZnO} \), enhanced the amount of weak acid sites, changed the copper chemical state on the catalysts surface and enhanced the catalytic activity and stability with the introduction of the \( \text{Al}_2\text{O}_3 \) contents. In addition, the influence of the reaction temperature and the space velocity on the catalytic performance of the catalysts modified by \( \text{Al}_2\text{O}_3 \) was also investigated. The optimal \( \text{Al}_2\text{O}_3 \) contents \( \{\text{Al}_2\text{O}_3 : \text{CuO–ZnO–Al}_2\text{O}_3 \text{ wt%}\} \) of the \( \text{CuO–ZnO–Al}_2\text{O}_3/\text{HZSM-5} \) catalysts was 7.0 wt% under the proper \( \text{Cu}/\text{Zn} \) ratio of 7:3. The \( \text{CZA}_7\text{H} \) catalyst for \( \text{CO}_2 \) hydrogenation to \( \text{DME} \) showed the maximum \( \text{CO}_2 \) conversion, \( \text{DME} \) selectivity and \( \text{DME} \) yield of 27.3%, 67.1% and 18.3%, respectively, under the reaction conditions of the optimal reaction temperature 260 °C, the appropriate space velocity of \( \text{GHSV} \) 1500 h\(^{-1}\) and the conventional pressure of 3.0 MPa.

### Conflicts of interest

There are no conflicts to declare.
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