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Zhen Liu, Xiaoqi An, Min Song, Zejia Wang, Yifan Wei, et al.. Dry gel assisting crystallization of bifunctional CuO-ZnO-Al₂O₃/SiO₂-Al₂O₃ catalysts for CO₂ Hydrogenation. Biomass and Bioenergy, 2022, 163, pp.106525. 10.1016/j.biombioe.2022.106525 . hal-04295947

HAL Id: hal-04295947

<https://hal.science/hal-04295947>

Submitted on 20 Nov 2023

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1 **Dry gel assisting crystallization of bifunctional**
2 **CuO-ZnO-Al₂O₃/SiO₂-Al₂O₃ catalysts for CO₂ Hydrogenation**

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12

13 **Abstract**

14 A series of bifunctional catalysts CuO-ZnO-Al₂O₃/SiO₂-Al₂O₃ (CZA/SA) with different
15 SA/CZA ratios were prepared by dry gel assisting crystallization method. The catalytic
16 performance of bifunctional catalysts for one-step synthesis of methanol (MeOH) and dimethyl
17 ether (DME) from CO₂ hydrogenation was investigated. The results showed that compared with
18 Cu/ZnO/Al₂O₃, CZA/SA catalyst significantly improved the selectivity of DME and MeOH and
19 reduced the CO selectivity with moderate CO₂ conversion. The catalyst structure was
20 characterized by X-ray photoelectron spectroscopy (XPS) and temperature-programmed reduction
21 (H₂-TPR), which further confirmed that the active site of methanol generation was the Cu-ZnO
22 interface with a strong interaction rather than solo Cu or ZnO crystallite, which could enhance the
23 hydrogenation function and inhibit reverse water gas shift reaction. Compared with the physical
24 mixing method, the dry gel assisting crystallization method could flexibly adjusted the acid
25 strength and the amounts of acid sites, which was benefit for enhancing dehydration function to
26 improve the selectivity of DME.

27

28 **Key words**

29 CO₂ hydrogenation, bifunctional catalysts, methanol; dimethyl ether; dry gel

30

31 **1. Introduction**

32 With the rapid industry development worldwide, CO₂ emission from the combustion of fossil
33 fuels and consumption of chemicals is increasing rapidly. Greenhouse effect and environmental
34 pollution problems were severe in recent years, which have become one of the important global
35 problems urgently needed to be solved[1]. Meanwhile, the growing energy demands requires
36 massive and sustainable energy resources supply, which is becoming crucial because of that most
37 of fossil energy are stored in politically unstable regions. A strategic research area for the
38 development of low-carbon and sustainable production of chemicals and fuels is the utilization of
39 biomass. The use of biomass, especially biowaste from forestry and wood processing, agro-food
40 production and municipal solid waste, to produce renewable energy or chemicals not only
41 provides steady energy resources supply but also aids the sustainable development of human
42 society[2].

43 However, renewable energy and heat produced from biomass are facing problems related to
44 storage and transport to long distances. High-density energy vectors, such as liquid fuels, are still
45 necessary in all future energy scenario, but they should be derived from alternative resources to
46 fossil fuels. Current technologies for biomass utilization out of combustion (for example,
47 production of bioethanol or biodiesel) are all characterized from two aspects: i) the use of only a
48 fraction of the biomass and ii) the need to use a limited type of resources. There is thus the need to
49 develop a novel technology, which can flexibly use a variety of biowaste to produce chemicals or
50 energy-rich liquid fuels.

51 Biomass can be converted into CO₂-riched syngas via thermo-chemical processes such as
52 gasification or pyrolysis. Direct production of methanol/dimethylether (DME) from CO₂-riched
53 syngas provide a flexible strategy, which has a wide industrial application prospects for further
54 produce alternative, environmentally-friendly fuels and chemicals usually come from
55 petrochemical industry [3, 4]. Therefore, selective hydrogenation of CO₂ to methanol not only
56 effectively reduces the accumulation of CO₂ and alleviates the greenhouse effect, but also provide
57 alternative route for produce high value-added fuel substitution and chemicals from biomass
58 resources other than petrochemical industry. Despite numerous extensive studies in the past

59 decades, there is still a lot of controversy about the active site for methanol formation over classic
60 Cu/ZnO based catalyst[5-18]. It was widely believed that Cu, Zn were the active sites for
61 hydrogenation reaction[6, 7]. However, recent studies have shown that perhaps the Cu-ZnO
62 interface is the real active site[8-10, 13, 15], and Cu, Zn can only be considered as the possible
63 precursor of the real active site[8, 12].

64 However, the one-pass yield of methanol via CO₂ hydrogenation is low because of
65 thermodynamic limitations[19]. In addition, reverse water gas shift reaction easily occurs under
66 the reaction conditions of methanol synthesis[5, 19, 20]. Although researchers found that the use
67 of noble metals or rare earth metal catalysts (such as Pd, Au, Ag, In₂O₃, etc.) instead of
68 conventional CuO-ZnO-Al₂O₃ catalysts can effectively restrain the reverse water gas shift
69 reaction[21-23], the high price of such catalysts limits its large-scale industrial application. The
70 direct synthesis of DME by CO₂ hydrogenation can reduce the thermodynamic limitation of
71 methanol synthesis and restrain the reverse water gas shift (RWGS) reaction. The conversion rate
72 of CO₂ and the selectivity of MeOH and DME are effectively improved. At the same time, it
73 requires only one reactor, reducing the production cost of DME[24, 25].

74 Dimethyl ether (DME) is known as new green energy in the 21st century because of excellent
75 combustion performance and no pollution[26]. In recent years, DME has attracted a wide spread
76 attention as alternative to liquid petroleum gas (LPG) and diesel[27]. Moreover, DME could be
77 play as an intermediate by methanol dehydration in MTO process, which meets the increasing
78 demand for olefins as a supplementary route to petrochemical industry[28]. At present, the
79 large-scale industrial production of DME is mainly using vapor phase dehydration of methanol.
80 Solid acid materials (such as alumina, molecular sieve) are often used as catalysts with relative
81 mild reaction condition[26].

82 The catalysts for direct CO₂ to DME conversion should have dual functions that simultaneously
83 catalyze methanol synthesis and dehydration reaction, while reverse water-gas shift reaction
84 should be minimized. Physical mixing method for bifunctional catalyst synthesis is simple, which
85 avoids the interference of two components in the synthesis process. This method can achieve
86 higher CO₂ conversion, but the selectivity of DME is low. Compared with the traditional physical
87 mixing method, the direct formation of metal oxides and acid sites into a homogeneous system at

88 the microscopic level can make the two components better synergistic effect and achieve relay
89 catalysis[25]. Many strategies for one-pot synthesis of bifunctional catalysts have been
90 implemented, such as impregnation[29], co-precipitation[24, 30, 31], combustion[32], sol-gel
91 method[33] and so on. Due to the close contact between the two components, the reported
92 catalysts prepared by one-pot synthesis strategy had higher CO₂ conversion and DME selectivity
93 (Table S1). However, catalysts also showed relative short lifetime due to relative higher acid
94 strength of zeolite as dehydration component. Yang et al.[34] prepared a core-shell bifunctional
95 catalyst for CO hydrogenation to dimethyl ether by co-precipitation crystallization. On the basis of
96 this, the core-shell structure provided a limited reaction environment, which greatly increased the
97 collision probability between methanol and acid centers and improved the selectivity to dimethyl
98 ether. Ren et al.[30] explored the influence of reaction temperature and reaction pressure on the
99 catalytic performance of bifunctional catalysts. The results show that the optimum reaction
100 temperature is 240 °C-260 °C and the optimum reaction pressure is 2.8 MPa-3.5 MPa.

101 In this paper, bifunctional CuO-ZnO-Al₂O₃/SiO₂-Al₂O₃ (CZA/SA) catalysts were prepared
102 by dry gel assisting crystallization method. The catalysts were characterized and compared with
103 the catalysts prepared by impregnation-recrystallization method. The active site properties for
104 methanol formation and dehydrogenation were further confirmed by various physical and
105 chemical characterization. At the same time, the optimized ratio of CZA and SA was explored.

106 **2. Experimental**

107 **2.1 Catalyst preparation**

108 **2.1.1 Preparation of CuO-ZnO-Al₂O₃**

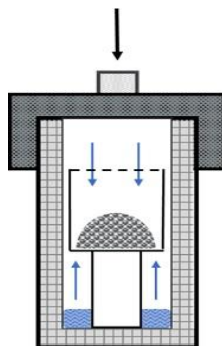
109 CuO-ZnO-Al₂O₃ catalysts with molar ratio of 6/3/1 was prepared by an improved
110 coprecipitation method[30]. The mixed nitrate aqueous solution (Cu(NO₃)₂, Zn(NO₃)₂ and
111 Al₂(NO₃)₃) and Na₂CO₃ aqueous solution were simultaneously added dropwise into a 400 mL
112 three-necked flask with preheated deionized water maintaining at 65 °C-70 °C under violent
113 stirring. During the coprecipitation process, the pH was monitored by a pH meter and maintained
114 at the range of 6.5-7.0 through careful control of dripping speed. At the end of coprecipitation, the
115 pH was adjusted to 7.0 by continue dripping Na₂CO₃ aqueous solution. The obtained suspension
116 was aged in a 70 °C beaker for 60 minutes under violent stirring. The filter cake obtained from

117 suction filtration was washed with deionized water for at least three times and dried in an oven at
118 110 °C for 12 h. At last, CZA sample was obtained by decomposing metal precipitates, which was
119 calcined in muffle furnace at 360 °C for 4 h.

120 2.1.2 Preparation of CuO-ZnO-Al₂O₃/SiO₂-Al₂O₃ catalyst

121 Dry gel assisting crystallization method was developed for prepare bifunctional CZA/SA
122 catalysts, among which the solid acid component prepared by traditional synthesis formula of
123 HZSM-5 (0.48TPAOH: 2.0TEOS: 8.0EtOH: 120H₂O: 0.026Al₂O₃). The solution of raw materials
124 was hydrolyzed under stirring at room temperature for 6 hours. The obtained precursor solutions
125 were put into an oven and dried at 110 °C for 12 h. The obtained dry gels were physically mixed
126 with certain amount of calcined CZA with different SA/CZA ratio from 1/0.5 to 1/2. A
127 hydrothermal autoclave lining with PTFE was employed for crystallization, in which a certain
128 amount of ethanol aqueous solution was added to the bottom of the lining and a small PTFE open
129 container loaded with abovementioned solid mixture was placed above the lining (Fig. 1). The
130 hydrothermal autoclave was placed in an oven and crystallized at 150 °C for 2 days. The obtained
131 samples were washed to neutral and dried in an oven at 110 °C for 12 h and calcined in a muffle
132 furnace at 550 °C for another 6 h to remove the organic template.

133 In order to study the superiority, traditional bifunctional catalyst was also prepared by
134 impregnating CuCl₂, ZnCl₂, AlCl₃ with commercial HZSM-5, and the as-prepared sample was
135 recrystallized to recover crystallinity with 0.3 M TPAOH at 150 °C for 2 days, then dried
136 overnight at 110 °C and calcined in a muffle furnace at 550 °C for another 6 h. The resulting
137 sample from impregnation-recrystallization method is denoted as CZA/HZSM-5.



138

139 Fig. 1. Improved hydrothermal autoclave for catalysts preparation by dry gel assisting crystallization method

140 2.2 Catalyst characterization

141 X-ray diffraction (XRD) was carried out to conduct crystalline structure of the prepared
142 sample on X-ray powder diffractometer X'Pert Pro MPD PXRD produced by PANalytical B.V.,
143 using Cu K α target ($\lambda = 0.15406$ nm), tube pressure 40 kV, tube flow 40 mA, scanning range $2\theta =$
144 $5^\circ - 50^\circ$.

145 The reduction properties of CZA after adding SA were analyzed by temperature-programmed
146 reduction (H_2 -TPR). The instrument is AutoChem II 2920 Chemisorption Analyzer produced by
147 Micromeritics. 0.1 g (20-40 mesh) sample was put into a U-shaped sample tube. Then the mixture
148 of hydrogen and argon (10% H_2) was pumped. The sample was heated from room temperature to
149 $600^\circ C$ at a heating rate of $10^\circ C/min$. Finally, H_2 -TPR curve was obtained.

150 The elemental composition and chemical valence of the samples were analyzed by X-ray
151 photoelectron spectroscopy (XPS) by Thermo Scientific Escalab 250Xi X-ray photoelectron
152 spectroscopy.

153 The acid properties of the sample were characterized by temperature programmed desorption
154 (NH_3 -TPD). The instrument was AutoChem II 2920 Chemisorption Analyzer produced by
155 Micromeritics. Prior to NH_3 adsorption under the mixed atmosphere of NH_3 & He at $70^\circ C$ for 0.5
156 h, the sample was pretreated in helium flow at $550^\circ C$ for 0.5 h. After that, the physically adsorbed
157 NH_3 was removed by purging helium for 0.5 h. Finally, the temperature was raised to the test
158 temperature to obtain the NH_3 -TPD curve. The amount of coke deposited on the spent catalyst was
159 measured by TG. The sample was heated to $900^\circ C$ at a rate of $10^\circ C \cdot min^{-1}$ under $100 mL \cdot min^{-1}$
160 flow of air.

161 The BET surface areas and pore volume of the samples were measured by TriStar 3020
162 physical adsorption instrument (Micromeritics). The samples were degassed at room temperature
163 for 30 min and then at $300^\circ C$ for 4 h before the test. The pore structure of the catalysts were
164 determined by measuring the adsorption-desorption data of N_2 at boiling point ($77 K$).

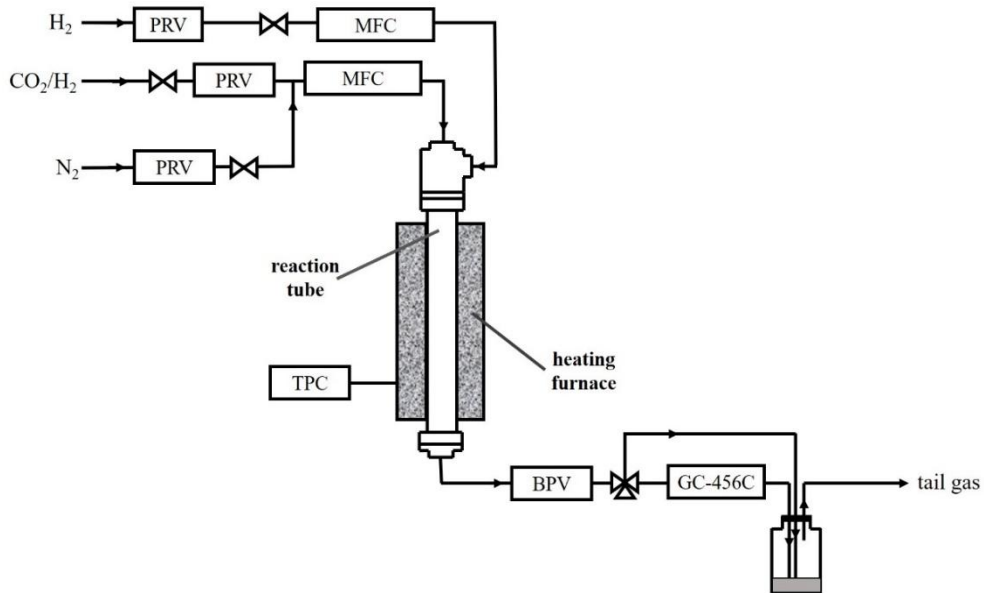
165 The morphology and atomic distribution of the catalyst surface were analyzed by SEM-EDS.
166 The SEM analysis was made by Hitachi S-4800 microscope with an acceleration voltage of 0.5-20
167 kV, fitted with an EDS analyzer.

168 **2.3 Catalytic test**

169 The catalytic evaluation of the catalysts was investigated in a self-designed fixed-bed reactor.

170 Fig. 2 shows the flow chart of the reactor. 1 g catalyst with particle size of 20-40 mesh (0.425
 171 mm-0.850 mm) was loaded in a stainless reactor tube with 8 mm inner diameter. The catalyst was
 172 reduced by H₂/N₂ (1/9, volume ratio) at atmospheric pressure and 280 °C for 4 h with a total flow
 173 rate of 100 mL·h⁻¹. After the heating furnace temperature drops to the reaction temperature, slowly
 174 increase the pressure to 3.0 MPa to start the reaction The reaction condition was 260 °C, 3.0 MPa,
 175 V(H₂)/V(CO₂) = 3.0 and GHSV = 1800 mL·gcat⁻¹·h⁻¹. The products were analyzed online by gas
 176 chromatograph Techcomp GC-456C with TCD detector and Porapak-Q (3m*3mm)
 177 packed-column.

178



179

180

Fig. 2. Flow chart of fixed-bed reactor for CO₂ hydrogenation

181

PRV: pressure reducing valve, MFC: mass flow controller, BPV: back pressure valve, GC: gas chromatography,

182

TPC: Temperature-programmed controller

183

184

The carbon conservation was used to calculate the CO₂ conversion and the selectivity of
 185 products such as MeOH and DME. The calculation formula is as follows:

$$X_{CO_2} = \frac{\sum_{i=1}^n n_i f_i A_i}{(\sum_{i=1}^n n_i f_i A_i + f_{CO_2} A_{CO_2})}$$

$$S_i = n_i f_i A_i / \sum_{i=1}^n n_i f_i A_i$$

186

where X_{CO₂}, i, S_i, n_i, f_i, A_i are CO₂ conversion, different product components, selectivity of
 187 product components, C atom number of product components, correction factor of product

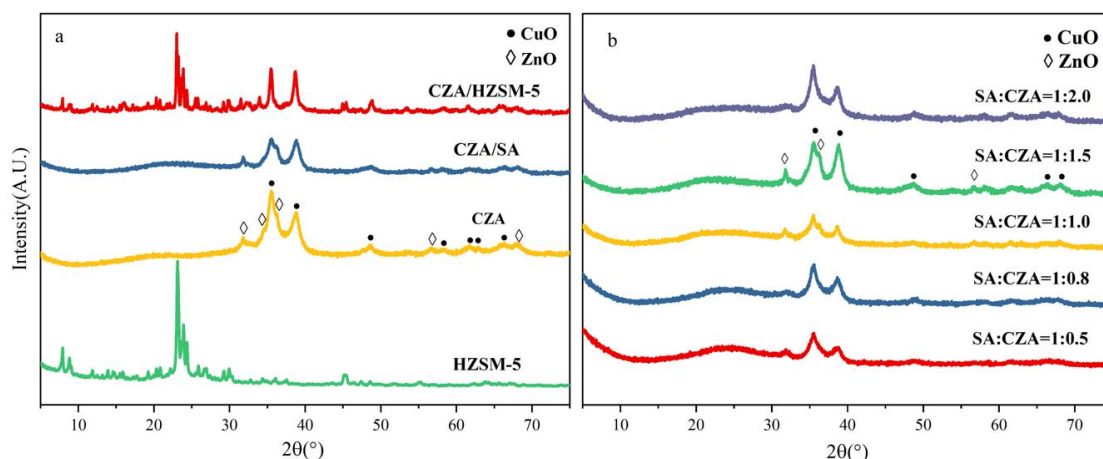
188 components, peak area of product components, respectively.

189 **3. Result and discussion**

190 **3.1 Structural property of catalysts**

191 Fig. 3 shows the XRD patterns of CZA, CZA/SA, CZA/HZSM-5 and HZSM-5 samples. It
192 can be seen from Fig. 3a that three diffraction peaks appeared in all samples at $2\theta = 30^\circ\text{-}40^\circ$,
193 which the peaks at $2\theta=31.8^\circ$ and 8.8° are ascribed to the diffraction patterns of ZnO and CuO,
194 respectively[35, 36]. The wide peak at $2\theta = 35.5^\circ$ might be caused by the overlapping of
195 diffraction peaks of ZnO at $2\theta = 34.5^\circ, 36.1^\circ$ and CuO at $2\theta = 35.4^\circ$ [37]. In addition, the classical
196 X-ray diffraction peaks of HZSM-5 also could be observed in the range of $2\theta = 7^\circ\text{-}9^\circ$ and $2\theta =$
197 $22^\circ\text{-}25^\circ$ on CZA/HZSM-5 catalyst synthesized by impregnation-recrystallization method.
198 However, the diffraction peak of HZSM-5 zeolite was not observed in the bifunctional catalyst
199 prepared by dry gel assisting crystallization method, which means that the addition of CZA into
200 system strongly inhibited the crystallization of HZSM-5[38]. It should be mentioned that no
201 corresponding diffraction peak of Al_2O_3 was observed in all catalysts, indicating that Al_2O_3 was
202 present in the catalyst in amorphous phase or implanted into aluminosilicate[31]. Compared with
203 CZA/HZSM-5 catalyst, the diffraction peaks of CuO and ZnO in CZA/SA catalyst became
204 weakened and broadened, which confirmed that the crystalline size of CuO-ZnO was smaller than
205 traditional CZA/HZSM-5 sample[31]. The XRD patterns of a series of bifunctional catalysts with
206 different SA/CZA ratios prepared by dry gel assisting crystallization method are shown in Fig. 3b.
207 No obvious diffraction peaks change on CuO and ZnO was obtained, indicating that CZA could
208 stably existed in the crystallization process from a very wide composition range during dry gel
209 assisting crystallization process. The diffraction peaks of CuO and ZnO showed a gradual increase
210 trend with the increase of CZA content.

211



212

213 Fig. 3. XRD patterns of the catalysts. (a: CZA, CZA/SA, CZA/HZSM-5 and HZSM-5; b: a series of bifunctional
214 catalysts with different SA/CZA ratios)

215 The BET Surface areas and the average pore diameter of the catalysts with different SA/CZA
216 ratios are listed in Table 1. From the table, it can be seen that the specific surface area increased
217 from 493 m²/g to 586 m²/g when SA/CZA ratio increased from 1/0.5 to 1/0.8, which showed that
218 SA crystallization process was not affected by introducing small amount of metal oxide. However,
219 sharp decrease on specific surface area was observed when further increasing proportion of CZA,
220 which confirmed that of the porosity of the bifunctional catalyst was mostly contributed by SA
221 component. The pore volume and average pore diameter of the catalyst reached the maximum
222 when SA/CZA=1/1.0. SEM and EDS mapping images of catalyst (SA/CZA =1/1.0) showed that
223 the surface of SA was covered by well dispersed CZA (Fig. S1).

224

Table 1. Pore structure properties of catalysts with different SA/CZA ratios

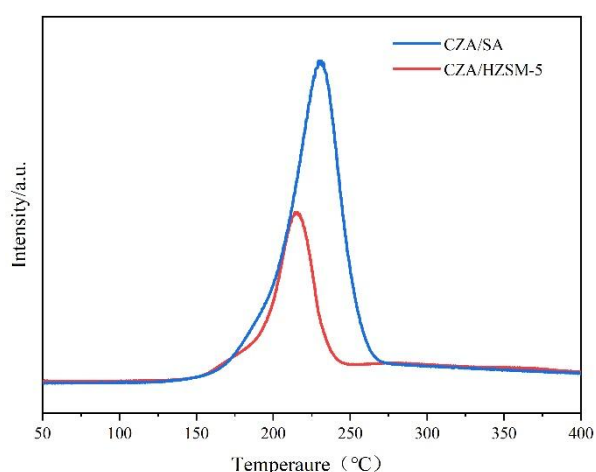
Sample	S _{BET} /(m ² /g)	V _t /(cm ³ /g)	d _{AVG} /(nm)
SA:CZA=1:0.5	493	0.354	3.0
SA:CZA=1:0.8	586	0.430	3.0
SA:CZA=1:1.0	382	0.559	6.1
SA:CZA=1:1.5	331	0.522	6.0
SA:CZA=1:2.0	198	0.213	4.3

225 3.2 Reduction of catalysts

226 The reduction properties of CZA/SA and CZA/HZSM-5 were characterized by H₂-TPR. The
227 reduction curve showed a wide reduction peak (Fig. 4). Given ZnO and Al₂O₃ cannot be reduced
228 during testing temperature range[32, 39, 40], the reduction peak was attributed to the reduction of

229 CuO species. From the reduction curve, it is clearly to see that the reduction peaks of the two
 230 catalysts were asymmetric, which indicated the overlap peaks resulting from the two reduction
 231 processes[41]. There might be two different Cu species with different reducibility in the catalyst,
 232 which was consistent to the presumption by Jiang et al[42]. The lower temperature reduction peak
 233 was attributed to the reduction of highly dispersed CuO and the higher temperature reduction peak
 234 was attributed to the reduction of bulk CuO [43].

235 The reduction onset temperature, peak temperature and hydrogen consumption of CZA/SA
 236 are higher than those of CZA/HZSM-5 (Table 2). It is interesting to note that compared with the
 237 impregnation method, the CZA prepared by dry gel assisting crystallization method had a strong
 238 interaction between Cu and ZnO, which increased the reduction temperature of CuO. Meanwhile,
 239 the high dispersion of Cu species also caused the result of higher the hydrogen consumption,
 240 which was consistent to XRD results.



241

242

Fig. 4. H₂-TPR profiles of the CZA/SA and CZA/HZSM-5catalysts.

243

Table 2. The reduction onset temperature, peak temperature and hydrogen consumption of CZA/SA and

244

CZA/HZSM-5			
Sample	T _o (°C)	T _M (°C)	H ₂ consumption(mmol/g _{cat})
CZA/SA	145.1	231.1	3.86
CZA/HZSM-5	139.0	215.6	2.22

245

3.3 Chemical state of catalysts

246

Fig. 5 showed the XPS spectra of bifunctional CZA/SA and CZA/HZSM-5 catalysts. The

247 peaks at 952.6 eV and 953.5 eV in Fig. 5a and Fig. 5b were attributed to the $\text{Cu}2p_{1/2}$ of
248 CZA/HZSM-5 and CZA/SA, respectively, while the peaks at 932.7 eV and 933.7 eV were
249 attributed to the $\text{Cu}2p_{3/2}$ of CZA/HZSM-5 and CZA/SA, respectively. The satellite peaks at about
250 941-942 eV and 961-962 eV indicated that the Cu species in the samples existed in Cu^{2+} [5, 44-46].
251 Compare with bulk CZA sample with XPS $\text{Cu}2p_{3/2}$ peak normally at 932.2 eV attributing to
252 Cu^{2+} [47], the binding energies of $\text{Cu}2p_{3/2}$ in CZA/HZSM-5 and CZA/SA were higher than that
253 in CZA. Similar higher binding energy shifts were also observed in the Zn2p spectra in Fig. 5c
254 and Fig. 5d [47]. The peaks of $\text{Zn}2p_{3/2}$ in CZA/HZSM-5 and CZA/SA catalysts appeared at
255 1021.25 eV and 1021.90 eV, respectively, which were higher than that in bulk CZA appeared at
256 1020.0 eV. The result might be explained that new Cu-Si(Al) and Zn-Si(Al) interfaces with the
257 Cu-O-Si(Al) and Zn-O-Si(Al) bonds in bifunctional catalysts was formed, which resulting in
258 strong interaction with Cu or Zn species. The strong interaction of Cu-Si(Al) and Zn-Si(Al)
259 interfaces makes the lower density of outmost electrons of Cu and Zn, which decreased the
260 shielding effect on X-ray and caused a higher binder energy results. However, the interaction was
261 not as strong as atomically implanted copper phyllosilicate phase with the Si-O-Cu structure,
262 which normally showed characteristic peaks at 935.5 eV in the $\text{Cu}2p_{3/2}$ XPS spectrum[38]. It is
263 worth noting that the binding energies of Cu $2p_{3/2}$ and Zn $2p_{3/2}$ in CZA/SA catalysts were higher
264 than those of CZA/HZSM-5 catalysts. It was inferred that the Cu-ZnO- Al_2O_3 catalyst prepared by
265 the Dry gel assisting crystallization method exhibited stronger interaction of Cu-O-Si(Al) and
266 Zn-O-Si(Al) bonds than those in samples prepared by impregnation-recrystallization method. The
267 nearly absence of peak at 935.5 eV to copper phyllosilicate phase demonstrated that dry gel
268 assisting method showed well Cu implant module as Cu-O-Si(Al) interfaces. Combined with XRD
269 results, the smaller crystalline size and better dispersion of Cu species might be resulting in
270 stronger interaction between CuO and ZnO, which might be also led to higher binding energy of
271 Cu and Zn.

272

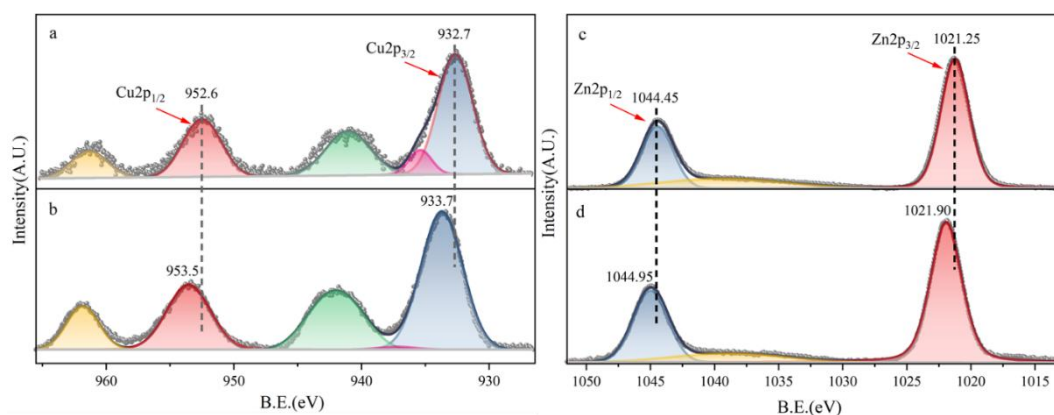


Fig. 5. Cu 2p and Zn 2p XPS spectra of CZA/HZSM-5 (a, c) and CZA/SA (b, d).

3.4 Surface acidity of catalysts

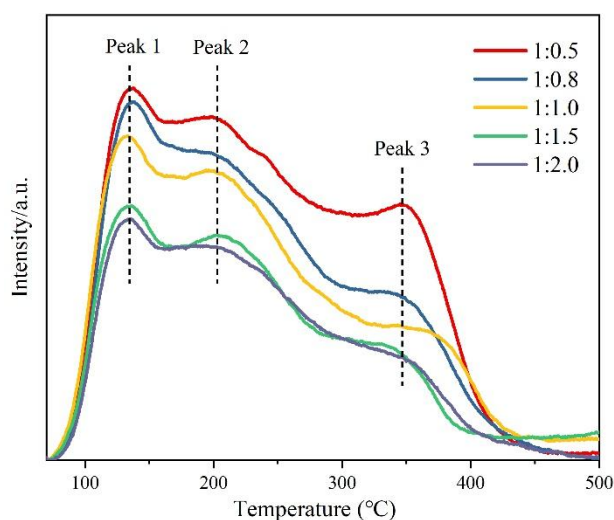
The catalysts with different SA/CZA ratios prepared by dry gel assisting crystallization method were characterized by NH_3 -TPD to study the role of acid sites in the synthesis of DME. The desorption curve is shown in Fig. 6 and the peak fitting results are shown in Table 3. It can be observed that each catalyst had three kind of acid site with peak temperatures between 120-130 °C, 200-210 °C and 320-340 °C, respectively, which corresponded to weak acid site, medium strong acid site and strong acid site. Compared with the acid site of HZSM-5 at 150-250 °C, 300-400 °C and 450-550 °C, respectively[48], the three kinds of acid site strength of bifunctional catalyst decreased obviously. The absence of ZSM-5 diffraction peaks in XRD patterns of CZA/SA sample demonstrated that poor crystallization into zeolite led to weaker acid strength. On the other hand, CuO, ZnO and Al_2O_3 might migrated into $\text{SiO}_2\text{-Al}_2\text{O}_3$ during the crystallization process which would covered some of the acid sites and led to a decrease in acidity[24, 49, 50]. With the increase of CZA content in the bifunctional catalyst, the total acid amount and the number of strong acid sites showed a decreasing trend. It is generally believed that the strong acid site has higher catalytic activity for methanol dehydration to hydrocarbon, while the medium strong acid site favors to form dimethyl ether[51-55]. Therefore, compared with the physical mixing method, the dry gel assisting method could adjust the acid strength and the amounts of acid sites during the preparation of bifunctional catalyst without additional modification of methanol dehydration component to improve the selectivity of DME.

Table 3. The acidity of the CZA/SA catalysts with different SA/CZA ratios

Sample	Acidity ($\mu\text{mol/g}_{\text{cat}}$) NH_3
--------	--

	Peak 1	Peak 2	Peak 3	Total
SA/CZA=1/0.5	42.36752	137.3683	61.81213	241.548
SA/CZA=1/0.8	32.25195	116.5342	64.80293	213.5891
SA/CZA=1/1.0	35.46852	93.25535	56.49033	185.2142
SA/CZA=1/1.5	35.96557	104.6865	35.73627	176.3883
SA/CZA=1/2.0	14.27406	81.47539	28.68501	124.4469

295



296

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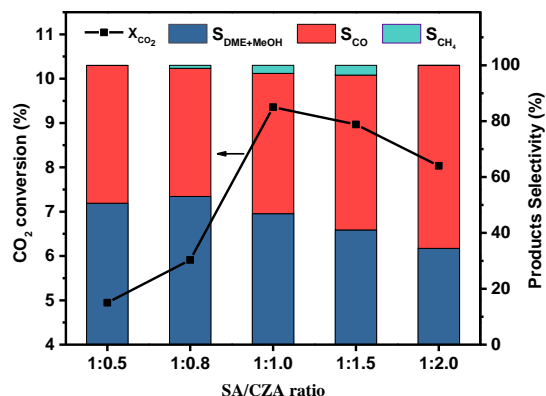
Fig. 6. NH_3 -TPD profiles of the catalysts with different SA/CZA ratios from 1/0.5 to 1/2.0

298 3.5 Catalytic results

299 The average value of the catalytic test results obtained from the stabilized period of the
300 reaction was taken as the result of CO_2 conversion and product selectivity, which are shown in
301 Table 4. The main by-product of the reaction was CO, in addition to a small number of CH_4 . It
302 should be mentioned that no C_2+ hydrocarbons were detected over all the catalyst under the
303 reaction condition. Compared with CZA catalyst, the bifunctional catalyst greatly reduced the
304 selectivity of CO by-products after the introduction of acidic component. The selectivity of MeOH
305 and DME increased from 31.50 % to 46.88 % was obtained over CZA/SA catalyst even with
306 weaker acid strength and no distinct ZSM-5 crystallinity. However, CO_2 conversion decreased
307 from 12.47% to 9.36%, which might due to the inhibition of the side reactions of reverse water gas
308 shift. It is interested to notice that CZA/HZSM-5 catalysts prepared by
309 impregnation-recrystallization method showed almost no catalytic activity even both metal

310 CuO-ZnO component and acid ZSM-5 patterns was observed. As for the CZA/SA catalyst, an
311 improved selectivity to MeOH and DME was obtained over the catalyst even with no distinct
312 ZSM-5, which could be explained by enhancing dehydration function from moderate acid strength
313 and the amounts of acid sites. Moreover, stronger interaction of Cu-O-Si(Al) and Zn-O-Si(Al) or
314 interaction between CuO and ZnO confirmed by XPS might be another reason for the activity
315 enhancement by improving hydrogenation function.

316 In order to study the optimal SA/CZA ratio of bifunctional catalysts, a series of SA/CZA_x (x
317 = 0.5, 0.8, 1.0, 1.5, 2.0) catalysts were prepared. As shown in Table 4 and Fig. 7, the CO₂
318 conversion increased from 4.95% to 9.36% when reducing SA addition proportion from 1/0.5 to
319 1/1.0, which demonstrated that methanol synthesis reaction was the rate controlling step and
320 partially increase the content of CZA component benefited to overall catalyst activity. However,
321 further reducing SA/CZA ratio from 1/1.0 to 1/2.0 led to a slight decrease on CO₂ conversion with
322 significant increase on CO selectivity, which might due to the reason that fewer SA components
323 depressed the subsequent dehydration reaction and strengthen the side RWGS reaction. Different
324 from the physical mixed bifunctional catalyst with the best catalytic performance at SA/CZA =
325 1/2.0[23]. The catalyst prepared by dry gel assisting crystallization method showed the best
326 performance with SA/CZA ratio of 1/1.0, on which CO₂ conversion and MeOH + DME selectivity
327 were 9.36 % and 46.88 %, respectively. Considering that higher reaction temperature could
328 dynamically accelerate reaction rate, which could benefit for the increase of catalysts activity.
329 However, from the perspective of reaction thermodynamics, increasing reaction temperature is
330 beneficial to RWGS reaction. Here in our case, relative higher selectivities on methanol and DME
331 were obtained, which indicated that SA/CZA with ratio of 1/1.0 could significantly inhibited
332 RWGS reaction at higher reaction temperature of 260 °C. Compared with the hydrothermal
333 method, the dry gel method could fix aluminosilicates precursor into acid component in the
334 water-free micro-region, avoiding the damage of metal components in the harsh hydrothermal
335 crystallization environment to the greatest extent.



336

337

Fig. 7. The CO₂ conversion and product selectivity of the catalysts with different SA/CZA ratios.

338

339

Table 4. The CO₂ conversion and product selectivity of different catalysts

Sample	Conversion (%)	Selectivity (%)				
		MeOH	DME	MeOH+DME	CO	CH ₄
CZA	12.47%	31.50%	0	31.50%	67.88%	0.62%
HZSM-5/CZA=1/1.0	0.57%	0	0	0	50.75%	49.25%
SA/CZA=1/0.5	4.95%	15.75%	34.88%	50.63%	49.28%	0.09%
SA/CZA=1/0.8	5.91%	17.65%	35.40%	53.05%	45.86%	1.09%
SA/CZA=1/1.0	9.36%	14.28%	32.60%	46.88%	50.20%	2.92%
SA/CZA=1/1.5	8.97%	16.89%	24.17%	41.06%	55.44%	3.50%
SA/CZA=1/2.0	8.03%	11.68%	22.77%	34.45%	65.54%	0.01%

340

E. Catizzone et al.[25] used Unisim Design R430 software (Honeywell, Morris Stown, NJ,

341

USA) to perform a simulation, which showed that theoretical equilibrium conversion of CO₂ was

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23.75% and theoretical equilibrium selectivity of DME, CO and MeOH was 49.5%, 33.5% and

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16.4%, respectively. However, the obtained conversion was usually lower than the theoretical

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equilibrium conversion due to limited contact time between catalysts and reactants, diffusional

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limitation between hydrogenation and dehydration sites. Additionally, the structure of CZA could

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be partially undermined to some extent during the crystallization process, which intensified the

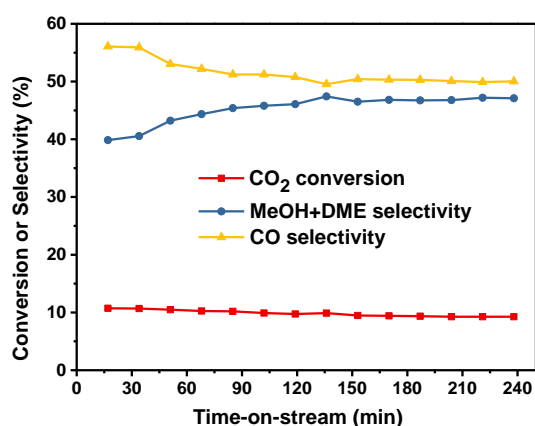
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occurrence of reverse water gas shift (RWGS) reaction and led to lower selectivity to MeOH and

348

DME. The duration test of SA/CZA = 1/1.0 catalyst was tested and shown in Fig. 8, while other

349 catalysts with different SA/CZA ratio were also tested and presented as Supporting Information
 350 Material (Fig. S2 to S4). From the duration data, we can find that the catalytic performance of
 351 catalyst reached a stabilized period after 2 hours of reaction time. During the stabilizing period,
 352 the CO₂ conversion decreased from 10.73% to 9.26%, while the selectivity of MeOH + DME
 353 increased from 39.6% to 47.1% with a synchronous decline on CO selectivity. With the progress
 354 of the reaction after reaching stabilized period, the CO₂ conversion rate showed no sign of
 355 significant decline with relative stable products selectivity. Previous studies indicated that the
 356 Cu-ZnO based CO₂ hydrogenation bifunctional catalyst could be deactivated by the reason of
 357 cokes, Cu sintering, and water poisoning[31, 56]. The spent catalyst after reaction was also
 358 characterized (Fig. S5 to S6 and Table S2 in Supporting Information Material) to confirm the
 359 catalyst stability. XRD patterns of fresh catalyst and spent catalyst revealed that no intensification
 360 on the diffraction peak of ZnO or CuO was observed but with some new peaks corresponded to
 361 the Cu⁰, which means that no obvious sintering or reoxidation was occurred during the reaction.
 362 However, BET analysis revealed that a decline on specific surface area was observed, which might
 363 due to relative lower stability of SiO₂-Al₂O₃ component. Negligible amount of coke was also
 364 determined by TG analysis. All the characterization on spent catalyst revealed that the as-prepared
 365 catalysts by dry gel assisting crystallization method showed improved performances on catalyst
 366 stability.



367
 368 Fig. 8. CO₂ conversion and products selectivity of SA/CZA=1/1.0 catalyst with time on stream.

369 4. Conclusion

370 In this paper, CuO-ZnO-Al₂O₃/SiO₂-Al₂O₃ bifunctional catalysts were prepared by dry gel
 371 assisting crystallization method for the hydrogenation of CO₂. The products selectivity to

372 methanol and dimethyl ether was significantly improved from 31.50 % to 46.88 % with a slight
373 decrease on CO₂ conversion over CuO-ZnO-Al₂O₃/SiO₂-Al₂O₃ with weaker acid strength and
374 even no distinct ZSM-5 crystallinity. Compared with the physical mixing method, the acid
375 strength and the amounts of acid sites could be flexibly adjusted during the preparation procedure
376 by dry gel assisting crystallization method, which could significantly improve the selectivity of
377 DME. The characterization of the samples by XPS and H₂-TPR confirmed that the active site of
378 methanol generation was the Cu-ZnO interface, rather than Cu and ZnO. Stronger interaction of
379 Cu-O-Si(Al) and Zn-O-Si(Al) or interaction between CuO and ZnO confirmed by XPS might be
380 another reason for the activity enhancement by improving hydrogenation function. The optimal
381 ratio of CuO-ZnO-Al₂O₃/SiO₂-Al₂O₃ was investigated with SA/CZA ratio of 1/1.0. Duration test
382 and characterization on spent catalyst implied that the catalyst prepared by dry gel assisting
383 crystallization method showed improved performances on catalyst stability.

384 **Acknowledgment**

385 This work was supported by the National Key Technologies R&D Program of China, Key
386 projects of intergovernmental international innovation cooperation (2018YFE0118200), Key
387 Research and Development Plan of Shandong Province (2019JZZY010506), and Key Research
388 and Development Program of Ningxia (2022ZDYF0937).

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