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The Structure Properties of CuZnAl Slurry Catalysts Prepared by a Complete Liquid-Phase Method and its Catalytic Performance for DME Synthesis from Syngas

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Abstract Four CuZnAl slurry catalysts with different contents of Al were directly prepared from the solution of these metal salts to catalyst slurry by a complete liquid-phase method. The structure properties of the catalysts were characterized by XRD, BET, XPS, FTIR, and their catalytic performances for the single-step synthesis of Dimethyl ether (DME) from syngas were evaluated in a slurry reactor of 250 mL with a mechanical magnetic agitator. The results indicate the main phase existed in the catalysts are Cu, Cu_2O, ZnO and boehmite (AlOOH) and the structures of pore and surface are comparable with those of the commercial methanol synthesis catalysts. Activity tests show that the slurry catalysts are quite effective for the single-step synthesis of DME from syngas. Among them, the catalyst with 2.09 mol% Al is best, whose DME selectivity reaches 93.08%. All of the catalysts prepared by the novel method exhibit good stability during the reaction time investigated for 18 days.

Keywords Complete liquid-phase method · Slurry reactor · Dimethyl ether · CuZnAl slurry catalysts · Syngas · Boehmite

1 Introduction

Dimethyl ether (DME) has received much attention as an alternative diesel fuel due to its lower NO_x emission and near-zero smoke [1–3], thus much consideration should be given to the production of DME in a large scale. Direct synthesis of DME from syngas (called STD process) is considered to be a promising process because of its dramatically economic values and theoretical siginificance. The catalyst used in this process is composed of a methanol synthesis catalyst and a methanol dehydration catalyst, which is made typically by mechanically mixing, and sometimes they are also prepared by coprecipitation or impregnation method in order to get a better catalyst. As STD process is a strong exothemic reaction process, the traditional fixed bed reactor is not appropriate because of its limited heat removed capacity, in which aspect the slurry reactor has many merits and has been successfully applied in F-T synthesis process. The slurry reactor is also considered as an ideal one for DME synthesis [4, 5].

To date, the catalysts reported in the literature for DME synthesis in a slurry reactor are all prepared by dispersing the traditional solid catalysts into the organic medium. This preparation method is complicated, furthermore, the activity of the so-prepared catalysts deactivates very quickly. The development of good stable catalysts has become the bottleneck of the process scale-up of the slurry phase DME synthesis.

A novel preparation method of slurry catalyst for slurry reactor was suggested by us [6], named a complete liquid-phase method. Its main innovative thought lies in preparing the catalysts directly from solution to slurry. Because the catalytic materials can grow in a similar surrounding as its final reaction surrounding by using the novel preparation method, it is expected that the stability of catalysts can be improved. Moreover, the novel preparation method is more simple and economic than the conventional method, and some disadvantages existed in conventional method can be avoided, such as high medium viscosity, bad fluidity as well as easy subsiding and aggregating, especially in

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scale-up test. The novel preparation method has been applied to the single-step synthesis of DME from syngas, CuZnAl and CuZr based slurry catalysts have been prepared and their activity has been investigated primarily. As we expect, the catalysts show good stability and the high selectivity to DME [6, 7].

In the present study, the structure properties of CuZnAl slurry catalysts prepared by the novel method were investigated, the catalytic performances of them with different Al contents were compared, and the information of the structure and activity was discussed.

2 Experimental

2.1 Catalyst Preparation

An appropriate amount of $(C_3H_7O)_3Al$ was added into water and kept at 353 K for 1.5 h in a slurry reactor, then a certain amount of 12 N HNO_3 was added dropwise and stirred for 1 h at 368 K. The resulting solution was mixed with another solution containing Cu $(NO_3)_2$ and Zn $(NO_3)_2$(Cu/Zn = 1:1 atomic ratio), and stirred at 368 K until gelation. After that, the gel was treated with acetone three times within 24 h, and then dispersed in paraffin under mechanical stirring. Thereafter the gel solution was heated in N_2 flow by a temperature program as following:

$$\mathrm{RT} \overset{1\mathrm{K/min}}{\rightarrow} 343\ \mathrm{K}\ (180\,\mathrm{min}) \overset{1\mathrm{K/min}}{\rightarrow} 393\ \mathrm{K}\ (120\,\mathrm{min}) \overset{2\mathrm{K/min}}{\rightarrow} 563\ \mathrm{K}(480\,\mathrm{min}) \overset{2\mathrm{K/min}}{\rightarrow} \mathrm{RT}$$

After the treatment of N_2, a slurry catalyst was obtained. For convenience, these catalysts will be designated by an abbreviation, C-*x*, where '*x*' denotes the content of Al (mol%).

2.2 Catalytic Activity Test

The DME synthesis reaction was carried out in a slurry reactor with a mechanical magnetic agitator. The CuZnAl slurry catalyst of the solid hold-up of 30% was reduced in 20% H_2 in N_2 under atmospheric pressure at 563 K for 10 h before reaction. The temperature was then decreased to reaction temperature in flowing N_2. A reactant gas mixture composed of H_2 and CO (H_2/CO = 1:1) was introduced into the reactor at the pressure of 4.0 MPa, a GHSV of 150 $mL/g_{cat}h$ or 250 $mL/g_{cat}h$ and the temperature of 473–553 K. The products were analyzed with a gas chromatograph equipped with FID and TCD detectors, using GDX-502 and TDX-01 column respectively.

2.3 Catalyst Characterization

In order to eliminate the effect of paraffin on catalyst characterization and show the actual property of the slurry catalyst, the slurry catalysts were extracted by chloroform and dried at room temperature before characterization.

X-ray diffraction (XRD) data of catalysts were collected on a Rigaku D/max 2500 diffractometer (CuKα radiation, 40 kV, 100 mA). FTIR were observed on FTS-165 spectrometer. The BET surface areas were calculated from the nitrogen adsorption isotherm at 77 K measured by an SORPTMATIC 1990 (CE instruments, Italy). XPS were acquired on an ESCALAB 250 spectrometer (VG Scientific Ltd., UK) equipped with an Al Kα ($h\upsilon = 1486.6$ eV).

3 Results and Discussion

3.1 The Catalyst Phase Structure

The XRD patterns of the un-reduced $CuZnAl_{-}$ slurry catalysts are displayed in Fig. 1a–d. All catalysts exhibit the diffraction lines of Cu, Cu_2O and ZnO, consistent with the phase structures of DME synthesis catalysts prepared by the conventional method [1, 8, 9], but not any Al_2O_3 phase structures were found. The appearance of metallic Cu and Cu_2O in the un-reduced catalysts is due to the reduction of CuO by isopropanol which is formed during preparing Al-gel [6]. Figure 1a–d shows that the diffraction intensities of metallic Cu increase with increasing the content of Al. This result further indicates that Cu and Cu_2O are from the reduction of CuO by isopropanol because the higher Al

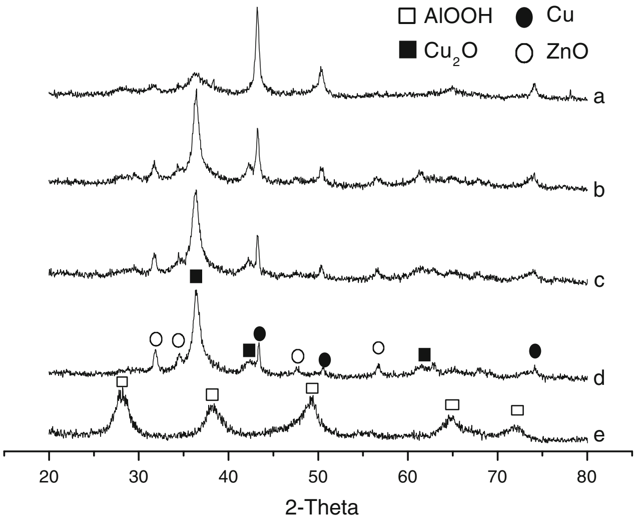

Fig. 1 XRD patterns of un-reduced catalysts and pure Al catalyst **a** C-2.90 **b** C-2.09 **c** C-1.84 **d** C-1.62 **e** pure Al

content, the more isopropanol can be produced during the preparation.

Up to now, the most common hybrid catalysts for the STD process are prepared by mechanically mixing methanol synthesis catalyst with methanol dehydration catalyst. The γ-Al_2O_3 are the most extensive to be used as methanol dehydration catalysts [9, 10]. Moreover, some researchers [1] also studied CuZnAl catalysts prepared by a coprecipitation method and found that the catalyst containing γ-Al_2O_3 could produce DME with a high selectivity. They concluded that crystallinity of Al_2O_3 was closely related to the catalytic activity. However, in our cases no peaks ascribed to any Al_2O_3 are presented in the XRD spectra of the catalysts investigated, but these catalysts are active for DME synthesis and with high DME selectivity (Sect. 3.4). This reveals that γ-Al_2O_3 is not essential to the synthesis of DME. In order to shed further light on the existing form of Al, a pure Al slurry catalyst without Cu and Zn was prepared by the novel method and characterized by XRD and FTIR (see Figs. 1e and 2). In Fig. 1e, the peaks of 28.18, 38.34, 48.93, 55.14, 64.98 and 71.90 can be ascribed to the diffraction line of boehmite (AlOOH).

Figure 2 shows the FTIR spectra of the pure Al catalyst, CuZnAl catalyst, γ-Al_2O_3 (purchased from Zhoushan Mingri Nanomaterial Inc., Zhejiang, China) and pure boehmite (purchased from Hejin Aluminum Inc., Shanxi, China). It can be found that the peak positions of the pure Al catalyst and γ-Al_2O_3 have significant difference at the lower frequency than 1,300 cm^{-1}. In case of pure Al catalyst, four peaks of 1,061 , 735 , 624 and 464 cm^{-1} are found, which are similar with those of pure boehmite and in case of γ-Al_2O_3, a strong peak is observed at 624 cm^{-1}, which are attributed to asymmetrical vibration of Al–O.

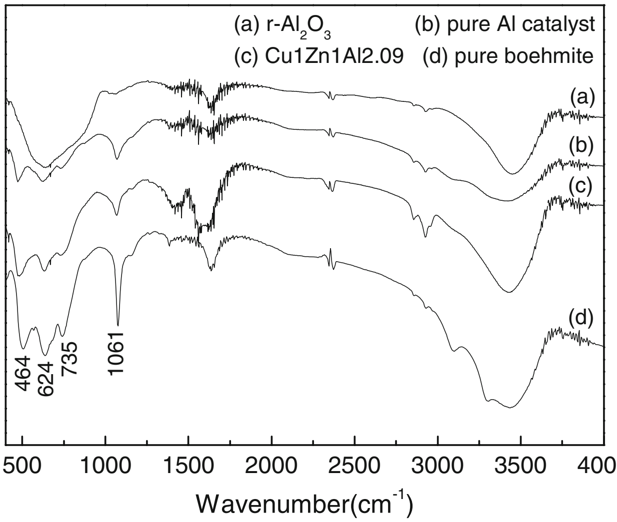

Fig. 2 FTIR spectra of γ-Al_2O_3 **a**, pure Al catalyst **b**, CuZnAl catalyst **c** and pure boehmite **d**

Because the peak number and position of CuZnAl catalyst are identical to that of pure boehmite (see Fig. 2), it can be concluded that the existing form of Al in CuZnAl catalyst is boehmite. The reason for the appearance of boehmite in CuZnAl catalyst may be the special heat-treatment process of complete liquid-phase method.

XRD patterns of reacted catalysts are similar to that of un-reduced catalysts (not shown), but the intensity of Cu peaks decreases. This suggests that boehmite does not converse to γ-Al_2O_3 and the dispersion of Cu is increased during the reaction of DME formation from syngas.

3.2 The Catalyst Pore Structure

The catalyst pore structures are listed in Table 1. From Table 1, it is easy to find that the BET surface area, pore volume and mean pore diameter of the CuZnAl catalysts prepared by the novel method are comparable with those of the commercial methanol synthesis catalysts, such as C207, NC208 and ICI51-1 [11, 12]. This indicates that the catalysts with similar pore structure to those prepared by conventional method can be obtained by using the complete liquid-phase method, in which no steps of drying and calcining are carried out.

3.3 The Catalyst Surface Structure

The XPS characterization (not shown) shows that the BE (binding energy) of the $Cu2p_{3/2}$ level of all un-reduced catalysts is about 932.5 eV and no shake-up satellite peak at 943.7 eV, indicating the absence of Cu^{2+} ions. The Cu LMM Auger peaks of the catalysts are broadened, resulting from the overlapping of two peaks at KE 918.8 and 917.6 eV. From the XPS results it is obvious that there are Cu^0 and Cu^+ in these catalysts. This is consistent with the XRD results. Moreover, the increase of Al content gives rise to a positive shift of the BE of $Cu2p_{3/2}$. Similar results have been recently reported in the work of Chen et al. [13]. This fact shows that some interaction between Cu and Al has taken place and the electron distribution of copper has changed. The BE of the Zn $2p_{3/2}$ level is located at

Table 1 The pore structure of CuZnAl slurry catalysts

Catalysts	A (m^2/g)	V_p (cm^3/g)	d_p (nm)
C-2.90	147.77	0.24	5.86
C-2.09	99.13	0.17	11.01
C-1.84	98.89	0.16	9.76
C-1.62	105.25	0.17	17.80
C207[a]	68.62	0.25	11.00
NC208[a]	86.21	0.26	13.40
ICI51-1[a]	70.00	0.21	11.82

[a] Reference catalysts prepared by conventional method

Table 2 Cu concentration on surface and Cu/Zn atomic ratio of CuZnAl slurry catalysts

Catalysts	Cu[a]	Cu/Zn[a]	Cu[b]	Cu/Zn[b]
C-2.90	0.93	0.302	1.44	0.465
C-2.09	1.10	0.358	1.23	0.359
C-1.84	0.93	0.357	1.17	0.368
C-1.62	0.68	0.169	0.75	0.223

[a] Un-reduced catalyst

[b] The reacted catalyst

1,022 eV and the corresponding Zn LMM Auger peak at KE 988.2 eV, indicating its oxidation state of +2. Based on the results mentioned above, it is concluded that the catalysts surface is composed of Cu^0, Cu^+ and ZnO. It has been reported that both Cu^+ and Cu^0 are essential for the methanol formation [14–16] and ZnO has synergism with Cu [13, 15]. Thus the slurry catalysts prepared by the complete liquid-phase method may have similar active site to those prepared by conventional method.

The atomic ratios on the surface of the un-reduced and the reacted catalyst are illustrated in Table 2. The Cu/Zn ratios of all un-reduced catalysts are lower than the bulk Cu/Zn ratio which, according to the nominal composition Cu/Zn = 1:1, should be one. Similar results has been reported in the literature [13, 17, 18], but it should be noted that in our case the maximum value for Cu/Zn ratio is 0.358, which is far lower than that of catalyst prepared by conventional method, indicating that more zinc ions enrich onto the surface of the catalysts in the liquid-phase preparation circumstance. For the reacted catalysts, an increase in Cu concentration accompanied by an increase in the Cu/Zn ratio is observed when compared to the un-reduced catalysts. In opposition to our result, Dai et al. [18] have reported that the surface Cu/Zn ratio decrease in the reduced and the reacted catalyst because the CuO can not be well dispersed by the surrounding zinc oxide and alumina in the preparation process and copper would agglomerate or undergo sintering and lead to the growth of copper particle size during the reduction and reaction process. Figueiredo et al. [19] have also found that the decrease of the Cu/Zn ratios in the reduced catalysts indicated a lack of copper dispersion. These findings in this work suggest that the slurry catalyst prepared by the complete liquid-phase preparation method can be highly dispersed and hinder the agglomerate or sintering of copper, which can also been confirmed by the XRD results.

3.4 The Catalytic Performance

The dependence of the catalytic performance on the content of Al in CuZnAl slurry catalysts are shown in Figs. 3 and 4. At each temperature, the reaction of 24 h was performed. The data listed in Figs. 3 and 4 is average value during the reaction of 24 h at a certain temperature. It is obvious that the conversion of CO and selectivity to DME changes regularly with the content of Al. The optimized CO conversion and DME selectivity is obtained over the catalyst with 2.09 mol% Al. The selectivity to DME is 93.08% at 553 K and still approaches 80% even at lower temperature. Generally speaking, Cu, Zn is active site for methanol formation, so it is reasonable to conclude that in CuZnAl catalyst in this work boehmite plays important role in methanol dehydration. Up to now, no researches have been reported on the methanol dehydration over boehmite,

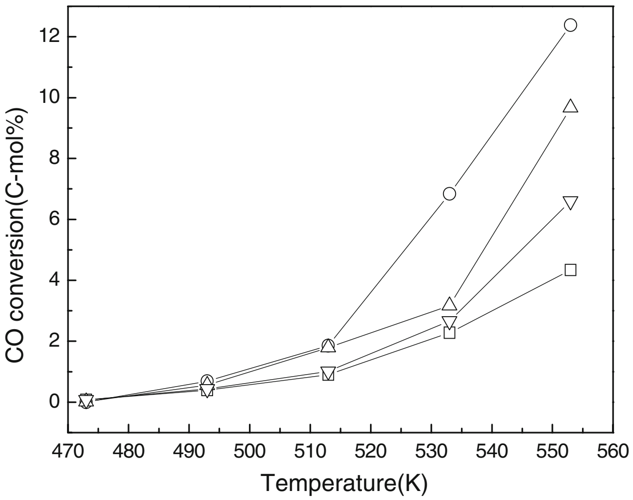

Fig. 3 Effect of Al content in CuZnAl slurry catalysts on CO conversion (□) C-2.90 (○) C-2.09 (△) C-1.84 (▽) C-1.62 (reaction conditions: P = 4.0 MPa; H_2/CO = 1.0; GHSV = 250 mL/g_{cat}h)

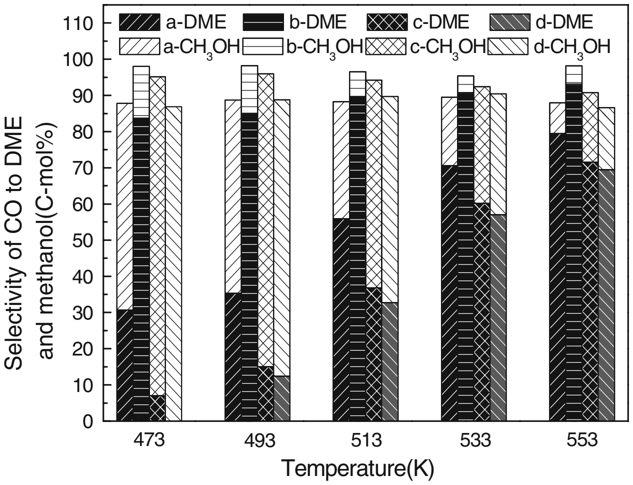

Fig. 4 Effect of Al content in CuZnAl slurry catalysts on selectivity of CO to DME and methanol **a** C-2.90 **b** C-2.09 **c** C-1.84 **d** C-1.62 (reaction conditions: P = 4.0 MPa; H_2/CO = 1.0; GHSV = 250 mL/g_{cat}h)

so this result will extent the research field of methanol dehydration.

When Al content is below 2.09 mol% (1.84 and 1.62 mol%), the DME selectivity is lower but methanol selectivity is higher, which reveals that the ability of methanol dehydration drops. When the content of Al becomes 2.90 mol%, the conversion of CO is the lowest but the selectivity to DME is higher than that of the catalysts with the Al content of 1.84 and 1.62 mol%, which indicates that the ability of methanol synthesis decreases. Therefore, it can be deduced that the mechanism of the direct conversion of CO and H_2 to DME over the CuZnAl slurry catalysts is still a two-step reaction involving methanol formation followed by methanol dehydration. It is interesting to note that the total selectivity of DME and methanol over each catalyst remains essentially constant at all of temperatures investigated, in other words, the ratio of the total selectivity of methanol and DME to that of methane kept unchanged with reaction temperature. Thus it can be concluded that methane formation under these conditions does not occur mainly by further hydrogenation of methanol but by an independent pathway from CO and H_2 parallel to that of methanol formation and there is a common intermediate for the above two reaction.

Figure 5 presents the change of CO conversion and DME selectivity with time-on-stream over the C-2.09 slurry catalyst. These data were collected first from 473 to 553 K, and then from 553 to 473 K. Through this way, the information of the catalyst life and stability can be observed. As shown in Fig. 5, at the same GHSV the CO conversion and the DME selectivity have no obvious change whether in the process of temperature rising or dropping, and it can also be concluded that the catalyst activity will rise as reaction time extends because an increase in the conversion of CO was observed at low reaction temperature in the process of temperature dropping. It clearly shows the performance of the catalyst is even during the 450 h varying duty reaction and no deactivation has been found. Air products and chemicals Inc. [20] have reported that the deactivation rate of catalyst used in laboratory to synthesize DME was 1.2%/d. Peng [21] have also found that the degradation of the activity of methanol synthesis and methanol dehydration was confirmed to be lower than 68 and 62 points of the initial value respectively after 117 h DME synthesis reaction in slurry reactor. Hence, it can be concluded that the catalyst in our work behaves a very good stability, which should attribute to the highly dispersed Cu component and the special Al form in the catalyst.

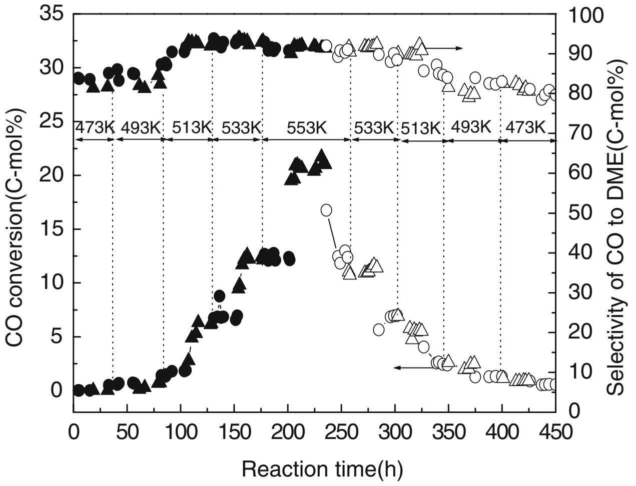

Fig. 5 CO conversion and DME selectivity as function of reaction time over the C-2.09 slurry catalyst (▲, △) GHSV: 150 mL/g_{cat}h (●, ○) GHSV: 250 mL/g_{cat}h (reaction conditions: P = 4.0 MPa; H_2/CO = 1.0; solid: raising temperature; open: dropping temperature)

4 Conclusion

In this work, the CuZnAl slurry catalysts with different contents of Al were prepared by the complete liquid-phase method. The characterization results indicate the main phase existed in the catalysts are Cu, Cu_2O, ZnO and boehmite (AlOOH), and the structures of pore and surface are comparable with those of the commercial methanol synthesis catalysts and active metals on the slurry catalysts are highly dispersed. Activity tests show that the slurry catalysts are quite effective for the single-step synthesis of DME from syngas and boehmite plays important role in methanol dehydration. Among the catalysts investigated in this work, the catalyst with 2.09 mol% Al is best, whose DME selectivity reaches 93.08%. All of the catalysts prepared by the novel method exhibit good stability during the reaction time investigated for 18 days.

In the end, we have to stress that this is an advantage for CuZnAl slurry catalysts in DME selectivity and stability, which may be contributed to the specificity of the preparation method. However, at this stage its CO conversion is lower than the traditional catalysts for DME synthesis. Hence, a variety of experimental approaches are still needed in a further work to provide corroborating and conclusive materials to fully understand the exact characteristic of slurry catalysts.

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