Liquid phase preparation of catalysts used in slurry reactors to synthesize dimethyl ether from syngas: Effect of heat treatment temperature

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The CuZnAl slurry catalysts have been prepared by a complete liquid phase technology and characterized by X-ray diffraction, H₂ temperature-programmed reduction and temperature-programmed desorption of ammonia. The activity of the catalysts for direct synthesis of DME from syngas is evaluated in a slurry reactor. The structure and performance of the catalysts under different heat treatment temperatures are investigated. The results indicate that the phase of copper species, reducibility of catalysts and acid distribution are affected by the heat treatment temperature. Moreover, the catalyst heat treated at 513 K shows the smallest crystal size of Cu, good dispersion, more weak acid sites and larger amount of stable Cu₂O species. In the DME synthesis reaction, it is found that the effect of heat treatment temperature on the catalytic activity is depended strongly on the ratio of Cu⁹/Cu¹⁺ and the proportion of weak acid sites in the catalyst. The catalyst shows maximum activity at 513 K.

Keywords: Catalysts, Liquid phase catalysts, Slurry catalyst, Dimethyl ether, Syngas

Dimethyl ether (DME) has recently received much attention as a clean alternative fuel for diesel engines with much lower NOx emission, near-zero smoke production, and less engine noise as compared with traditional diesel fuels. This has led to a growing requirement to produce large scale of DME to meet the future market.

Single-step synthesis of DME from syngas over bifunctional catalysts in slurry reactor has been recently reported by many researchers because of its advantages of simplicity, economic rationality, lower investment, better heat transfer, direct use of CO-rich syngas, and so on. However, a major problem in commercial application of slurry DME synthesis technology is the poor stability of bifunctional catalysts. Thus, the causes of catalyst deactivation, including sintering, aggregating, coking and poisoning were investigated and extensive researches have been focused on preparing catalyst with good stability. It is worth mentioning that the catalysts reported in the literatures for DME synthesis in a slurry reactor are all prepared by dispersing the traditional solid catalysts into the organic medium. This preparation method may cause a mismatch between the hydrophilicity of the catalyst surface and the oiliness of the organic medium, leading to non-ideal interfacial wettability. This further induces misdistribution, aggregation and rheological deterioration of the catalyst particles in the reactor, and thus significantly reduces the catalyst's performance.

Considering that the formation and growth of the catalyst material should take place in the same environment where the catalyst is finally used, we have proposed a novel catalyst preparation technology used specially for slurry reactors, i.e., complete liquid phase technology. Its novelty lies in heat treating the catalyst precursor directly in organic medium, instead of traditional drying and calcination processes. In the literature, it has been reported that the technological conditions in traditional drying and calcination processes greatly influence the structures of the precursors and catalysts, which finally result in differences in the catalytic performance. The effect of calcination temperature on Cu-based catalysts has been studied extensively by many researchers. Xu et al. investigated the effect of calcination temperature on CuMnZrO₂ catalysts for synthesis of higher alcohols from syngas. It is reported that the calcination temperature strongly influenced the interaction between the active species and support, and hence, the structure and catalytic performance. Low calcination temperature yielded poorly crystallized catalysts and favored the formation of a Cu(OH)₂-like structure. In the case of CuO-CeO₂ catalyst for selective oxidation of CO, Jung et al. found that the oxidation state of copper in the CuO-CeO₂ catalyst changed from cuprous oxide to cupric oxide with the increase of calcination temperature. Mahato et al. observed that the CuO particles grew with calcination temperature. Also, the size distribution changed; the material calcined at lower temperature has a narrow size distribution whereas the material calcined at higher temperature shows a wide size distribution. Yang et al. proved...
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that with the increase of calcination temperature, 
CuO, ZnO and Al$_2$O$_3$ were formed with evident 
crystallization and the reduction peak of CuO shifted 
to high temperature. Guo et al.\textsuperscript{19} showed that the 
dispersion of copper species decreased with the increase in calcination temperature.

In the presently used complete liquid phase 
technology, the heat treating process is also a key 
step. This study discusses the effect of heat treating temperature on the properties of the synthesized 
CuZnAl slurry catalysts. The relationship between 
the physiochemical properties and the catalytic 
performance are also discussed.

**Experimental**

CuZnAl slurry catalysts were prepared by complete 
liquid phase technology\textsuperscript{20,21}. The CuZnAl atomic 
ratio in the catalyst was 2/1/4. The process was 
divided into three stages. The first stage was the 
preparation of Al sol, wherein Al(i-C$_3$H$_7$O)$_3$ (55.09 g) 
was hydrolysed by adding 300 mL distilled water at 
353 K, and stirring the resulting mixture for 1.5 h. 
Subsequently, 2.29 mL of 12 N HNO$_3$ was added 
dropwise with stirring for 1 h at the same temperature 
(353 K) when the Al sol was immediately formed. 
The second stage was the preparation of CuZnAl gel. 
Cu(NO$_3$)$_2$.3H$_2$O (32.75 g) and Zn(NO$_3$)$_2$.6H$_2$O 
(19.83 g) were dissolved in 50 mL ethanol and the 
resulting solution was slowly added to the Al sol. 
The resulting CuZnAl solution was stirred at 353 K 
until a gel was obtained. The CuZnAl gel was then 
aged for 7 days at ambient temperature. The third 
stage was the preparation of CuZnAl slurry catalysts. 
The CuZnAl gel was dispersed in liquid paraffin 
under mechanical stirring and heated from room 
temperature to 473 K, 493 K, 513 K, 533 K and 
553 K, at a heating rate 10 K/min and a N$_2$ flow of 
200 mL/min at normal pressure and was kept for 16 h 
at the heat treatment temperature, when the CuZnAl 
slurry catalysts were obtained. These catalysts are 
abbreviated as CATX, where ‘X’ denotes the heat 
treatment temperature.

DME synthesis reaction was carried out in a 0.25 L 
slurry reactor with a mechanic agitator. The CuZnAl 
slurry catalysts were not pre-reduced by hydrogen 
before reaction. The synthesis gas (H$_2$/CO = 1) was 
directly introduced into the reactor at 4.0 MPa 
pressure, gas hourly space velocity of 250 mLg$_{cat}$ h$^{-1}$ 
and temperature of 473-553 K. Outlet gaseous 
products were analyzed with a gas chromatograph 
equipped with a flame ionization detector and 
a thermal conductivity detector, using GDX-502 
and TDX-01 columns, respectively. From the 
chromatographic results of the outlet gas, the 
conversion of CO (X$_{CO}$) and the selectivities ($S$) of 
DME and methanol can be calculated respectively 
as Eqs (1), (2) and (3),

$$X_{CO} = \frac{N(2y_{DME} + y_{CH3OH} + y_{CH4} + 2y_{C2H4} + 3y_{C3H6} + y_{CO2})}{N_{0}(y_{CO})_0} \times 100 \quad \ldots (1)$$

$$S_{DME} = \frac{2y_{DME}}{2y_{DME} + y_{CH3OH} + y_{CH4} + 2y_{C2H4} + 3y_{C3H6}} \times 100 \quad \ldots (2)$$

$$S_{CH3OH} = \frac{y_{CH3OH}}{2y_{DME} + y_{CH3OH} + y_{CH4} + 2y_{C2H4} + 3y_{C3H6}} \times 100 \quad \ldots (3)$$

where $N_0$ and $N$ are the flow rates of the feed 
and product (mL/min), $y_i$ is the mole fraction of component $i$ in the product stream and $(y_{CO})_0$ is 
the mole fraction of CO in the feed stream. All 
experimental data were obtained under steady-state 
conditions that were usually maintained for 24 h at 
one tested point.

Prior to characterization, the catalysts were extracted 
by petroleum benzine and dried at room temperature 
in order to eliminate the effect of liquid paraffin 
on catalyst characterization and show the actual 
properties of the slurry catalyst.

X-ray diffraction (XRD) data of catalysts were collected on a Rigaku D/max 2500 diffractometer 
(Cu-Kα radiation, 40 kV, 100 mA). H$_2$-TPR was 
carried out in a laboratory-made micro reactor. For 
each TPR experiment, 50 mg catalyst was packed 
into the reactor and heated at the rate of 10 K/min to 
773 K in a stream of H$_2$/N$_2$ (5/95) at a flow rate of 
30 mL/min. The amount of H$_2$ uptake during the 
reduction was measured by a thermal conductivity 
detector (TCD). XPS were acquired on an 
ESCALAB 250 spectrometer (VG Scientific Ltd., 
UK) using Al-Kα radiation ($h\nu = 1486.6$ eV) and C$_1s$ 
(BE = 284.6 eV) was used as an internal standard. 
NH$_3$-TPD was carried out in a tubular reactor. The 
NH$_3$ was passed for 30 min over 50 mg catalyst at 
423 K. After adsorption, the sample was purged with 
He for 30 min at 323 K. TPD data were collected 
from 323–1073 K at a heating rate of 10 K/min.
Results and discussion
The catalytic performance of the CuZnAl slurry catalysts were tested for DME synthesis at different reaction temperature (Fig. 1). With an increase in reaction temperature, CO conversion with all the catalysts increased. On the other hand, the heat treatment temperature showed significant influence on the CO conversion. As shown in Fig. 1, the conversion of CO initially increased with heat treatment temperature, passing through a maximum at 513 K, and then decreasing. The relationship between DME selectivity and the heat treatment temperature showed a similar tendency as that of the CO conversion. The selectivity of different catalysts at the reaction temperature of 553 K is shown in Fig. 2, the selectivity of CAT513 was the highest for DME. When the heat treatment temperature was higher than 513 K, DME selectivity decreased, accompanied by an increase in the methanol selectivity. This result indicates that the catalytic activity for methanol synthesis and methanol dehydration was affected by the heat treatment temperature. The above results show that the catalyst performed best when the heat treatment temperature was 513 K. It was interesting to note that DME can be produced from syngas over these catalysts, although the catalysts were not pre-reduced by hydrogen before reaction, indicating that certain active sites for methanol synthesis and methanol dehydration had been formed during the heat treatment process.

The XRD patterns of the CuZnAl slurry catalysts before and after 120 h reaction time are collected in Fig. 3. As shown in Fig. 3a, before the reaction, broad and diffuse peaks of AlOOH are observed in all
samples, indicating that AlOOH was already formed at all temperatures of heat treatment and the thus-formed AlOOH was highly amorphous with a low level of crystallinity. However, the copper species in the catalyst was affected obviously by the temperature of heat treatment. The CAT473 catalyst exhibited strong and sharp diffraction lines of Cu$_2$ (OH)$_3$ (NO$_3$), while the diffraction peaks of CuO were weak, suggesting that the copper nitrate did not decompose completely when heat treatment temperature was 473 K. With increasing heat treatment temperature to 513 K, the diffraction lines of Cu$_2$(OH)$_3$(NO$_3$) disappeared and the main diffraction lines were for CuO and Cu$_2$O. On further raising the heat treatment temperature to 553 K, the main diffraction peaks were of Cu$_2$O and Cu. These results show that the copper species in the catalyst varied under different heat treatment temperature. Also, it was found that the partial CuO can be reduced to low-valent copper (Cu$_2$O or Cu) during the heat treatment process when the temperature was higher than 513 K. The possible reason for forming low-valent copper is that liquid paraffin was partially cracked under heat-treatment conditions, and CuO was then reduced by hydrogen and the hydrocarbon free radical produced from the cracking of liquid paraffin.

The XRD patterns of the CuZnAl slurry catalysts after 120 h reaction are presented in Fig. 3b. All the catalysts exhibited similar diffraction lines of Cu, revealing that copper species (CuO or Cu$_2$O) undergoes further reduction during the reaction in the H$_2$/CO atmosphere. Thus, it may be concluded that the final phase structure of the catalyst depends mainly on its composition and the reaction environment and less on the heat treatment temperature. However, the peak intensity of Cu changed significantly under different heat treatment temperatures. The width of the most intensive peak Cu (111) at half-height of the peak was used for estimation of the average crystal size of Cu by the Scherrer equation. The average crystal size of Cu after 120 h reaction for CAT473, CAT493, CAT513 and CAT553, was 28.7, 23.4, 14.7, 17.5 and 18.2 nm respectively. The catalyst heat treated at 513 K had the smallest crystal size of Cu (14.7 nm) and higher disperisty. These observations establish the fact that the heat treatment temperature had tremendous effects on the crystal size of Cu during the process and can be controlled by selecting the proper heat treatment temperature, while keeping all other conditions the same. In conjunction with the activity evaluation results, it may be concluded that small crystal size of Cu and good dispersion were beneficial for DME synthesis from syngas.

The H$_2$-TPR profiles of the catalysts treated at different heat treatment temperatures before and after 120 h reaction are reported in Fig. 4. In the H$_2$-TPR profiles before reaction of CAT473 and CAT493, three peaks appear at 533 K, 563 K and 600 K (Fig. 4a). With the increase of heat treatment temperature to 513 K, the lower temperature peak at 533 K disappears and the peak at 563 K shifted to even lower temperature with gradual decrease in the area of higher temperature peak at 600 K. A poorly resolved peak was observed for CAT533 with a shoulder (556 K) on the right side of the maximum (549 K) while the shape of the peak for

Fig. 4 – H$_2$-TPR profiles of catalysts at different heat treatment temperatures (a) before reaction, and, (b) after 120 h reaction time. [1, CAT473; 2, CAT493; 3, CAT513; 4, CAT533; 5, CAT553].
CAT553 (547 K) was sharper and more symmetrical. Combined with the XRD results, it seems reasonable to relate the different H$_2$-TPR signals to copper species with different composition, which will have different reducibility.

On the other hand, it can be seen from Fig. 4b that after 120 h reaction, two peaks appeared at 500 K and 526 K for CAT473 catalyst. The other four catalysts showed a single peak at ~520 K. The attribution of the reduction peak was further examined by XPS analysis of the catalysts obtained after 120 h of reaction. The result showed that the Cu$^2+$ $p_{3/2}$ binding energy value of all catalysts was about 931.8 eV and no shake-up satellite peak at 943.7 eV existed, indicating the absence of Cu$^{2+}$ ions$^{22,23}$. The Cu L$_{2,3}$ Auger peaks of the catalysts were broadened, due to the overlapping of two peaks at KE 918.8 and 917.6 eV. It was obvious that Cu$^0$ and Cu$^+$ were co-present in the catalysts. According to XRD results, only metallic copper was found for all catalysts after reaction. No peaks attributed to Cu$_2$O were seen in XRD patterns. One explanation is that Cu$_2$O is amorphous or its crystal sizes too small to be detected by XRD. Another explanation is that the Cu$_2$O exists mainly in the catalysts surface. Thus, it may be concluded that the reduction peaks in Fig. 4b are due to reduction of Cu$_2$O. The reduction peak areas for the CAT473, CAT493, CAT533 and CAT553 decreased remarkably after 120 h reaction, while that for CAT513 changed only slightly and had the larger area amongst the five reduced catalysts. This indicates that after 120 h reaction the amount of Cu$_2$O in the CAT513 was more than in the others and also difficult to reduce during the reaction. It was thus inferred that difficulty in reduction of Cu$_2$O may be contributing to the higher catalyst activity. In general, catalysts used for synthesis of DME from syngas possess the ability for methanol synthesis and methanol dehydration. Earlier reports show that Cu$^+$ and Cu$^0$ are essential for the formation of methanol and that the Cu$^+$/Cu$^0$ ratio determined the specific activity$^{24,25}$. The H$_2$-TPR results indicate that the heat treatment temperature affects the ratio of Cu$^+$/Cu$^0$ on the catalyst surface and consequently, significantly different catalytic performances are observed. This result demonstrates that an optimum Cu$^+$/Cu$^0$ ratio may exist.

NH$_3$-TPD was performed to monitor the acid strength and the amount of acid sites of the different catalysts. As shown in Fig. 5, the catalysts heat treated at 473 K and 493 K showed only one typical NH$_3$-TPD spectrum at higher temperature (728 K-733 K), which may be attributed to the strong acid sites. This indicates that the CAT473 and CAT493 catalysts have not formed any weak acid site. However, when heat treatment temperature was above 493 K, the catalysts showed two NH$_3$ absorption peaks at 608 K-638 K and 728 K-733 K, corresponding to NH$_3$ eluted from the weak and strong acid sites, respectively. On comparing the ratio of weak to strong acid sites of the different catalysts before reaction, it is found that CAT513 had the highest ratio of weak to strong acid sites, which is in good agreement with the higher activity of this catalyst. This result indicates that the weak acid sites were responsible for the formation of DME, in accordance with earlier reports in literature$^{26,27}$.

In summary, the heat treatment temperature showed strong influence on the catalytic performance of the CuZnAl slurry catalysts prepared by complete liquid phase technology. On varying the heat treatment temperature from 473 K to 553 K, the phase of copper species, the reducibility of catalysts, the state of hydroxyl group and the acid distribution changed. The characterization results showed that the catalyst heat treated at 513 K had the smallest crystal size of Cu, good dispersity, more weak acidic sites and larger amount of Cu$_2$O, which was stable and difficult to be reduced during the reaction. The final phase structure of the catalyst depended mainly on its composition and the reaction environment and less on the heat treatment temperature. The activity evaluation results indicated that the effect of
heat treatment temperature on the catalytic activity depended strongly on the ratio of \( \text{Cu}^{0}/\text{Cu}^{+} \) and their dispersity. It was observed that a higher proportion of weak acid sites were in good agreement with the higher catalytic activity. Maximum catalytic activity was observed when the heat treatment temperature was 513 K.

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