Journal of Zhejiang University SCIENCE A
ISSN 1673-565X (Print); ISSN 1862-1775 (Online)
www.zju.edu.cn/jzus; www.springerlink.com
E-mail: jzus@zju.edu.cn

Attrition resistant catalyst for dimethyl ether synthesis in fluidized-bed reactor

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Received Mar. 3, 2008; revision accepted May 12, 2008

Abstract: Fluidized-bed reactor is a candidate for dimethyl ether (DME) synthesis from syngas because of its excellent heat removal capability. In order to improve the attrition resistance of catalyst, an amount of silica sol as binder was added to the catalyst composed of methanol synthesis component $CuO/ZnO/Al_2O_3$ and methanol dehydration component HZSM-5, which was prepared by coprecipitation and shaped by spray drying to get spherical particles. The effect of silica sol on the catalytic activity was investigated in a fixed-bed flow microreactor. Based on the experiment results, silica sol in the range of 0~20wt% had small effect on the catalytic activity. Generally, the CO conversion and DME yield decreased with the increase in concentration of silica sol, while the attrition resistance of catalysts increased with increasing silica sol, indicating that it was feasible to improve the attrition resistance without greatly sacrificing the activity of catalyst. In addition, the characterizations of catalysts were carried out using Brunauer-Emmett-Teller (BET), X-ray powder diffraction (XRD) and temperature programmed reduction (TPR).

Key words: Dimethyl ether (DME), Attrition resistance, Catalytic activity, Silica sol
doi:10.1631/jzus.A0820155 **Document code:** A **CLC number:** TQ426.63

INTRODUCTION

Dimethyl ether (DME) has attracted wide attention as a useful chemical intermediate for the preparation of many important chemicals, such as methyl acetate and lower olefins. Especially, DME can be used as a fuel for diesel engines with thermal efficiencies equivalent to traditional diesel fuel, much lower NO_x emission, near-zero smoke production and less engine noise. The physical properties of DME are similar to these of liquefied petroleum gas (LPG), so DME can replace LPG as domestic fuel. In addition, DME is also used as an aerosol propellant to substitute for chlorofluorocarbons which harm the ozone layer (Takeguchi *et al.*, 2000; Omata *et al.*, 2002; Luan *et al.*, 2007; Moradi *et al.*, 2007a). Therefore, when air pollution and energy crisis are two of the most serious problems all over the world, the study on DME as an alternative and clean fuel is again emphasized (Qi *et al.*, 2001; Kim *et al.*, 2004; Sun *et al.*, 2004; Fei *et al.*, 2006; Semelsberger *et al.*, 2006; Moradi *et al.*, 2007b).

Since the 1980s, direct synthesis of DME from syngas has been continuing research focus for its marked economic values and theoretical significance (Gogate *et al.*, 1992; Peng *et al.*, 1999; Yaripour *et al.*, 2005; Andreasen *et al.*, 2006; Wang *et al.*, 2006a). However, the three reactions, i.e., methanol synthesis ($CO+2H_2 \rightleftharpoons CH_3OH+90.4\ kJ$), methanol dehydration ($2CH_3OH \rightleftharpoons CH_3OCH_3+H_2O + 23.7\ kJ$) and water gas shift ($CO+H_2O \rightleftharpoons CO_2+H_2+40.9\ kJ$) included in the process of direct DME synthesis from syngas are all highly exothermic reactions. Therefore, there is need for reactors to easily remove reaction heat. Slurry bubble column reactors (SBCRs) are attractive for their heat removal capability (Guo and Huang, 1997; Liu *et al.*, 2002). However, SBCRs encounter serious mass transfer problem due to the introduction of inert liquid phase such as waxy liquid for efficient heat removal, which becomes the drawback of industrial production of DME. Xiao and Lu (2002) proposed to synthesize DME in fluidized-bed reactor. Fluidized-bed reactors show better heat removal property because of the movement of catalyst particles in the bed. It has been calculated that the coefficient of heat transfer in fluidized-bed reactor is five times as much as that in SBCRs. Furthermore, it was reported (Wang *et al.*, 2001) that in the slurry reactor the CO conversion was about 17%, the selectivity of DME was 70% at the conditions of T=260 °C, P=4.0 MPa, H_2/CO=1.0 (v/v), and gas space velocity of 3000 ml/(g·h). Under the same conditions, in the fluidized-bed reactor CO conversion and DME selectivity can be as high as up to 48.5% and 97.0% (Teng, 2004), while in a fixed-bed reactor, the corresponding levels are 10.7% and 91.9% (Lu *et al.*, 2002). Obviously, the fluidized-bed reactor demonstrates a considerable DME productivity improvement over both the fixed-bed and the slurry reactor. Therefore, one can conclude that among different reactors the fluidized-bed is the most promising candidate for conducting the DME synthesis from syngas.

However, catalysts used in fluidized-bed reactor are subject to attrition from collision between catalyst particles and the reactor wall which can result in loss of catalyst and plugging of filter (Ray *et al.*, 1987; Petukhov and Kalman, 2003). So attrition resistance is one of the critical parameters in the development of catalysts. The objective of this study is to develop a kind of catalyst suitable for fluidized-bed application with high catalytic performance and high attrition resistance. The catalyst presented in this paper is based on Cu base catalyst and HZSM-5, prepared by a conventional coprecipitation method (Ramos *et al.*, 2005). The method to improve attrition resistance is to introduce silica sol as binder to the active components, followed by spray drying which yields spherical particles favorable for fluidized-bed reactor application (Bukur *et al.*, 2005). However, improvement in attrition resistance at the expense of activity and selectivity of catalyst is undesirable. To determine if the silica sol is feasible in improving the attrition resistance without sacrificing the activity of catalyst, the effect of silica sol on the catalytic performance and attrition resistance was studied.

EXPERIMENTS

Catalyst preparation

The catalysts used in this study were prepared by a conventional coprecipitation method and shaped by spray drying. These catalysts had the same composition of CuO, ZnO, Al_2O_3 and HZSM-5 but with different concentrations of silica sol. The process of catalyst preparation was described in detail as follows. First, it was precipitated from an aqueous solution of $Cu(NO_3)_2$ and $Zn(NO_3)_2$ by dropwise addition of a 1 mol/L aqueous solution of Na_2CO_3 at 80 °C to a final pH value of 7. Then, the mixture was thoroughly washed by deionized water to remove the sodium ion and then $Al(OH)_3$ power was added to the precipitate. At this time the composition of catalyst was 38 CuO/38 ZnO/8 Al_2O_3 by weight, which was the active component for methanol synthesis. It contained 9.5 parts by weight (pbw) of Al_2O_3. Following this, the acid dehydrogenation component HZSM-5 was thoroughly mixed with the above precipitate. The ratio of the methanol synthesis component to the acid dehydrogenation component is 5:1 by weight. After that, silica sol (pH 4~5, less than 0.05 wt% of sodium, 25 wt% of silica, provided by Qingdao Sea Chemical Research Institute) of different parts by weight as binder was added and blended completely. Finally, the slurry was spray dried in a spray drier with dimensions of 1.8 m inside diameter and 6.8 m total high to obtain spherical particles. The spray-dried catalyst was calcined at 350 °C for 3 h in a muffle furnace.

Spray dryer operating conditions have much effect on the particle characteristics. In order to obtain the suitable operating conditions, the effect of operating conditions on the particle size distribution and morphology was studied. Based on the experimental results obtained, it was determined that the appropriate parameters were nozzle diameter of 0.9 mm, pressure of 2 MPa, feed rate of 30 L/h, the inlet temperature of 300 °C and outlet temperature of 140 °C. The detail results were described in (Teng, 2004).

Reaction studies

The catalytic property of catalysts for DME synthesis from syngas was tested in a laboratory-scale high-pressure and high-temperature stainless fixed-bed reactor. The reactor had a size of Φ10 mm×300 mm and contained 2.0 g of packed catalysts (40~80 meshes). These catalysts were supported between two layers of quartz, the upper layer of which was used to preheat the reactants. A thermocouple was located at the level of the catalysts in the reactor. Gas flow rate was controlled by mass flow controller. The reaction pressure was controlled by back pressure valve. The downstream line from the reactor exit to the analysis system was coated by heating belt to avoid the condensation of water and methanol formed during reaction. Before the feed gas was introduced, catalysts need to be reduced with pure H_2 at the normal pressure and a flow rate of 100 ml/min according to the following heating program: heating up from room temperature to 300 °C at a heating rate of 1 °C/min and then keeping for 3 h.

Following catalyst reduction, the reactor temperature was decreased to reaction temperature and H_2 flow was stopped, followed by syngas at a space velocity of 3000 ml/(g·h). The syngas was a premixed gas of CO and H_2 (H_2/CO=1, v/v). The reactor system was then pressurized to 3 MPa. After achieving the desired process condition of 260 °C, 3 MPa, 3000 ml/(g·h), the sample was analyzed every other 0.5 h till the activity of catalyst reached a stable state.

All the products and feed gas were analyzed by an online 7890T gas chromatograph made by Shanghai Tianmei Scientific Instrument Factory in China that was coupled with a CDMC-1EX integrator. The different gases to be analyzed were separated by a column filled with GDX-101. A thermal conductivity detector (TCD) was used to detect reaction products. The CO conversion and DME yield were defined as follows:

$$X_{\mathrm{CO}}=\frac{F_{\mathrm{in}}y_{\mathrm{co,in}}-F_{\mathrm{out}}y_{\mathrm{co,out}}}{F_{\mathrm{in}}y_{\mathrm{co,in}}}\times 100\%\ \ (\mathrm{mol/mol}),$$

$$Y_{\mathrm{DME}}=\frac{2F_{\mathrm{out}}y_{\mathrm{DME,out}}}{F_{\mathrm{in}}y_{\mathrm{co,in}}}\times 100\%\ \ (\mathrm{mol/mol}),$$

where F_{in} is gas flow rate at inlet of reactor (mol/min); F_{out} is gas flow rate at outlet of reactor (mol/min); $y_{\mathrm{co,in}}$, $y_{\mathrm{co,out}}$, $y_{\mathrm{DME,out}}$ are percent by molar of CO at inlet, outlet and molar of DME at outlet, respectively.

Catalyst characterization

Detailed physical and chemical characterization of catalysts was carried out using the following analytical techniques. Morphology information for each sample with different binder parts by weight was achieved by a Japanese JSM-6360 LV from JEOL scanning electron microscope (SEM) at an accelerating voltage of 15.0 kV. The samples were coated with palladium before SEM measurements to avoid charging problems.

The attrition of the catalysts was measured using test method ASTM-D-5757-95 in a fluidized-bed test system with 26 mm (diameter)×2500 mm (height). Particle sizes less than 20 μm are considered fines. The fine collection was weighed before and after the test. The system consists of a vertical attrition tube made from stainless steel with 2000 mm long and 26 mm inside diameter. There is an orifice plate attached to the bottom of this tube. Above the attrition tube is the setting chamber with a 100 mm inside diameter. The gas outlet of the setting chamber is connected with a filter in order to prevent fine particle loss. The attrition loss is calculated from the fine particles to give a relative estimation of the attrition resistance of the catalyst. The attrition loss is based on the fine loss after 4 h. To further illustrate the attrition resistance of the catalyst prepared, a kind of industrialized catalyst Cu/SiO_2 for fluidized-bed reactor was used for comparison. The attrition loss of different catalysts was tested under the same test condition.

Particle size distribution (PSD) of catalyst particles was analyzed using an American LS (AccuSizerTM 780) particle size analyzer from company of Particle Sizing Systems (PSS). This system was controlled with a computer system, and the output from the computer provided a plot of volume percentage vs particle size interval. The sample was measured before and after attrition measurement.

The Brunauer-Emmett-Teller (BET) specific surface area of the catalysts was determined, based on N_2 physic sorption at liquid nitrogen temperature on a micromeritics ASAP 2010 system. The samples were degassed at 393 K for 1 h prior to each measurement.

X-ray powder diffraction (XRD) patterns were obtained on a Rigaku D/max 255 VB/PC X-ray unit, and the XRD patterns were recorded for 2θ from 5° to 75° using Cu K_α radiation. Analyses were conducted using a continuous scan mode at a scan rate of 8°/min.

For determination of the reduction behavior of the catalysts, temperature programmed reduction

(TPR) experiments were carried out on Autochem II 2920 system. A sample of close to 0.025 g was dried and degassed under Ar flow at 400 °C for 1 h, and followed by cooling down to ambient temperature. Reduction was performed under H_2/Ar gas mixture (5/95, v/v). The total gas flow was 50 ml/min and temperature program was 25~600 °C at a heating rate of 5 °C/min.

RESULTS AND DISCUSSION

Effect of binder silica sol on catalytic activity

When catalytic activity was inspected in a fluidized-bed reactor, a lot of gas was needed and the operation was complicated. Since the main purpose of the evaluation of catalytic activity was to inspect the change of the catalytic activity after adding binder, namely the relative values of the activity, the evaluation on the catalytic activity mainly in the fixed-bed micro-reactor was conducted.

The effect of binder silica sol on the catalytic activity was shown in Fig.1. Generally, the CO conversion and DME yield decreased with an increase in concentration of binder silica sol. However, as can be seen, the catalytic activity was not remarkably decreased in the range of 0 to 20 wt% silica sol; beyond 20 wt% addition of silica sol catalytic activity and DME yield decreased significantly. Gas chromatography analysis showed that the main by-product was methanol. The content of methanol increased with the increase of the silica sol. This is mainly due to existing a preferential affinity of the methanol dehydration component for the silica sol leading to surface blocking proved by the following XRD patterns, which inhibited the reaction of methanol to DME. For the catalyst without silica sol, CO conversion and DME yield were 66.8% and 46.2%, respectively. When 20 wt% silica sol was introduced to the catalyst, the CO conversion decreased to 60.5% and the yield of DME decreased to 42%, indicating that it is possible to improve the attrition resistance by addition of binder silica sol to the catalyst components followed by spray drying without greatly sacrificing the activity of catalyst.

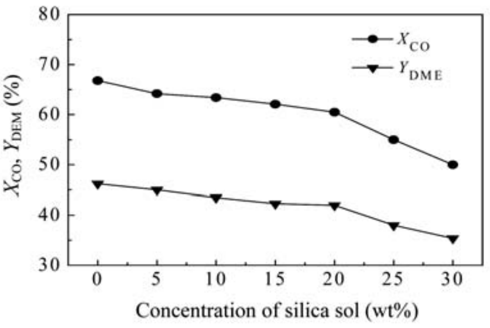


Fig.1 Effect of silica sol on catalytic activity

The catalyst containing 20 wt% silica sol was evaluated in a laboratory-scale fluidized-bed reactor. The experimental results showed that the catalyst had a good activity and selectivity. The detail results were described in (Teng, 2004). Then, the morphology information, PSD and other characteristics of the particles were characterized.

Catalyst characterization

There was a great influence of physical and chemical property of catalysts on the catalytic property. Different characterization methods were used to explain and identify the experiment results.

1. BET

The BET specific surface area, pore volume, average pore diameter and attrition loss of catalysts with binder silica sol from 0 to 30 wt% were listed in Table 1. The attrition loss was based on the weight of the fine particles after 4 h. As shown, the attrition loss decreased with an increase in concentration of silica sol, indicating silica sol is favorable for the improvement of attrition resistance. The BET specific surface area and pore volume of catalysts showed the maxima, while average pore diameter decreased with increasing silica sol. The results may be explained by that silica sol enters the pores of the original network of the catalysts, which helps to prevent a collapse of

Table 1 Effect of silica sol on physical properties of catalysts

Content of silica sol (wt%)	Surface area (m^2/g)	Pore volume (ml/g)	Average pore diameter ($\times10^{-10}$ m)	Attrition loss (4 h) (%/h)
0	128.64	0.3738	172.628	—
5	131.86	0.4429	166.532	14.3
10	140.96	0.5213	162.012	9.2
15	142.96	0.5735	159.351	7.1
20	143.89	0.5997	157.350	6.1
25	140.24	0.5672	154.287	4.6
30	135.67	0.5099	150.873	3.2

pore structure. On the other hand, there are interlocking forces created between the binder silica sol and catalyst components. It was also found that the catalysts with different content of binder silica sol had a density of about 0.53~0.60 g/cm^3 (not shown in Table 1), indicating that for the density there was no significant change with the addition of binder.

2. XRD

XRD of the catalysts containing 10 wt% binder, 20 wt% binder and the catalyst without silica sol were shown in Fig.2. The patterns had been plotted over 2θ value ranging from 5° to 75°. The identification of different species referred to Wang *et al.*(2006b). The XRD patterns of the catalysts with binder were nearly identical to that of catalyst without binder, indicating that binder silica sol had no remarkable effect on the crystal structure of catalyst components, no new species produced and the binder highly dispersed among the catalyst components in the amorphous state. Whereas, with addition of silica sol, diffraction peaks of HZSM-5 became sharper which meant that there was an interaction between the HZSM-5 and SiO_2, resulting in the gathering of HZSM-5. This reduced the catalytic activity for methanol dehydration.

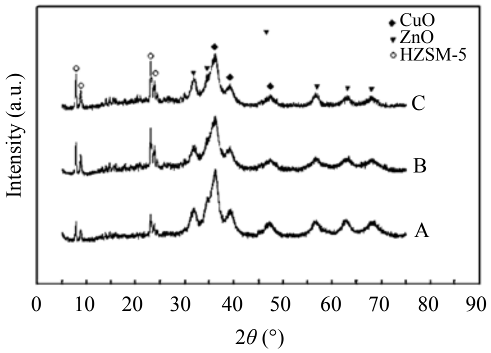


Fig.2 XRD patterns of catalysts

A: catalyst without binder; B: catalyst with 10 wt% binder; C: catalyst with 20 wt% binder

3. SEM

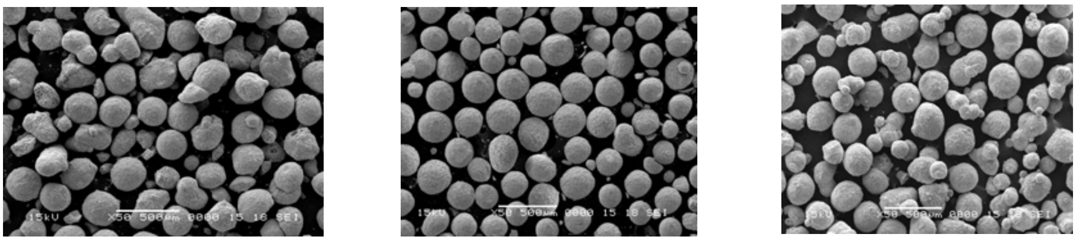
Fig.3 illustrated the morphologies of catalysts with 10 wt%, 20 wt% and 30 wt% binder silica sol. It can be observed that, generally, the catalysts were spherical in shape. This showed that binder silica sol was favorable for the formation of spherical particle. When the amount of silica sol was 10 wt%, the smaller and larger particles were basically irregularly shaped. The medium sized particles were relatively more spherical. For the catalyst particles with 30 wt% binder, they were not as spherical as expected, probably partly due to particle agglomerate during spray drying. Catalyst with 20 wt% binder was found to be the best in terms of sphericity of particles, indicating an optimum binder level of about 20 wt%. On the other hand, the PSD of catalyst with 20 wt% silica sol showed that the average particle size of catalyst shaped by spray drying was 180 μm as shown in Fig.4, which was just needed for DME production in fluidized-bed reactor.

4. TPR

A summary of the TPR characterization results for the catalysts was given in Table 2. The TPR results indicated that hydrogen consumption during TPR decreased with an increase in the concentration of the binder content. This was considered to be mainly due to decrease in the content of copper oxide in the catalyst. However, there was almost no change for the main peak temperature of the samples, with all at roughly 165 °C corresponding to the reduction CuO→Cu. These results suggested that there was no effect on the interaction of the catalyst components by the addition of an amount of binder.

Attrition mechanism

In order to investigate how particles were attrited, the morphological changes before and after a kind of attrition test were measured using a microscope. The



(a) (b) (c)

Fig.3 SEM image of the catalysts shaped by spray drying. (a) Catalyst with 10 wt% binder; (b) Catalyst with 20 wt% binder; (c) Catalyst with 30 wt% binder

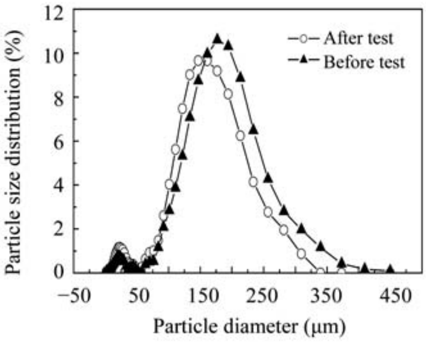
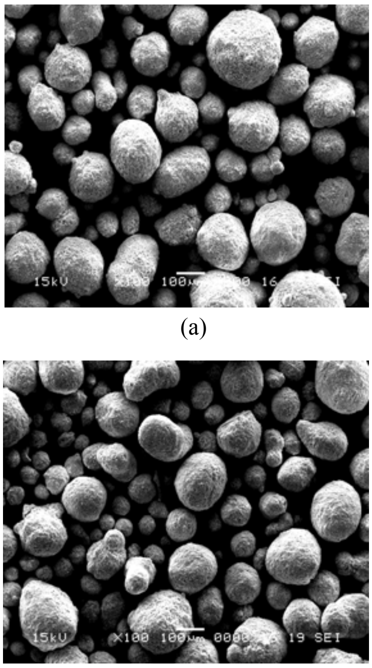


Fig.4 Particle size distribution of catalyst with 20 wt% binder

Table 2 TPR results of the catalysts

Amount of binder (wt%)	H_2 consumed peak (mmol H_2/g cat.)	Temperature (°C)
0	43.0	165
10	39.0	164
15	38.8	163
20	34.5	165
25	32.8	163
30	31.6	162

SEM images of catalysts particles with 20 wt% binder before and after attrition test were shown in Fig.5. From Fig.5, we can see clearly that the particles after attrition test did not show any significant change in sphericity. However, the number of bigger particles was obviously disappearing and the amount of smaller size particles increased after attrition test. Furthermore, after attrition test, the average particle size decreased from 180 μm to 170 μm and the particles in the range of 0~50 μm increased as shown in Fig.4. Therefore, combining the results of PSD and SEM, it would appear that particle attrition in the fluidized-bed test system is mainly caused by fracture of larger particles. A mother particle is disintegrated into two or more parts because of the collision between particles and equipment wall, among particles as well, decreasing the average particle size. Then the fragments were rounded off by the abrasion of gas, creating fine particles. The conclusion is in agreement with the theory proposed by Welt (1977) and Boerefijn *et al.*(2000), that the larger the particle diameter, the greater its rate of attrition. The attrition mechanism proposed in this paper can be described as Fig.6. According to this attrition mechanism, to further improve the attrition resistance, addition of other structural promoters could be considered in the next work.



(a)

(b)

Fig.5 SEM image of catalysts with 20 wt% binder. (a) Before attrition test; (b) After attrition test

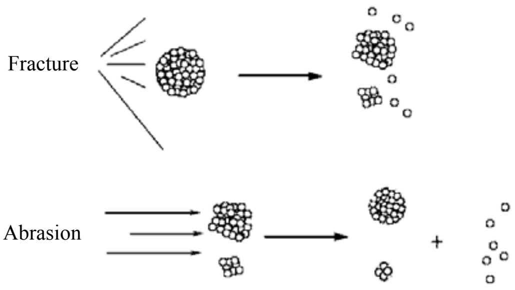


Fig.6 Mechanism of particle attrition

CONCLUSION

To develop a catalyst with high catalytic activity and attrition resistance used for DME synthesis in fluidized-bed reactor, addition of silica sol as binder to the active components of catalyst followed by spray drying was employed to improve the attrition resistance but with minor effects on the reduction of the catalytic activity. Within the range of 0~20 wt% silica sol, there was no remarked decrease in catalytic activity, although CO conversion and DME yield decreased with the increase in silica sol content, indicating that the attrition resistance was improved without greatly sacrificing the activity. The characterization of catalysts showed that binder silica sol had little effect on the chemical property of catalysts. Therefore, the catalyst studied in this paper has a great potential for fluidized-bed reactor application to directly synthesize DME. On the basis of further analysis by SEM and PSD, it is suggested that particle attrition is strongly affected by the fracture of bigger size particles and then the abrasion of the fragments by removal of outer surface that contains a lot of sharp corners.

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