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A novel liquid-phase technology for the preparation of slurry catalysts

Zhi-hua Gao, Li-feng Hao, Wei Huang*, and Ke-chang Xie

Key Laboratory of Coal Science and Technology, Taiyuan University of Technology, Ministry of Education and Shanxi Province Taiyuan, 030024, Shanxi, P.R. China

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A novel catalyst preparation method aimed to a slurry reactor has been suggested. Its main innovative thought lies in preparing the slurry catalysts directly from solution. Activity tests indicate that the $CuO–ZnO/Al_2O_3$ catalyst prepared by the novel method can efficiently catalyze syngas to DME and the selectivity to DME reaches 93.08%. The catalyst shows a good stability during the reaction of 440 h.

KEY WORDS: catalyst preparation; slurry reactor; DME synthesis; sol-gel.

1. Introduction

Currently, solid catalysts can be prepared by several methods, such as coprecipitation, impregnation and sol-gel processing. The common characteristics of these technologies are that metal salts or compounds are dissolved firstly and then treated through a series of steps such as dry and calcine, and finally, a solid powder is obtained. According to different reactors, the solid powder is taken to different shapes to use.

The slurry reactor has recently received more attention because of its advantages in caloric transfer. The current catalysts used in slurry reactor are all prepared by dispersing the traditional solid catalysts into the organic medium, which leads easily to catalyst subsiding, medium viscosity increasing, defluidity decreaseing and activity dropping.

In this paper, we would like to suggest a novel preparation method of slurry catalyst for slurry reactor. Its main innovative thought lies in preparing the catalysts directly from solution to the slurry. This novel method was first tried to prepare the catalysts for the direct synthesis of dimethyl ether from syngas in a slurry reactor.

As we known, DME is an important chemical and a chemical intermediant for production of gasoline, ethylene, aromatics and other chemicals. Growing attention is being paid to its applications as a transportation fuel or as a fuel additive [1–5], thus the demand for DME is expected to increase rapidly. Direct synthesis of DME from syngas in slurry reactor is considered to be promising for its dramatic economic values and theoretical siginificance.

2. Experiment

2.1. Catalyst preparation

The catalyst $CuO–ZnO/Al_2O_3$ was prepared by so-called complete liquid-phase technology in this work. An appropriate amount of $(C_3H_7O)Al$ was dissolved in water and kept at 35 K for 1.5 h in a water bath, then a certain amount of 12 N HNO_3 was added and stirred under reflux for 1 h at 36 K. The resulting solution was mixed with the another solution containing $Cu(NO_3)_2$ and $Zn(NO_3)_2$, and stirred under reflux at 36 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 put into a slurry reactor, in which activity tested will be carried out, and heated in N_2 flow by a temperature program as following:

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

After the treatment, a slurry catalyst was obtained.

2.2. Catalytic activity test

The DME synthesis reaction was carried out in a slurry reactor with a mechanical magnetic agitator. The slurry catalyst $CuO–ZnO/Al_2O_3$ of the solid hold-up of 18.8% was reduced with 20 vol% H_2 under atmospheric pressure at 56 K for 10 h before reaction. Thereafter the temperature was decreased to reaction temperature in flowing N_2. A mixed gas of 50 vol% H_2 and 50 vol% CO was fed into the reactor at a rate of 60 ml/min or 100 ml/min. The reaction pressure was kept at 4.0 MPa. The products were analyzed with a gas chromatograph equipped with FID and TCD detectors, using GDX-502 and TDX-01 column, respectively.

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* To whom correspondence should be addressed.
E-mail: huangwei@tyut.edu.cn

2.3. Catalyst characterization

The crystal structures of the catalysts were measured using a Rigaku D/max 2500 X-ray powder diffractometer with monochromated CuKα (40 kV/100 mA) radiation. Before XRD characterization, the slurry catalyst was extracted by chloroform and dried naturally. The slurry catalyst after reaction was also characterized by leica microscope and rotating viscometer.

3. Results and discussions

XRD patterns of CuO–ZnO/Al_2O_3 slurry catalyst before and after reaction were presented in figure 1. Figure 1 shows that the main crystal phase of both the un-reduced and used catalyst are Cu, ZnO and Cu–Al spinel, which indicates that on one hand, the catalyst has the same crystal structures with those prepared by traditional method, on the other hand, a part of CuO was reduced during preparation. Comparing curve b with curve a, one can see that the intensity of XRD peaks decreases after reaction. This suggests the increase in the dispersion of the used catalyst. J.-L. Shi et al. [6] has found that the existence of ethanol can cause the reduction of CuO during the preparation of ultrafine particle CuO/ZrO_2. Thus, it is not surprising that metallic Cu appears in the un-reduced catalyst because it is possible that $(C_3H_7O)Al$ hydrolyzed and isopropanol formed during preparing Al-gel, and then CuO was reduced by isopropanol.

Figure 2 presents microscope photograph of the used CuO–ZnO/Al_2O_3 slurry catalyst. From figure 2, it can be seen that the size of particle is uniform about 3–5 μm. The measure of viscosity indicates 2.5 mPa s at 28 K for the slurry catalyst, at which temperature that of pure solvent is 1.3 mPa s. It is obvious that the viscosity of the slurry catalyst is very low compared with those prepared by traditional method.

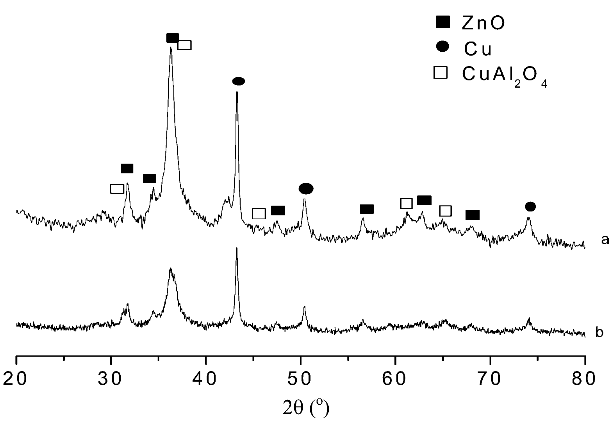

Figure 1. XRD pattern of CuO–ZnO/Al_2O_3 slurry catalyst, (a) before reaction, (b) after reaction.

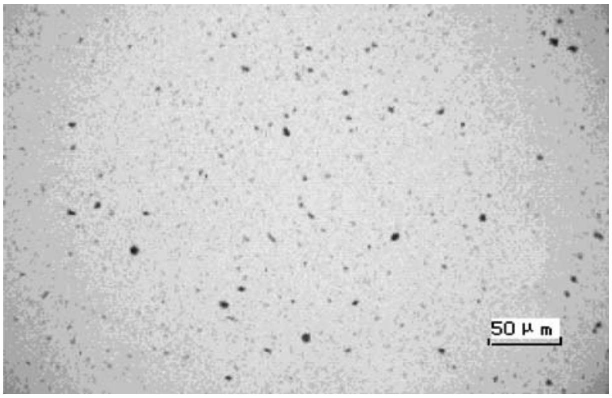

Figure 2. Microscope photograph of CuO–ZnO/Al_2O_3 slurry catalyst after reaction.

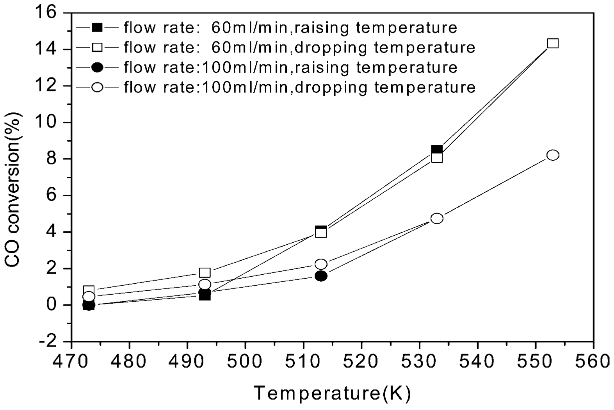

Figure 3. CO conversion over CuO–ZnO/Al_2O_3 slurry catalyst at different temperatures and flow rate.

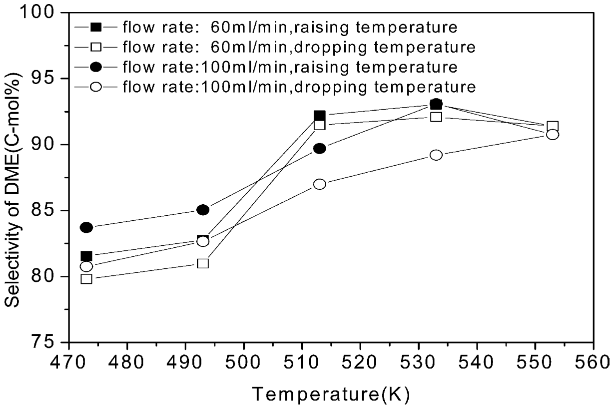

Figure 4. Selectivity o DME over CuO–ZnO/Al_2O_3 slurry catalyst at different temperatures and flow rate.

Figure 3 shows the activity data of the slurry catalyst. These data were collected first from 47 K to 55 K, and then from 55 K to 47 K. At each temperature, the reaction of 24 h was performed. The data listed in figure 3 are average value during the reaction of 24 h at a certain temperature. Through this way, the information of the catalyst life and stability can be observed. As shown in figure 3, the conversion of CO has no obvious

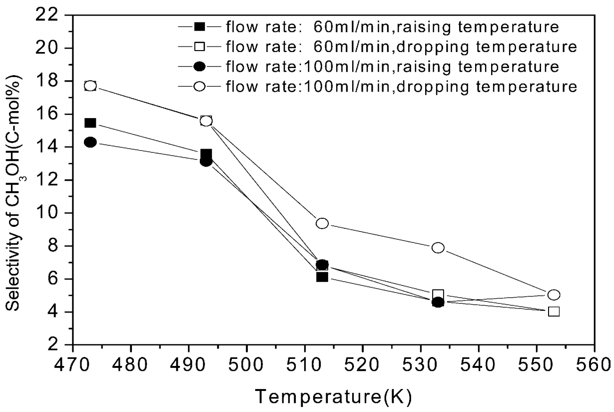

Figure 5. Selectivity to CH_3OH over $CuO–ZnO/Al_2O_3$ slurry catalyst at different temperatures and flow rate.

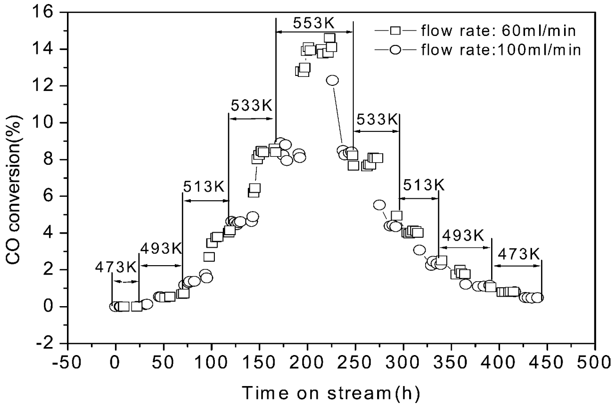

Figure 6. CO conversion as function of time-on-stream over $CuO-ZnO/Al_2O_3$ slurry catalyst.

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.

Figures 4 and 5 presents, respectively the change of the selectivity to DME and to methanol with temperature. It can be found from them that the selectivity to DME over the catalyst prepared by the new method is very excellent, reaching 93.08% at 55 K. The selectivity to DME still approaches 80% even at lower temperature. In this work, CO_2 was found very little and the primary byproducts are methanol and methane. The selectivity of methane is ca. 3% at all of temperatures investigated.

The effect of the feeding rate of the gases was also compared in this work. As shown in figures 3 and 4, with the flow rate decreasing CO conversion and DME selectivity increase from 51 K to 55 K.

Figure 6 shows the change of CO conversion with time-on-stream. It indicates that the performance of the catalyst is even during the reaction of 440 h and behaves a very good stability, no significant deactivation has been found.

4. Conclusions

The slurry catalyst prepared by the novel method has small and uniform granularity, high dispersion degree, and lower viscosity. Using $CuO–ZnO/Al_2O_3$ slurry catalyst can directly synthesis DME from syngas without adding additional methanol dehydration component, DME selectivity is more than 79.81% and the highest value reaches 93.08% at 55 K . The stability of slurry catalyst is good during the reaction of 440 h.

Acknowledgments

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