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Modification of Cu-based methanol synthesis catalyst for dimethyl ether synthesis from syngas in slurry phase

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Abstract

The Cu-based methanol synthesis catalyst was modified with Mn to improve its activity and stability for dimethyl ether (DME) synthesis from syngas in slurry phase. Mn was added by impregnating co-precipitated CuZnAl catalyst with aqueous solution of manganese nitrate (Mn/CuZnAl) or co-precipitation of the nitrates of Cu, Zn, Al and Mn (CuZnAlMn). The catalyst characterizations by H_2-TPD and XRD showed that CuO in CuZnAlMn catalyst was easily reduced, and Cu particles were well dispersed. XRD results indicated that the eutectic CuZn existed only over CuZnAlMn catalyst, and the promoter MnO did not appear over both of Mn/CuZnAl and CuZnAlMn catalysts. In DME synthesis reaction, it was found that Mn-modified CuZnAl catalyst have high activity and good stability. The proper content of Al and Zn can enhance the DME yield.

Keywords: Dimethyl ether; Syngas; Slurry phase; Mn-modified catalyst

1. Introduction

Dimethyl ether (DME) as an important chemical material and potential clean fuel substitute for LPG and diesel oil [1,2], so-called green fuel for 21st century [3], has attracted much more attention in recent years. Traditionally, DME is the by-product of high-pressure methanol synthesis. The high purity DME used as an aero-propellant can be also produced through methanol dehydration [4,5]. But the cost of DME is mainly controlled by the methanol price. When DME is produced as fuel, the production cost becomes more important than its purity. Therefore, one-step synthesis of DME from syngas has been known as a potential process comparing to the methanol dehydration process for its lower thermodynamic limitation and lower investment. One-step DME synthesis is a strong exothermic reaction process because it consists of methanol formation, methanol dehydration and water–gas shift reaction, which are all highly exothermic. The traditional fixed bed reactor is not appropriate for this process for its limited heat removal capacity. The slurry phase reactor has many merits for syngas conversion to synfuel process, and has been successfully applied in F–T synthesis process. It can also be an ideal reactor for DME synthesis [6,7].

It has been reported in the recently published literatures that the composite catalyst, which is active for vapor phase DME synthesis cannot be directly used for slurry phase DME synthesis. The catalyst deactivates at a very high rate [8]. The development of high activity and good stability catalyst has become the bottleneck of the process scale-up of the slurry phase DME synthesis.

Mn has been known as a promoter for improving the dispersion and the heat-resistance of CuZnAl methanol synthesis catalyst [9]. In this paper, the promotional effect of Mn on the activity and the stability of CuZnAl catalyst for slurry phase DME are studied.

2. Experimental

2.1. Catalyst preparation and catalytic activity test

2.1.1. Preparation of methanol synthesis catalyst

2.1.1.1. CuZnAl catalyst. The CuZnAl catalyst was prepared by co-precipitation of the corresponding aqueous

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solution of nitrate ($Cu(NO_3)_2$, $Zn(NO_3)_2$, $Al(NO_3)_3$) with sodium carbonate solution at 60–70 °C in a 1000 mL beaker with continuous stirring. The pH value was controlled at about 7.0. The precipitate was aged for 2 h, then filtered and washed with distilled water eight times. The gel was dried at 110 °C for 12 h and finally calcined in air at 360 °C for 4 h. The sodium content in catalyst was determined to be less than 0.01 wt.% by atomic scan spectroscopy (Atom Scan 16). The CuZnAl catalyst was then crushed into 200-mesh powder.

2.1.1.2. CuZnAlMn catalyst. The catalyst was prepared as above mentioned procedures, and manganese nitrate was mixed with other nitrates before precipitation.

2.1.1.3. Mn/CuZnAl catalyst. The Mn/CuZnAl catalyst was prepared by incipient wetness, impregnating manganese nitrate on CuZnAl, then dried at 110 °C for 12 h and calcined in air at 360 °C for 4 h. The CuZnAl/Mn catalyst was crushed into 200-mesh powder.

2.1.2. Preparation of DME synthesis catalyst

The DME synthesis catalysts were obtained by physically mixing the methanol catalyst and the equal granular size γ-Al_2O_3 at a weight ratio of 2:1.

2.2. Test of catalytic activity

The catalyst activity test was carried out in a 500 ML autoclave equipped with six-bladed impeller, in which the catalyst was suspended in liquid paraffin (treated to remove any trace poisons before use) with boiling point of higher than 340 °C. The catalyst was reduced in the autoclave reactor using diluted hydrogen (10% H_2 + 90% N_2) at a programmed temperature, rising from room temperature to 260 °C, and then kept at this temperature for 16 h. After this pre-treatment, the syngas (H_2/CO = 2.1) was introduced into the autoclave under 5.0 MPa. All of the effluent gaseous products were analyzed by on-line gas chromatographs using carbon molecular sieve column and a thermal conductivity detector (TCD) for hydrogen, carbon monoxide, carbon dioxide and methane, GDX-401 column and a flame ionization detector (FID) for DME, methanol and hydrocarbons. The results were connected by methane concentration.

2.3. H_2-TPR

The temperature programmed reduction of hydrogen was described elsewhere [10].

2.4. X-ray diffraction XRD

Powder X-ray diffraction was carried out using CuNi radiation at 40 kV and 40 mA on a Rigaku D/max-γA diffraction meter.

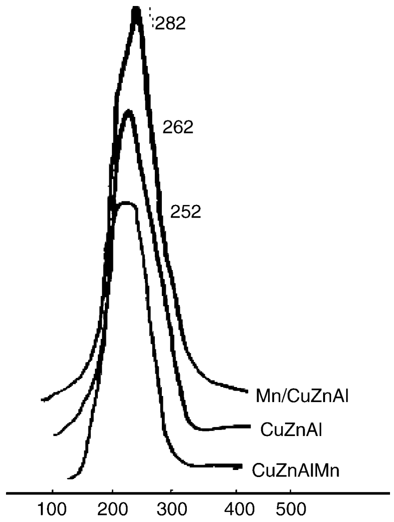

Fig. 1. H_2-TPR profiles of the catalysts.

3. Results and discussion

3.1. Results of H_2-TPR

Fig. 1 shows the H_2-TPR profiles of three methanol catalysts. All of them have only one reduction peak that appears at about 260–280 °C, which is known as the reduction of CuO. Comparing the profile of CuZnAl with Mn/CuZnAl, it is clear that the reducible CuO peak appears at 262 °C on the CuZnAl catalyst, while it appears at 282 °C on the Mn/CuZnAl catalyst. It means that the impregnation of Mn on CuZnAl made CuO more difficult to be reduced. On the other hand, the result of H_2-TPR of CuZnAlMn catalyst, prepared by co-precipitation, shows that the reducible CuO peak shifted from 262 to 252 °C, indicating that the CuO can be reduced more easily than that in other catalysts. The peak area of CuZnAlMn catalyst is less than the others; it may imply that Mn modification restricts the reduction of CuO. It can also be concluded that the Cu particle is dispersed more uniformly in the CuZnAlMn catalyst than that in the Mn/CuZnAl catalyst from Fig. 1.

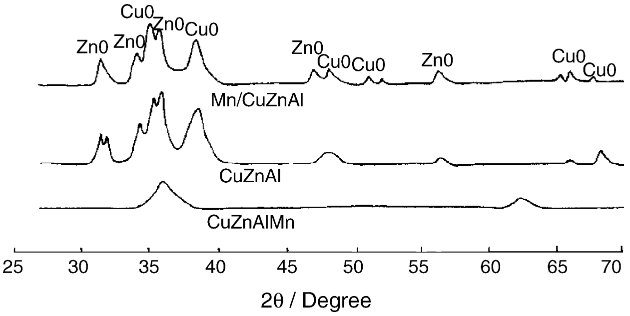

Fig. 2. Spectra of XRD.

Table 1
Effect of Mn-modified CuZnAl methanol catalyst on DME synthesis

Catalyst	CO conversion (C mol%)	Selectivity (C mol%)					Yield (C mol%)
		DME	MeOH	CH_4	CO_2	Other H.C.	
CuZnAl	56.7	54.5	5.79	8.25	22.2	9.27	30.9
CuZnAlMn	67.5	74.1	4.38	1.66	16.5	3.36	50.0
Mn/CuZnAl	38. 9	66.8	3.88	3.96	18.3	7.11	26.0

Reaction conditions: H_2:CO = 2:1, 5.0 MPa, 280 °C, 2.0 L/g cat h, methanol catalyst:dehydration catalyst = 2:1 (w/w).

Table 2
Promotional effect of Mn on CuZnAl catalyst for methanol synthesis

Catalyst	CO conversion (C mol%)	Selectivity (C mol%)			MeOH yield (C mol%)
		CO_2	MeOH	Other H.C.	
CuZnAlMn	72.4	0	99.3	0.73	71.8
CuZnAl	65.7	2.75	93.7	3.58	61.5
Mn/CuZnAl	59.9	0	99.1	0.91	59.4

Reaction conditions: H_2:CO = 2:1, 8.0 L/g cat h, 240 °C, 10.0 MPa, catalyst/solvent = 15 g/150 g (w/w).

3.2. The results of X-ray diffraction

Fig. 2 shows the XRD spectra of different catalysts (before reaction). The XRD spectra indicate that the CuO and ZnO exist in the CuZnAl and Mn/CuZnAl catalyst, but the CuO and ZnO become some distinctness on Mn-modified Mn/CuZnAl catalyst by impregnating method, comparing to the part eutectic of CuO and ZnO on the CuZnAl. Therefore, the Mn-modified catalyst prepared by impregnating depressed the formation of CuO–ZnO eutectic. On the other hand, there is almost no CuO and ZnO peak appearing on the Mn-modified catalyst prepared by co-precipitation, besides one peak appearing at the position of CuO and ZnO. The fact that CuO and ZnO diffraction peaks disappear, respectively on CuZnAlMn catalyst reveals that the active components disperse uniformly. This result is consistent with the result of H_2-TPR. Moreover, neither Al_2O_3 nor MnO crystal appear in all of the catalysts.

3.3. The performance of DME synthesis on different catalyst

The experimental results of DME synthesis over CuZnAl, Mn/CuZnAl and CuZnAlMn catalysts are summarized in Table 1. The CuZnAlMn prepared by co-precipitation exhibits the best performance for DME synthesis, where CO conversion and DME yield are 67.54 and 50.04%, respectively, while the methane selectivity is relatively low. However, the performance of DME synthesis over Mn/CuZnAl catalyst prepared by impregnating is even worst than that of the CuZnAl catalyst, which accords with the results of H_2-TPR and XRD diffraction because there is lack of eutectic CuO–ZnO over it. The reaction result and the characterization together reveal that the method of promoter Mn addition plays very important role in catalyst modification.

One-step synthesis of DME from syngas includes four reactions: CO hydrogenation, CO_2 hydrogenation, methanol dehydration and water–gas shift reaction.

$$CO + 2H_2 \Leftrightarrow CH_3OH \tag{1}$$

$$CO + 3H_2 \Leftrightarrow CH_3OH \tag{2}$$

$$2CH_3OH \Leftrightarrow CH_3OCH_3 \tag{3}$$

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \tag{4}$$

Two functionally different catalysts catalyzed the four reactions. The reaction (1), (2) and (4) took place over methanol synthesis catalyst while the reaction (3) is catalyzed by acidic catalyst. Up to now, the widely used catalysts for this process are composed of these two kinds of catalysts. Therefore, it is inevitable that the activity of methanol catalyst will influence the result of DME synthesis because methanol formation has been believed the rate limitation step among the series of reactions. Y. Kanai [11]

Table 3
Effect of Mn:Al ratio in catalyst on reaction results

Mn:Al ratio (w/w)	CO conversion (C mol%)	Selectivity (C mol%)					DME yield (C mol%)
		DME	MeOH	CH_4	CO_2	Other H.C.	
1:1	67.5	74.0	4.38	1.66	16.5	3.36	50.0
1:2	76.5	67.9	3.91	2.39	20.7	5.12	51.9

Reaction conditions: H_2:CO = 2:1, 5.0 MPa, 280 °C, 2000 mL/g cat h, methanol catalyst:dehydration catalyst = 2:1 (w/w).

Table 4
Effect of Cu:Zn ratio in catalyst on reaction results

Cu:Zn ratio (w/w)	CO conversion (C mol%)	Selectivity (C mol%)					DME yield (C mol%)
		DME	MeOH	CH_4	CO_2	Other H.C.	
5:2	68.6	66.0	2.81	3.65	18.9	8.69	45.4
4:3	67.5	74.1	4.38	1.66	16.5	3.36	50.0
3:4	73.6	67.2	3.00	3.43	18.5	7.9	49.4

Reaction conditions: H_2:CO = 2:1, 5.0 MPa, 280 °C, 2.0 L/g cat h, methanol catalyst:dehydration catalyst = 2:1 (w/w).

Table 5
Effect of reaction temperature on DME synthesis

Temperature (°C)	CO conversion (C mol%)	Selectivity (C mol%)					DME yield (C mol%)
		DME	MeOH	CH_4	CO_2	Other H.C.	
240	53.0	76.1	6.08	0.53	16.6	1.19	40.3
260	66.7	76.5	3.11	1.11	15.9	3.43	51.0
280	73.6	67.2	3.00	3.43	18.5	7.9	49.4

Reaction conditions: H_2:CO = 2:1, 5.0 MPa, 2.0 L/g cat h, methanol catalysis:dehydration catalysis = 2:1 (w/w).

found that in the CO and CO_2 hydrogenation to methanol over CuZn catalyst, ZnO_x ($x = 0$–1) transfers from ZnO particle and covers the Cu crystal to form the new adsorption center for CO, and this kind of adsorption center is more stable than metal Cu adsorption center. G. E. Paris [12] indicated that the Cu^+ dissolved in zinc crystal lattice is the activity site for methanol synthesis from carbon monoxide hydrogenation. Also, Edwards and Schrade's [13] experimental results showed that CO adsorbed on Cu^+ firstly forms carbonyl copper, then carbonyl copper inserts into the hydroxyl group to form salt formyl on the ZnO, and finally CH_3OH forms following the hydrogenation of CHO– and OCH_3–. All of the above viewpoints suggest that the methanol formation is catalyzed by the interaction of Cu, Zn in different valence state. It has been proved that eutectic CuZn exist in the CuZnAlMn catalyst from the XRD results, which leads to high the methanol formation more effective, as shown in Table 2.

The methanol synthesis performance over CuZnAlMn catalyst, which contains more CuO–ZnO eutectic, is significantly better than that over CuZnAl and Mn/CuZnAl catalyst. Obviously, CuO and ZnO are isolated in the CuZnAl and Mn/CuZnAl catalyst, resulting in decrease of the active site number for the methanol synthesis. The other reason is that there is a lack of fine Cu crystal in the CuZnAl and Mn/CuZnAl catalyst, and the bigger Cu crystalline is not favorable to the methanol synthesis [14].

In all experiments, same dehydration catalyst was employed to compose with different methanol synthesis catalysts for DME synthesis. Therefore, the performance of DME synthesis catalyst is exclusively affected by the methanol synthesis catalyst. The CuZnAlMn catalyst has the best activity for methanol synthesis among the three catalysts, and the same result happens in the DME synthesis process when these methanol synthesis catalysts are used to make the composite catalyst.

3.4. *Effect of the catalyst composition on the DME synthesis*

Table 3 shows the effect of Mn/Al ratio on DME synthesis. With the decreases of Mn content, the CO conversion increases, but the DME selectivity decreases at the same time because the catalyst has higher selectivity to CO_2 and other hydrocarbons. Although Mn addition is believed as the effective way to improve the activity and stability of the catalyst, the method and the amount of addition of Mn can affect the modification result.

Table 4 shows the effect of Cu/Zn ratio on DME synthesis. The CO conversion changes slightly with the change of the Cu/Zn ratio from 5:2 to 4:3, while DME selectivity is improved distinctly from 68.9 to 74.1%, and the by-product formation is depressed. Although the CO conversion reaches as high as73.6%, when the Cu/Zn ratio is 3:4, the DME selectivity still maintains 67.2%, and the DME yield could not be increased so far.

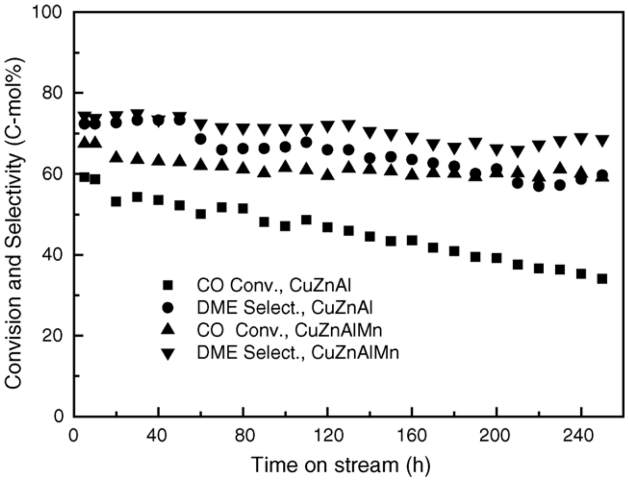

Fig. 3. Catalyst stability test of CuZnAl and CuZnAlMn. Reaction conditions: H_2:CO = 2:1, 5.0 MPa, 260 °C, 1000 mL/g cat h.

3.5. Effect of reaction temperature on DME synthesis

The effect of reaction temperature on DME synthesis over CuZnAlMn catalyst is listed in Table 5. It is easily confirmed that the appropriate reaction temperature for DME synthesis over CuZnAlMn is 260 °C. High temperature results in higher CO conversion but, on the other side, more methane and other hydrocarbons are produced. At higher temperature, the methanol dehydration proceeds at relatively high rate, resulting in stronger synergetic effect on syngas conversion. The total reaction rate is no longer controlled by thermodynamic of methanol but by the kinetics. It should be noted that the high temperature causes higher selectivity to methane, other low hydrocarbons and CO_2.

3.6. Catalyst stability test

Fig. 3 illustrates the experimental results of the catalyst stability test. It is confirmed that the Mn-modified catalyst has better stability than unmodified CuZnAl catalyst. This result should attribute to the highly dispersed CuZn component and less coalescence of the fine Cu crystal. Also Mn as a promoter of DME synthesis catalyst, is likely to prevent the sintering of catalyst, and promote the activity and stability for DME synthesis catalyst. The selectivity to DME has no obvious difference between the two catalysts.

4. Conclusions

Mn addition to the traditional CuZnAl methanol catalyst is an effective way to modify the catalyst to give better performance in slurry phase DME synthesis. The present study can be summarized as follows:

(1) CuO in CuZnAlMn catalyst prepared by co-precipitation can be reduced easily, and the reduced Cu is well dispersed. In the case of Mn/CuZnAl catalyst prepared by impregnating, the result is contrary with the former.
(2) CuZnAlMn catalyst prepared by co-precipitation method has better performance for DME formation because the CuO–ZnO eutectic is the main existing form of Cu and Zn, which is the active site for CO hydrogenation to methanol.
(3) The ratio of Cu, Zn, Al, and Mn affects the product selectivity of DME synthesis, and higher amount of Al, Zn is advantageous to enhance the DME yield.
(4) In the experiment range, 260 °C is the optimum operation temperature for DME synthesis over Mn-modified CuZnAl catalyst, at which the CO conversion and DME selectivity are 76.5 and 66.7%, respectively.
(5) Mn modification can significantly improve the catalyst stability in slurry phase DME synthesis.

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