Effect of ZrO_2 on the Stability of Cu-ZnO-ZrO_2/HZSM-5 Catalyst for Syngas Conversion to Dimethyl Ether

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(Received October 27, 1997; CL-970831)

The stability of Cu-ZnO/HZSM-5 and Cu-ZnO-ZrO_2/HZSM-5 catalysts for syngas conversion to dimethyl ether has been evaluated using a fixed-bed flow microreactor at 290 °C, 40 atm, 1500 h^{-1}. ZrO_2 addition showed a marked improvement in the stability of catalyst.

In recent years, Dimethyl ether synthesis direct from syngas has attracted wide attention in many fields, especially in chemical industry, for its marked economic values and theoretical significance.[1-4] The most common bifunctional catalysts used in the literature for syngas conversion to dimethyl ether consist of a physical admixture of methanol synthesis catalyst and zeolites or other acidic components such as alumina.[2,5-6] Among these catalysts, Cu-ZnO/HZSM-5 catalyst exhibits excellent catalytic activity and selectivity for dimethyl ether production; however, the stability of Cu-ZnO/HZSM-5 catalyst is not sufficient and should be increased further. We now report the successful improvement in stability of Cu-ZnO/HZSM-5 catalyst for syngas to dimethyl ether by adding ZrO_2 to the catalyst.

The catalysts were prepared by a 'coprecipitating-sedimentation' method which was developed in our laboratory; *i.e.* a nitrate solution of 66 wt-% copper, 34 wt-% zinc (or 64 wt-% copper, 16 wt-% zinc, 20 wt-% zirconium) and a solution of Na_2CO_3 were coprecipitated by being added to water simultaneously and dropwise over a period of thirty minutes at 70 °C, pH=7 under continuous stirring. The precipitates were then filtered, washed and added to the suspended liquid including H-ZSM-5 and water. The mixtures were stirred, filtered, dried, and calcined at 350 °C for 8 h. The resultant powder was molded under pressure into tablets.[7] For evaluation, the catalyst was placed in a fixed-bed flow microreactor and reduced at 240 °C with hydrogen for 4 h. Catalytic hydrogenation was carried out with a mixture of CO_2, CO and H_2 (5:27:68) under 40 atm pressure. The product stream and feed gas were analysed by gas chromatography using a flame ionization detector (FID) and a thermal conductivity detector (TCD), respectively.

As measures of the catalytic activity, the conversion of carbon monoxide and the selectivity of dimethyl ether (DME) were used. They were defined as follows:

$$\text{CO conversion (mol\%)} = \frac{CO_2 + \text{total hydrocarbons} + CH_3OH + 2DME}{CO + CO_2 + \text{total hydrocarbons} + CH_3OH + 2DME} \times 100\%$$

$$\text{DME selectivity (mol\%)} = \frac{2DME}{\text{total hydrocarbons} + CH_3OH + 2DME} \times 100\%$$

The stability of Cu-ZnO/HZSM-5 and Cu-ZnO-ZrO_2/HZSM-5 catalysts for syngas conversion to dimethyl ether was evaluated under the same conditions (290 °C, 40 atm, 1500 h^{-1}) for 100 h (Figure 1). The results exhibited that ZrO_2 addition showed a marked improvement in the stability of catalyst.

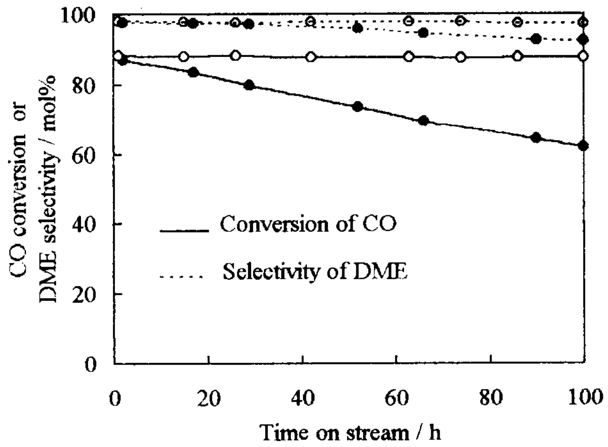

Figure 1. Stability of catalysts for syngas conversion to dimethyl ether (●: Cu-ZnO/HZSM-5, ○ : Cu-ZnO-ZrO_2/HZSM-5).

To explain the reason that ZrO_2 addition has a marked increase in the stability of catalyst, many physical chemical characterization methods such as XRD, TPR, TEM, XPS, EA were used.

XRD results of catalysts show that ZrO_2 component in Cu-ZnO-ZrO_2/HZSM-5 catalyst is high dispersed, its XRD peaks were not observed; Other components in Cu-ZnO-ZrO_2/HZSM-5 catalyst are more dispersed than those in Cu-ZnO/HZSM-5 catalyst, their XRD peaks in Cu-ZnO-ZrO_2/HZSM-5 are lower than those in Cu-ZnO/HZSM-5. After reaction 100 h, XRD spectra of Cu-ZnO/HZSM-5 shows CuO peak, this is the result of Cu active components being oxidized during the reaction; however, XRD spectra of Cu-ZnO-ZrO_2/HZSM-5 have no evident change. Therefore, it is thought that ZrO_2 in Cu-ZnO-ZrO_2/HZSM-5 prevented Cu active component from being oxidized, then kept the catalytic activity of catalysts and increased the stability of catalysts.

TPR results exhibit that Cu-ZnO-ZrO_2/HZSM-5 reduction peak temperature is higher than that of Cu-ZnO/HZSM-5 catalyst. It is advantage to keep the thermal stability of catalyst during the reaction at 290 °C, the temperature is close to the reduction peak temperature of Cu-ZnO-ZrO_2/HZSM-5 and higher than that of Cu-ZnO/HZSM-5. Therefore, Cu active components in the catalyst can keep high dispersed during reaction, and then the stability of catalysts increases.

TEM characterization results show that TEM graphs of Cu-ZnO/HZSM-5 catalyst become nebulous after reaction 100 h while Cu-ZnO-ZrO_2/HZSM-5 catalysts have no evident changes in their TEM graphs. Considering XRD results, we supposed that the formation of CuO during reaction for 100 h in Cu-ZnO/HZSM-5 catalyst caused the changes of TEM graphs.

Element analyses (EA) of the catalyst surface exhibit that

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Table 1. XPS results of catalysts

Catalyst		Cu-ZnO/HZSM-5		Cu-ZnO-ZrO_2/HZSM-5	
		Before reaction	After reaction 100h	Before reaction	After reaction 100h
Binding energy, ev	Cu $2P_{3/2}$	932.4	934.1	932.2	932.0
	Cu L_3VV (Auger Electron Spectra)	335.3	336.7	334.9	335.3
	Zn $2P_{3/2}$	1022.1	1022.3	1021.8	1021.1
	Zn LMM (Auger Electron Spectra)	265.8	265.7	265.1	264.8
	Cu/Zn (atom ratio)	0.48	0.48	0.98	1.26

carbon coke is not the main reason of Cu-ZnO/HZSM-5 catalyst deactivation for the reaction of syngas to DME.

XPS characterization obtained in vacuum of Cu-ZnO /HZSM-5 and Cu-ZnO-ZrO_2/HZSM-5 before reaction and after reaction 100 hours are shown in table 1. It is observed that for Cu-ZnO/HZSM-5, Cu $2P_{3/2}$ binding energy is 932.4 ev, Zn $2P_{3/2}$ is 1022.1 ev. Considering binding energy of Cu L_3VV and Zn LMM, we conclude that valence of Cu is zero, valence of Zn is two (ZnO). While after reaction 100 h, Cu$2P_{3/2}$ binding energy shows valence of Cu is two (CuO), Zn$2P_{3/2}$ binding energy have no evident changes. For Cu-ZnO-ZrO_2/HZSM-5, Cu $2P_{3/2}$ binding energy have no evident change, Zn $2P_{3/2}$ binding energy decreased after reaction 100 h, Cu active valence is zero and Zn active component is ZnO_{1-x}. So, it is concluded that ZrO_2 keep active species existence and avoid active components being oxidized, thus increased the stability of catalysts. In addition, Cu/Zn atom ratio of catalyst surface has no evident change before reaction and after reaction 100 h for Cu-ZnO/HZSM-5; while for Cu-ZnO-ZrO_2/HZSM-5, Cu/Zn atom ratio of catalyst surface increases. In other words, on catalyst surface, active component Cu atom increased, then increased catalyst performance and stability.[8] Therefore, ZrO_2 can increase the Cu atoms on catalyst surface. Of course, it will be necessary to reveal the reason why ZrO_2 in Cu-ZnO-ZrO_2/HZSM-5 catalyst can increase the Cu/Zn atom ratio of catalyst surface after reaction 100 h.

In conclusion, addition of ZrO_2 to Cu-ZnO/HZSM-5 resulted in marked increase in the stability of the catalyst for syngas conversion to dimethyl ether. It not only prevents Cu active component from being oxidized to CuO inactive components but increases the content of surface Cu atoms.

References and Notes

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