Chinese Chemical Letters Vol. 12, No. 6, pp. 527 – 528, 2001

Natural Mordenite Catalyst Used on the Ammoniation of Methanol

Li Qiu MAO[1], Tong Lai ZHANG[1], Chang Gen FENG[1], Qing Ze JIAO[2], Da Zhen JIANG[2]

[1]Department of mechano-electronic Engineering, Beijing Institute of Technology, Beijing 100081
[2]Department of Chemistry, Jilin University, Changchun 130023

Abstract: The catalytic properties of natural mordenite as acidic catalysts were investigated using the ammoniation of methanol.

Keywords: Ammoniation of methanol, natural mordenite, catalytic activity.

Silicon-magnesium catalyst, aluminum phosphate, ZSM, synthetical mordenite exchanged with alkaline-earth metals ion and acidic oxide, their catalytic properties in the ammoniation of methanol have been reported[1~5]. However, so far the ammoniation of methanol catalyzed by natural mordenite has not been reported. In the present work, we report the characterization and catalytic properties of natural mordenite catalysts.

NH_3-TPD was used to measure the acidic properties of these zeolites. The amounts of ammonia desorbed from these samples, the maximum and the minimum temperatures are summarized in **Table 1**. There are two desorption peaks for all samples within a temperature range of 383-723 K. Increasing the Si/Al ratio from 5.53 to 16.31 (corresponding to catalysts M-0 and M-7) will obviously decrease in NH_3 uptake. The maximum temperatures of NH_3 desorption on M-4 and M-7 samples are the same as that of HM. These results show that natural mordenite after dealumination has strong acidic properties.

Table 1 results of NH_3-TPD and ammoniation of methanol

Catalyst	Si/Al	NH_3-TPD				CH_3OH	S/%		
DME		T_{max}[a]	T_{min}[a]	NH_3 uptake[b]		conv/%	MMA	DMA	TMA
M-0[c]	5.53	685	588	1.14	95.5	87.2	11.7	0.9	0.2
M-2	11.48	692	590	0.86	71.4	86.1	12.3	1.0	0.6
M-4	14.42	721	611	0.53	32.1	83.2	13.6	2.6	0.7
M-7	16.31	721	617	0.47	30.9	77.0	17.4	5.6	1.0
HM	5.56	723	515	1.84	96.2	72.2	19.2	5.2	3.4
γ-Al_2O_3	0.00	668	582	0.94	75.4	68.8	13.7	7.8	9.8

Condition: 673 K, NH_3/CH_3OH (mol) = 3:1, Catalyst: 0.96 g, 40-60 mesh, Space velocity: 0.59 h^{-1}. [a]T_{max} and T_{min} are the maximum and minimum temperature (K) observed during the TPD experiments. [b]Ammonia uptake is given in mmol of ammonia per gram of catalyst. [c]Mordenite content in the mineral is 92.2%.

In the ammoniation of methanol, HM has slightly higher activity and selectivity for DMA than M-0, due to it has a higher NH_3 uptake. The catalytic activity of natural mordenite catalysts decreases with a decrease of NH_3 uptake.

The reaction results in different NH_3/CH_3OH ratio are shown in **Table 2**. The catalytic activity of M-0 (raw mine) and selectivity of MMA increase with an increase in ratio of NH_3/CH_3OH, and the selectivity of DMA and TMA decreases with an increase of it. 1:1 is the best ratio of NH_3/CH_3OH.

Table 2 effect of ratio of NH_3/CH_3OH on the catalytic properties

NH_3/CH_3OH (mol)	CH_3OH conv/%	S/%			
		MMA	DMA	TMA	DME
5:1	100.0	87.0	10.2	0.3	2.5
4:1	99.2	80.7	14.5	1.1	3.7
3:1	96.9	76.1	19.9	3.0	1.0
2:1	95.6	74.2	20.4	4.2	1.2
1:1	90.9	55.3	34.4	9.8	0.5

Condition: 673 K, Space Velocity: 0.37 h^{-1}, Catalyst: M-0, 1.5 g, 40-60 mesh.

Experimental

NH_3-TPD was carried out from 373 to 723 K with a heating rate β of 8 K min^{-1} and with N_2 (30 ml min^{-1}) as carrier gas. The NH_3 uptake was determined using TCD by comparing with the integrated area of a known volume of NH_3.

The ammoniation of methanol was performed on atmospheric pressure in a fixed-bed reactor. The reaction products were analysed by GC on a 2 m stainless column with a TCD.

Acknowledgments

We thank the financial support by the Natural Sciences Foundation of Jilin Province (97JJY2058).

References and notes

1. H. Stach, H. G. Jersohewitz, U. Lohse *et al*., *J. Phys. Chem.*, **1992**, *96*, 3473.
2. M. R. Basila, T. P. Kantner, *J. Phys. Chem*., **1966**, *70*, 5.
3. K. R. Wu, X. Z. Yao, *J. Petrochemistry (Chinese)*, **1987**, *16*(1), 7.
4. J. Wang, Y. Z. Zhang, *J. Fine Petrochemistry (Chinese)*, **1993**, *5*, 23.
5. M. Isao, Y. Akinori, F. Hiroshi, *et al*., *J. Catal*., **1983**, *82*, 313.
6. MMA is monomethylamine; DMA is dimethylamine; TMA is trimethylamine; DME is dimethyl ether.

Received 16 October, 2000