Selective catalytic reduction of NO_x with methanol under lean burn condition over transition metal modified zeolite catalysts

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Abstract: In present work a series of Co exchanged zeolite catalysts were prepared, and their properties in the selective catalytic reduction (SCR) of NO_x with methanol were investigated under simulated lean burn exhaust gas condition. Co-ZSM-5 shows higher conversion of NO_x comparing with Ag/Al_2O_3 between 300 to 400 ℃. The effect of the thermal treatments on the local structure and activities of Co-ZSM-5 was investigated.

Keywords: Methanol, SCR, Cobalt, ZSM-5

1. Introduction

The vanadia-based oxide and copper-based zeolite NH_3-SCR catalysts were employed to control NO_x emissions from stationary and mobile NO_x sources.[1,2] However, vanadia-based oxide and copper-based zeolite catalysts are usually suffered reversible and irreversible deactivation under SO_x condition due to formation of ammonium bisulfate.[3,4] Thus, these catalysts are too sensitive towards SO_x to be used in the exhaust systems with high concentration of SO_x.

Instead of ammonia, hydrocarbons and oxygenated compounds have drawn a lot of attentions as reductants for selective catalytic reduction of NO_x because of non-poison and no formation of ammonium bisulfate. Methanol with a simple molecular structure is very cheap, which make it more attractive among of these compounds. Ag/Al_2O_3 has been proved as an effective catalyst for the methanol SCR reaction.[5] Nevertheless, it remains a challenge for the design of methanol SCR catalysts with high activities especially at low temperature.

2. Experimental

Co modified zeolite catalysts were prepared by aqueous ion exchange method. ZSM-5 zeolite was purchased from Nankai University Catalyst Co., Ltd. The molecular ration of SiO_2/Al_2O_3 (SAR) of ZSM-5 was 38. A typical ion exchange procedure is as follows: 5 g of ZSM-5 and 3.57 g of Cobalt nitrate were dissolved into 10 g of deionized water to form a suspension followed by ion exchange at 353 K for 2 h to get Co-ZSM-5. Co-ZSM-5 zeolites were further thermal treated at 973 K in air or N_2 to get Co-ZSM-5-A and Co-ZSM-5-N, respectively. On the other hand, ZSM-5 zeolite was thermal treated at 973 K in air before the ion exchange process, followed by ion exchange with Co to get Co-ZSM-5-B.

The catalytic performance test was carried out in a continuous flow with a fixed-bed reactor, in which is positioned 1ml of catalyst pellets with the particle size in the range of 0.6 to 1 mm. Methanol solution was vaporized and mixed with other gases to get a feed gas containing 500 ppm NO, 1000 ppm CH_3OH, 14%O_2, 5%H_2O in N_2 (balance gas). Total flow rate was 1667 ml/min (GHSV=100,000 h^{-1}). Concentration of outlet gases was detected by online FT-IR. Stabilization and collection time for every temperature point were 15 mins and 30 mins respectively. Conversion (X) of NOx was calculated as formula:

$$X = \frac{(NO + NO_2)_{inlet} - (NO + NO_2)_{outlet}}{(NO + NO_2)_{inlet}}$$

3. Results and discussion

The sample prepared by the ion exchange of cobalt ions with the fresh ZSM-5 zeolites (Co-ZSM-5) show no methanol SCR activity, as shown in Fig. 1. The activities of Co-ZSM-5 increase after the

calcination at 973 K both in Air and in N_2. Interestingly, Co-ZSM-5-B exhibits the highest activities with two distinct peaks, indicating that the pre-treatment of ZSM-5 in air have a great effect on the local structure of ZSM-5 zeolites. The high temperature treatment of zeolites can usually cause the change of the structure of zeolites, as well as the formation of extra framework aluminum species, which will in turn led to a different local structure of Co-ZSM-5-B from those of Co-ZSM-5-A and Co-ZSM-5-N.

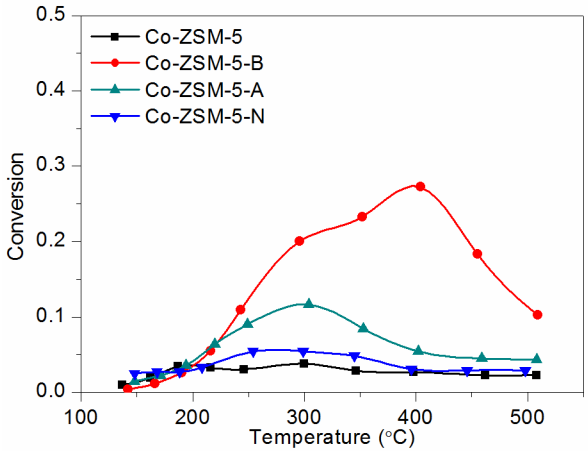

Figure 1. The Conversion of NOx on Co-ZSM-5, Co-ZSM-5-B, Co-ZSM-5-A, and Co-ZSM-5-N catalysts.

4. Conclusions

Co-ZSM-5 catalysts prepared by the ion exchange of cobalt ions with ZSM-5 zeolites calcined at high temperature in air show higher activities for the methanol SCR reactions than those of Co-ZSM-5 catalysts calcined after the ion-exchange process.

References

1. G. Busca, L. Lietti, G. Ramis, G; Berti, Appl. Catal. B 18 (1998) 1.
2. J. H. Kwak, R. G. Tonkyn, D. H. Kim, J. Szanyi, C. H. F. Peden, J. Catal. 275 (2010) 187.
3. Y. J. Shi, H. Shu, Y. H. Zhang, H. M. Fan, Y. P. Zhang, L. J. Yang, Fuel Process. Technol. 150 (2016) 141.
4. P. S. HammershØi, Y. Jangjou, W. S. Epling, A. D. Jensen, V. W. T. Janssens. Appl. Catal. B https://doi.org/10.1016/j.apcatb.2017.12.018.
5. Marika Männikkö, Magnus Skoglundh, Hannae Härelan Ingelsten. Appl. Catal. B 119-120 (2012) 256-266.