Promotion effect of Fe dispersion on the activity of Fe-ZSM-5 for NH_3-SCR of NO

Jin Shi, Mingxia Chen, Zhixiang Zhang and Wenfeng Shangguan*

Research Center for Combustion and Environmental Technology. School of Mechanical Engineering, Shanghai Jiao Tong University, Shanghai 200240, P. R. China;

**E-mail: shangguan@sjtu.edu.cn*

Abstract: The effect of Fe dispersion and distribution with different solvents in Fe-ZSM-5 on the NH_3-SCR performance was evaluated. The results indicated that water promoted more iron clusters occupied the joint of the ZSM-5 support, while the little amount of Fe^{3+} resulted in poor performance at low temperature. When using absolute methanol, the iron particle was like silk thread distributed over the entire surface with good activity at low temperature, but poor performance at high temperature. However, the iron cluster of Fe-ZSM-5 with the mixed solvent was in excellent dispersion and the appropriate ratio of Fe^{3+}/Fe^{2+}, which expanded the active temperature window.

Keywords: NH_3-SCR, Dispersion, Distribution

1. Introduction

Nitrogen oxides (NO_x) in the exhaust gases from combustion of fossil fuels remain a major source for air pollution. They are considered to be environmental pollutants associated with the greenhouse effect, acid rain, and photochemical smog. Selective catalytic reduction (SCR) of NO with NH_3 is the most widely employed method in NO_x abatement, which uses ammonia as reductant to reduce NO_x to nitrogen. V_2O_5-WO_3/TiO_2 (VWT) system catalysts. However, for the practical application in diesel engines (150-450 °C), V-based catalysts are restrained because of the toxicity and narrow operation temperature window [1].

Over the last decade, metal loaded/dropped ZSM-5 catalysts, such as Fe-ZSM-5, Cu-ZSM-5, Mn-ZSM-5 and Co-ZSM-5 show excellent performance. Among them, iron and copper zeolites have gained significant attention because of their adsorptive properties of NO and environmental friendliness. Fe- and Cu-ZSM-5 show good catalytic activity in the low temperature SCR reaction for more than one valence states of the iron or copper (Fe^{3+} and Fe^{2+}, Cu^{2+} and Cu^{+}), which could promote the mutual transformation between the electrons and formation of oxygen vacancy. However, Fe-ZSM-5 was considered to be an effective catalyst for NH_3-SCR because of the low cost, wide operating temperature range, durability at high temperature and resistance to SO_2 [2].

ZSM-5 molecular sieve is full of sub-nanometer porous structure with abundant acidic sites, which can adsorb NH_3 and convert NH_3 to intermediate NH_4^+. Besides, the interior space can be regarded as a kind of reactor, providing a favorable reaction space and electronic environment for the generation of highly dispersed transition metal oxide clusters. In these published papers, monomeric Fe^{3+} and clusters are considered to be the most active species in NH_3-SCR. Recently, the promotion effect of different methods (ultrasonic impregnation or methanol solvent) on good dispersion of active component, adsorption and reaction process of NO and NH_3 on the catalyst surface were investigated deeply [3]. However, the effect of different iron distribution on the ZSM-5 surface in the Fe-ZSM-5 system has not been studied.

In this study, series of Fe-ZSM-5 catalyst has been prepared by impregnation method using different solvent. Physicochemical properties of the catalysts were evaluated by various techniques to characterize the morphology and reduction performance of catalyst. Effect of different solvent impregnation on dispersion of active component, iron distribution on the ZSM-5 surface and the reaction process of NO and NH_3 were investigated deeply.

2. Experimental

The Fe loading was 10 wt.% and the catalysts were denoted as 10 wt.% Fe-ZSM-5/W, 10 wt.% Fe-ZSM-5/WM and 10 wt.% Fe-ZSM-5/M, where W, WM and M represented the different solvent, e.g., WM for the 50% deionized water and 50% absolute methanol. Finally, the mixture was dried at 110 °C overnight and calcined at 550 °C for 4 h at a ramp rate of 5 °C/min. Before evaluation, the catalyst powders were thoroughly grinded in a mortar, pressed, crushed and sieved to obtain an appropriate particle size (0.2-0.4 mm).

The SCR activity measurement was carried out in fix-bed quartz tube reactor during 100-650 °C with gas hourly space velocity (GHSV) of 60,000 h^{-1}. The reactant gas typically consisted of 350 ppm NO, 385 ppm NH_3, 15% O_2 and balance N_2 with flow rate of 150 ml/min. The temperature where the NO_x conversion ratio over 85% was considered to be the active temperature window. All data was collected after 30 min at the desired temperature in order to achieve steady-state condition. The outlet concentrations of NO, NO_2, N_2O and NH_3 were measured by FT-IR (Thermo NICOLET 6700).

3. Results and discussion

3.1 Activity

The NO_x conversion activity and N_2 selectivity of Fe-ZSM-5 with different solvent were depicted at Fig. 1 (a) and (b). The mixed solvent for Fe-ZSM-5 significantly expanded the active temperature window. Compared with Fe-ZSM-5/W and Fe-ZSM-5/M, the NO_x conversion activity of Fe-ZSM-5/WM increased by 57% and 16% at

200 °C and the active temperature window was expanded to 200-500 °C. The N_2 selectivity of Fe-ZSM-5/WM maintained a high value until high temperature, indicating that by-product of this reaction was very little.

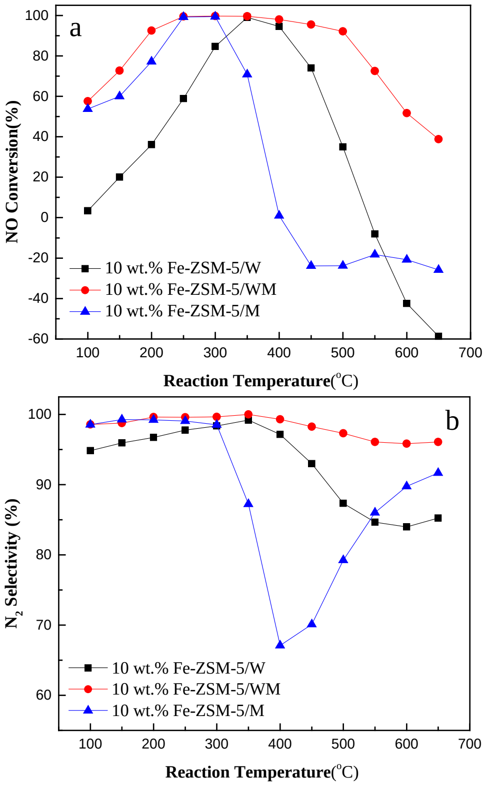

Fig. l. NO_x conversion (a) and N_2 selectivity (b) of Fe-ZSM-5 with different solvent.

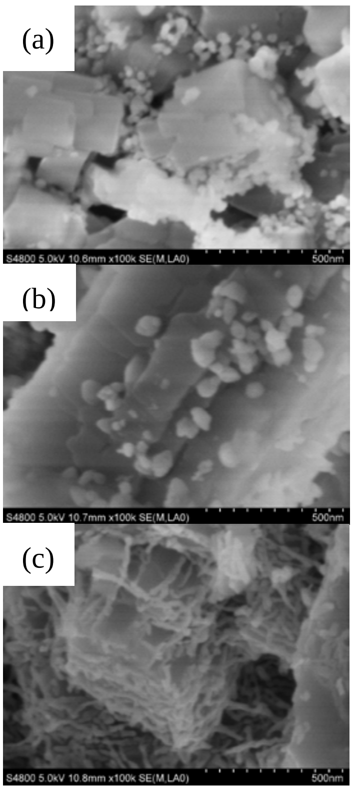

Fig. 2. SEM images of 10 wt.% Fe-ZSM-5/W (a), 10 wt.% Fe-ZSM-5/WM (b), 10 wt.% Fe-ZSM-5/M (c).

3.2 Characterization of catalyst

The morphologies of the catalysts were investigated by SEM images in Fig. 2.

The XPS analyses were applied to investigate the chemical state of Fe in near-surface region further, and the photoelectron spectra of Fe $2p_{3/2}$ was depicted at Fig. 3.

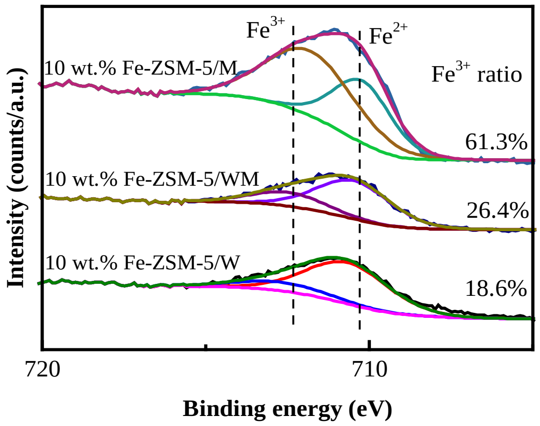

Fig. 3. XPS spectra of Fe 2p for Fe-ZSM-5 with different solvent.

4. Conclusions

A series of Fe-ZSM-5 catalysts were prepared by impregnation method using different solvent and evaluated in NH_3-SCR. Water promoted more iron clusters formed and occupied the joint of the ZSM-5 support, while the little amount of Fe^{3+} in Fe-ZSM-5/W resulted in poor performance at low temperature. When Fe-ZSM-5 impregnated with absolute methanol, the iron particle of the Fe-ZSM-5/M was like silk thread without cluster form distributed over the entire surface of the ZSM-5. Besides, large amount of Fe^{3+} in Fe-ZSM-5/M led to good activity at low temperature, but poor selectivity and performance at high temperature for excess high valence state of iron ions. However, the iron cluster of Fe-ZSM-5/WM with the mixed solvent was in good dispersion and well distributed on the support surface. Accordingly, the mixed solvent can promote the performance of Fe-ZSM-5 due to the good distribution of iron clusters on the support surface and the appropriate ratio of Fe^{3+}/Fe^{2+} formed for excellent dispersion.

References

1. J. H. Li, H. Z. Chang, L. Ma, J. M. Hao, T. Ralph. R. T. Yang. Catal. Today. 175 (2011) 147-156.
2. M. Iwasaki, H. J. Shinjoh. J. Catal. 273 (2010) 29-38.
3. L. Zhu, L. Zhang, H. Qu, Q. Zhong. J. Mol. Catal. A: Chem. 409 (2015) 207-215.