

Deactivation Mechanism of Fe/Zeolite Catalysts by C₃H₆ Coking for Selective Catalytic Reduction of NO with Ammonia

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Introduction

Selective catalytic reduction of nitric oxide with ammonia (NH₃-SCR) is considered as a primary approach to meeting stringent NO_x emission regulations of diesel engine. As the potential SCR catalysts for practical application, Fe supported on zeolites for NH₃-SCR of NO_x have been extensively investigated in past decades due to their good performance even at high space velocities^[1]. However, the catalysts are gradually deactivated by hydrocarbon coking during operation of diesel engine^[2-3]. In this work, the activities and deactivation behavior of various Fe/zeolite catalysts for NH₃-SCR have been studied, and a mechanism of catalyst deactivation is proposed.

Materials and Methods

Fe-zeolite catalysts were prepared by using the conventional ion-exchange procedure. Six types of zeolite, H-ZSM-5, Beta, Mordenite, Y, Ferrierite, and 4A zeolite were employed as the support. For each catalyst, 5 g zeolite was added to 200 mL of 0.05 M FeCl₂ solution with constant stirring at room temperature. After 24 h, the mixture was filtered and washed several times with deionized water. The obtained solid was dried at 110 °C overnight and then calcined at 600 °C for 5 h in air. The obtained catalysts are denoted as Fe-ZSM-5, Fe-Beta, Fe-MOR, Fe-Y, Fe-FER, Fe-4A, respectively. These catalysts were characterized by BET surface area, TGA, XRD, TPR, TPD, and In situ FT-IR spectroscopy methods.

Results and Discussion

As shown in Figure 1, Fe-ZSM-5, Fe-Beta, and Fe-MOR showed high activities for NH₃-SCR; NO conversions are all > 80 % in a wide temperature range of 300-500 °C, and NO conversion reached nearly 100 % at 400 °C. In comparison, the other three catalysts, Fe-Y, Fe-FER, and Fe-4A, showed low catalytic activities, and the decrease order of their maximum NO conversion at 400 °C is Fe-Y > Fe-4A > Fe-FER. When 1000 ppm propene was added to the mixture of reaction gas, the NO conversion decreased to some extent for all catalysts at various reaction temperatures. Figure 1 shows the catalytic activities for NH₃-SCR of NO over various catalysts at 400 °C before and after C₃H₆ coking for 30 min. It can be seen that Fe-MOR has still kept high activity with almost 90 % NO conversion even after C₃H₆ coking for 30 min, while the activities clearly decreased over other catalysts.

When C₃H₆ was removed from the reaction gas, the activity of catalyst could be recovered gradually in the reaction gas. The higher is the temperature, the faster is the recovery. Separate experiments showed that the activity of catalyst could be completely regenerated if the coked catalysts were heated at 500 °C in air. This result indicates that the carbonaceous deposit or coke could be burned off by excess oxygen in the reaction gas.

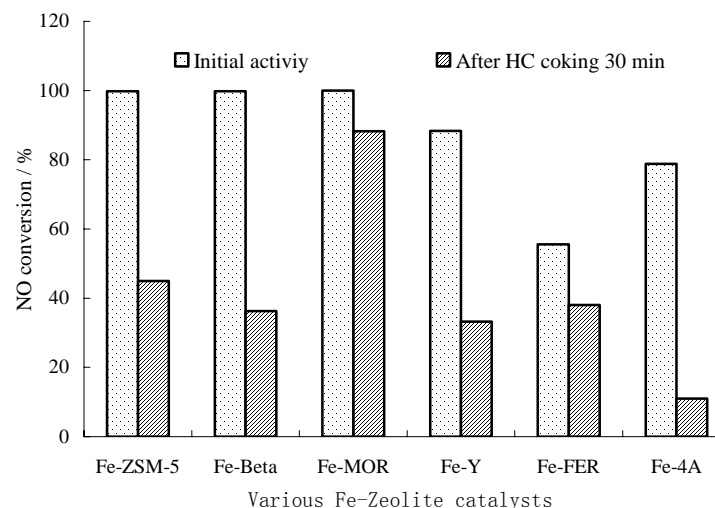


Figure 1 Activity comparison of NH₃-SCR of NO over various catalysts (Fe ion-exchanged zeolites) at 400 °C before and after C₃H₆ coking for 30 min. Reaction conditions: 0.1 g catalyst, 1000 ppm NH₃, 1000 ppm NO, 5 % O₂ and balance He, GHSV=3.8×10⁵ h⁻¹.

For Fe-MOR, BET characterization results showed that the surface area, pore volume and average pore diameter all decreased upon HC coking; these parameters decreased from 422 to 23 m²/g, 0.217 to 0.126 cm³/g, and 2.57 to 2.04 nm, respectively. TGA analysis suggested that the hydrocarbon coking was generated during NH₃-SCR in the presence of C₃H₆. It possibly covered the active sites and blocked the pores of zeolite cages then suppressed the catalyst activity. Furthermore, the results of NH₃-TPD indicate that the amount of adsorption of NH₃ on acid sites clearly decreased, and the NO-to-NO₂ oxidation activity on Fe³⁺ active sites was also suppressed. Based on in-situ FT-IR analysis, it is clear that the reaction rate of NH₃-SCR was suppressed in the presence of C₃H₆. The NH₄⁺ adsorbed on the Brönsted acid sites would be completely reacted with NO and O₂ in 3 min; however, in the presence of 1000 ppm C₃H₆, the NH₄⁺ adsorbed on the Brönsted acid sites clearly remained even after NO and O₂ were introduced for 30 minutes. Meanwhile, carbonaceous species were observed based on the FT-IR spectra, such as formate, acetate, and NCO. The deactivation of Fe-Zeolite was due to the carbonaceous deposit on catalyst, which covers both acid sites and metal active sites. Therefore, the HC coking inhibited the oxidation of NO to NO₂, as well as the NH₃-SCR reaction rate due to the carbonaceous deposit on acid sites.

References

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