

Superior Fe-ZSM-5 Catalyst for Selective Catalytic Reduction of Nitric Oxide by Ammonia

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Nitrogen oxides in the exhaust gases from combustion of fossil fuels remain a major source for air pollution and acid rain. The current technology for reducing NO_x (NO + NO₂) emissions from power plants is selective catalytic reduction (SCR) with ammonia in the presence of oxygen. For the SCR reaction, V₂O₅ + WO₃ (or MoO₃) supported on TiO₂ are the commercial catalysts.¹ The mechanism of the reaction on the vanadia catalysts has been studied extensively, and several different mechanisms have been proposed.^{1,2} Ion-exchanged zeolite catalysts have also been studied, e.g., Fe-Y,³ Cu-ZSM-5,⁴ and Fe-ZSM-5,⁵ but the reported activities were lower than that of the commercial vanadia catalysts. The SCR technology based on vanadia catalysts is being used in Europe and Japan and is being quickly adopted in the US. However, problems associated with vanadia catalysts remain, e.g., high activity for oxidation of SO₂ to SO₃, toxicity of vanadia, and formation of N₂O at high temperature. Hence, there are continuing efforts in developing new catalysts.¹ In this paper, we report a superior Fe-ZSM-5 catalyst that is much more active than the commercial vanadia catalysts and does not have the deficiencies that are associated with the vanadia catalysts.

The Fe-ZSM-5 catalysts were prepared by using specific ion-exchange procedures, and the iron in the catalysts was present in the form of Fe³⁺ ions.⁶ The catalytic activity experiments were performed at 1 atm with a conventional fixed-bed flow reactor.⁸

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(6) Fe(58)-ZSM-5 was prepared by exchanging 2 g NH₄-ZSM-5 (Si/Al = 10) with 200 mL of 0.05 M FeCl₂ solution. The number in the parentheses following Fe indicates % ion exchange determined by neutron activation analysis. Ce-Fe(42)-ZSM-5 was obtained from 3 g of NH₄-ZSM-5 exchanged with 200 mL of 0.05 M Ce(NO₃)₃ solution, followed by exchanging with 200 mL of 0.05 M FeCl₂ solution. All of the exchange processes were performed at room temperature for 1 day. Fe(130)-ZSM-5 was obtained from exchanging 2 g of H-ZSM-5 (Si/Al = 10) with 0.73 g of iron powder mixed in 200 mL of 0.1 M HCl solution at 50 °C for 10 days in flowing He. H-ZSM-5 was prepared by calcining NH₄-ZSM-5 at 500 °C for 3 h. The obtained solid samples were first dried at 120 °C in air for 12 h and then calcined at 600 °C for 6 h. Fe²⁺ in the zeolite framework was oxidized to Fe³⁺.⁷ The Fe contents were 1.59% (wt) in Fe(58)-ZSM-5 (i.e., 57.7% ion exchange), 1.14% in Ce-Fe(42)-ZSM-5 (0.054% for Ce, i.e., 42.3% total ion exchange) and 3.57% in Fe(130)-ZSM-5 (i.e., 130% ion exchange). Besides the Fe-ZSM-5 catalysts, (4.4% V₂O₅ + 8.2% WO₃)/TiO₂ catalyst was also prepared by incipient wetness impregnation.⁸ This catalyst had SCR activity and behavior nearly identical to that of the commercial SCR catalyst supplied by a major catalyst manufacturer.⁸

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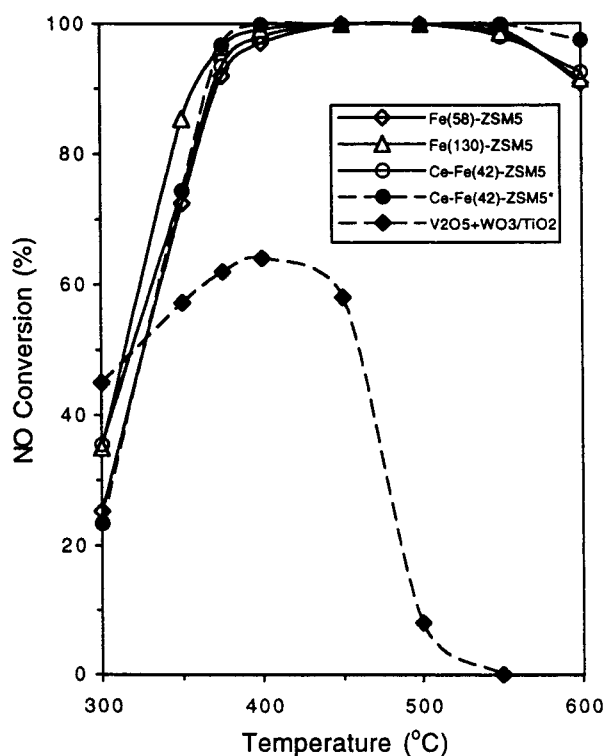


Figure 1. Catalytic activities for NO reduction by ammonia on Fe-ZSM-5 and 4.4% V₂O₅+8.2% WO₃/TiO₂ catalysts. Reaction conditions: 50 mg (0.065 mL) catalyst, 1000 ppm NO, 1000 ppm NH₃, 2% O₂, balance He, and GHSV = 4.6 × 10⁵ l/h (ambient conditions). * denotes addition of 500 ppm SO₂ and 5% water vapor. The numbers in the parentheses following Fe indicate % ion exchanges.

The results on % NO conversion with different catalysts are compared directly with a commercial-type catalyst⁸ in Figure 1. Surprisingly high NO conversions were obtained on the Fe-ZSM-5 catalysts, with a broad temperature window (375–600 °C) under a high gas hourly space velocity (GHSV) of 4.6 × 10⁵ l/h (Figure 1). At 450–500 °C, NO conversions reached nearly 100%. It appears that the activities were little influenced by the Fe content between 1.14 and 3.57 wt % in Fe-ZSM-5. The addition of a small amount (0.054 wt %) of cerium further increased the activities (Figure 1). In comparison, the commercial 4.4% V₂O₅ + 8.2% WO₃/TiO₂ catalyst⁸ showed substantially lower activities in NO reduction under the same conditions, and the NO conversions decreased sharply when the temperature was above 450 °C (Figure 1) due to oxidation of ammonia by oxygen.¹ However, when the amount of the commercial catalyst was increased from 50 to 800 mg while keeping all other conditions identical, the maximum NO conversion was increased from 64.0% at 400 °C to 99.8% at 375 °C. This indicates that Fe-ZSM-5 catalysts were more than 16 times as active as the commercial catalyst. In addition, on the Fe-ZSM-5 catalysts, no N₂O was detected in the entire temperature range of 300–600 °C, with only N₂ and H₂O as the reaction products. With the (V₂O₅ + WO₃)/TiO₂ catalyst, about 5% of N₂O yield was observed in the reaction at 375 °C, but N₂O yield would be decreased when the feed stream contained water vapor.

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When H₂O and SO₂ were added to the reactants, the SCR activity increased on Ce–Fe(42)-ZSM-5 at temperature above 350 °C, and the temperature window was widened (Figure 1). The Ce–Fe-ZSM-5 was also stable in the SCR reaction. During a run of 60 h on stream at 375 °C, under the conditions of 100 mg sample, 1000 ppm NO, 1000 ppm NH₃, 2% O₂, 5% H₂O, and 500 ppm SO₂, NO conversion was only changed from 99.9 to 99.0%. However, the activity on Fe(58)-ZSM-5 decreased from 99.5 to 80.0% under the same conditions. This indicates that cerium also plays a stabilization role for Fe-ZSM-5. The preparation of even more stable catalyst is in progress. Activities for SO₂ oxidation were measured by collecting SO₃ from the products as BaSO₄ precipitates.⁸ The Ce–Fe-ZSM-5 showed a much lower activity for SO₂ oxidation to SO₃ (0.7 vs 3.8% for (V₂O₅ + WO₃)/TiO₂) at 375 °C under the same reaction conditions.

The mechanism of NO reduction by NH₃ on the Fe-ZSM-5 catalyst was studied by in situ FT-IR. NH₄⁺ ions (bands at 3351–2730, 2154, 1944, and 1466 cm⁻¹⁹) were observed on the NH₃-adsorbed Fe(58)-ZSM-5 at 100 °C. An increase in temperature resulted in desorption of NH₃ from the sample. However, some NH₄⁺ ions still remained on the Fe-ZSM-5 catalyst at 450 °C. This suggests that strong Brønsted acid sites existed on the sample. In a separate experiment, when the Fe-ZSM-5 was exposed to 1000 ppm NO and 2% O₂ at 200–400 °C, three bands at 1880, 1624, and 1580 cm⁻¹ were detected, which can be assigned to weakly adsorbed NO, NO₂, and NO₃⁻ species, respectively.¹⁰ This suggests that NO was oxidized to NO₂ by O₂. After the sample was purged with He for 5 min at 400 °C, all of the bands vanished.

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In another experiment, NH₃ was first adsorbed on the Fe-ZSM-5 to form NH₄⁺, and the sample was subsequently exposed to (NO + O₂)/He at 300 °C. The NH₄⁺ bands vanished gradually in 5 min. This indicates that NH₄⁺ reacted with NO/NO₂ to form N₂, as identified by gas chromatograph. When the Fe-ZSM-5 was exposed to the reactant mixture (NO + NH₃ + O₂)/He at 200–450 °C, only adsorbed NH₄⁺ ions were detected. The above results taken together indicate the following scheme for NO reduction by NH₃ on the Fe-ZSM-5 catalyst. NH₃ is first activated to NH₄⁺ on Brønsted acid sites of the zeolite and then weakly adsorbed, and gaseous NO and NO₂ (resulting from NO oxidation by O₂) and NO₃⁻ species react with NH₄⁺ to form N₂ and H₂O. The reaction between NO_x adspecies and NH₄⁺ is much faster than that between NO and O₂.

In conclusion, the Fe-ZSM-5 catalyst shows remarkably high activities for the NH₃ SCR reaction, which is more than 67 times as active as the Fe-ZSM-5 (Si/Al = 29) reported by Komatsu et al.,⁵ judging by the first-order rate constants. In their work, an Fe-ZSM-5 catalyst was prepared by exchanging ZSM-5 with FeCl₃ solution and thus resulted in a low Fe content (0.28 wt %) in the sample. Also, a higher Si/Al ratio in their catalyst led to a weaker acidity. Both of these would result in a lower activity in their sample. The high activity of the Fe-ZSM-5 catalyst achieved in this work may be attributed to its strong Brønsted acidity (thus, a high concentration of NH₄⁺ ions) and a high activity for oxidation of NO to NO₂. It is known that both of them are important for the SCR reaction on zeolite-type catalysts.^{9b}

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