

Low temperature selective catalytic reduction (SCR) of NO with NH₃ over Fe–Mn based catalysts

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Fe–Mn based transition metal oxides (Fe–Mn, Fe–Mn–Zr and Fe–Mn–Ti) show nearly 100% NO conversion at 100–180 °C for selective catalytic reduction of NO with NH₃ under the applied conditions with a space velocity of 15 000 h^{−1}.

Nitrogen oxides (NO, NO₂ and N₂O) have been a major source of air pollution. They contribute to photochemical smog, acid rain, ozone depletion and the greenhouse effect. An efficient technology for removing NO from power plants is selective catalytic reduction (SCR) with ammonia (4 NO + 4 NH₃ + O₂ = 4 N₂ + 6 H₂O). The industrial operations are carried out on V₂O₅ + WO₃(MoO₃)/TiO₂ catalysts at 350–400 °C.^{1–3} However, the high concentration of ash (*e.g.*, K₂O, CaO and As₂O₃) in the flue gas reduces their performance and longevity, although they are resistant to SO₂.^{2,4} To solve this problem, one attractive option is to place the SCR unit downstream of the desulfurizer and electrostatic precipitators where SO₂ and ash have been removed. Since the temperature in the downstream is typically below 200 °C, this makes it necessary to develop low temperature SCR catalysts to avoid reheating of the flue gas and thus decrease the capital cost.

Some transition metal containing catalysts have been investigated for the low temperature SCR reaction, such as amorphous chromia,⁵ NiSO₄/Al₂O₃,⁶ MnO_x/Al₂O₃,⁷ V₂O₅/activated carbon⁸ and MnO_x/TiO₂.⁹ They showed various SCR activities at below 200 °C under different conditions. It is known that ammonium nitrite decomposes quickly into N₂ (majority) and NO (minority) below 100 °C.¹⁰ The formation of ammonium nitrite from NO, O₂ and NH₃ requires oxidation of NO to NO₂ by O₂. In our previous work,^{11,12} we have shown that an increase in NO oxidation to NO₂ on Fe–ZSM-5 will result in a significant improvement of the SCR activity and, moreover, the reaction rate of NH₃ with NO₂ + NO is much higher than that with NO. Therefore, it is expected that a high activity for NO conversion to NO₂ at low temperatures may facilitate a high SCR activity because it can enhance the formation of ammonium nitrite. More recently, we found that Fe–Mn based transition metal oxides were highly efficient sorbents for NO removal.¹³ In particular, these sorbents showed very high activity for NO oxidation to NO₂ at room temperature; 63–76% NO conversions were obtained on Fe–Mn, Fe–Mn–Zr and Fe–Mn–Ti oxides under the conditions of 500 ppm NO, 10% O₂ and GHSV (gas hourly space velocity) = 6000 h^{−1}. Therefore, we investigated these mixed oxides as low temperature SCR catalysts in this work.

The Fe–Mn based transition metal oxides (Fe–Mn, Fe–Mn–Zr and Fe–Mn–Ti, with equal mol of metals) were prepared by the coprecipitation method as described in detail previously.¹³ The BET surface areas were 54, 178 and 183 m² g^{−1}, respectively, for Fe–Mn, Fe–Mn–Zr and Fe–Mn–Ti oxides. The SCR activity measurements were carried out in a fixed-bed quartz reactor. The reaction conditions were as follows: 0.5 g sample (0.4 ml), 1000 ppm NO, 1000 ppm NH₃, 2% O₂, 2.5% water vapor (when used), 37.5 or 1000 ppm SO₂ (when used), balance He, 100 ml min^{−1} total flow rate and GHSV = 15 000

h^{−1} (ambient conditions). The premixed gases (1.01% NO/He, 1.00% NH₃/He and 0.99% SO₂/He) were supplied by Matheson. Water vapor was generated by passing He through a gas-wash bottle containing deionized water. The tubings of the reactor system were heat-traced to prevent formation and deposition of ammonium sulfate/bisulfate and ammonium nitrate. The NO and NO₂ concentrations were continually monitored by a chemiluminescent NO/NO_x analyzer (Model 42C, Thermo Environmental Instruments Inc.). To avoid errors caused by the oxidation of ammonia in the converter of the NO/NO_x analyzer, an ammonia trap containing phosphoric acid solution was installed before the sample inlet to the chemiluminescent analyzer. The products were analyzed by a gas chromatograph (Shimadzu, 14A) at 50 °C with 5A molecular sieve column for N₂ and Porapak Q column for N₂O. All the data were obtained after 60–200 min when the SCR reaction reached a steady state. The SCR activities of Fe–Mn, Fe–Mn–Zr and Fe–Mn–Ti oxides at 80–180 °C are shown in Fig. 1. These mixed oxides showed excellent activities at low temperatures. At 80 °C, 68–74% NO conversions were obtained at a space velocity of 15 000 h^{−1}. With increasing temperature, NO conversion increased significantly and reached nearly 100% at above 120 °C. The products were N₂ and H₂O only and N₂O formation was not observed by GC. However, on pure MnO_x, we observed 8–35% N₂O selectivity (with 72–93% NO conversion) at 80–180 °C under the same reaction conditions. The SCR activity at low temperatures decreased in the following order: Fe–Mn > Fe–Mn–Zr > Fe–Mn–Ti. As mentioned above, the Fe–Mn catalyst has a much lower surface area than Fe–Mn–Zr and Fe–Mn–Ti oxides. Hence it seems that the SCR activity does not have a correlation with the surface area.

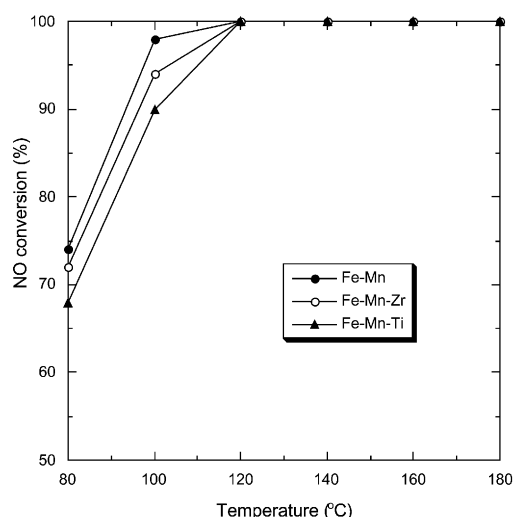


Fig. 1 SCR activities on the Fe–Mn based transition metal oxides in the absence of H₂O. Reaction conditions: 0.5 g catalyst, [NO] = [NH₃] = 1000 ppm, [O₂] = 2%, He = balance, total flow rate = 100 ml min^{−1} and GHSV = 15 000 h^{−1}.

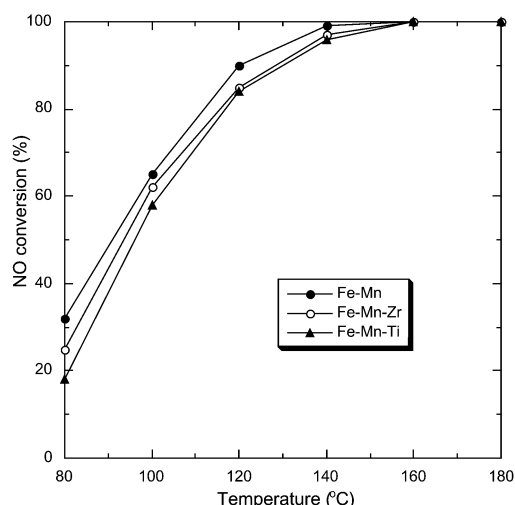


Fig. 2 SCR activities on the Fe–Mn based transition metal oxides in the presence of H₂O. Reaction conditions: 0.5 g catalyst, [NO] = [NH₃] = 1000 ppm, [O₂] = 2%, [H₂O] = 2.5%, He = balance, total flow rate = 100 ml min⁻¹ and GHSV = 15 000 h⁻¹.

Since the combustion gases contain water vapor, we further studied the effect of H₂O on the SCR activities of the mixed oxides. As shown in Fig. 2, when 2.5% H₂O was added to the reactants, NO conversion decreased sharply at lower temperatures, *e.g.*, 80 °C. It is likely that H₂O occupies some of the active sites for the SCR reaction. When the reaction temperature was increased, the H₂O inhibition effect became less significant. At 160–180 °C, nearly 100% NO conversion was still obtained on the three catalysts. In addition, the Fe–Mn based catalysts did not show any decrease in activity after 10 h on stream at 140 °C in the presence of H₂O. Also, the inhibition by H₂O is reversible. When H₂O was removed from the reaction gases, NO conversions were recovered on these catalysts.

The above results indicate that the Fe–Mn based transition oxides are highly active for the low temperature SCR reaction and they are resistant to water vapor at 140–180 °C. Their SCR activities are much higher than those on 20% MnO_x/Hombikat TiO₂, the 'best' low temperature catalyst reported in ref. 9. For instance, at 100 °C, 89–98% NO conversions were observed on the Fe–Mn based catalysts at GHSV = 15 000 h⁻¹ (Fig. 1), whereas only 82% NO conversion was reported on the MnO_x/TiO₂ at GHSV = 8000 h⁻¹. The superior SCR activity on these Fe–Mn catalysts is probably related to their high activity for NO oxidation to NO₂ at low temperatures. Since NO₂ + NO is very active in reacting with NH₃ adsorbed species at low temperatures,¹² the formed NO_x can be reduced to nitrogen by NH₃. It is noted that there are still small concentrations of SO₂ in combustion gases even after the desulfurizer (except when using very clean fuels such as liquefied natural gas). Effects of SO₂ on the SCR activity are also important for the low temperature SCR catalyst. Our result indicated that, when 1000 ppm SO₂ was added to the reaction gas and the space velocity was kept at 15 000 h⁻¹, NO conversions on Fe–Mn–Zr oxides were decreased significantly to 8–23% at 80–180 °C under steady state conditions. This is consistent with the previous observations that MnO_x catalysts were deactivated by SO₂.^{7,14}

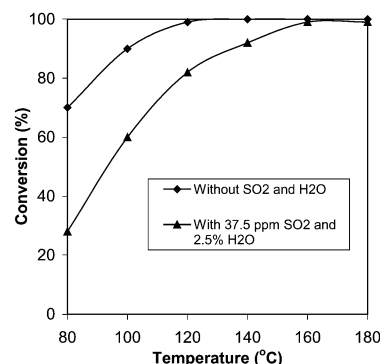


Fig. 3 SCR activities on the Fe–Mn based transition metal oxides in the presence of SO₂ + H₂O. Reaction conditions: 0.5 g catalyst, [NO] = [NH₃] = 1000 ppm, [O₂] = 2%, [SO₂] = 37.5 ppm and [H₂O] = 2.5% (when used), He = balance, total flow rate = 100 ml min⁻¹ and GHSV = 15 000 h⁻¹.

In the presence of SO₂, SO₂ can be oxidized to SO₃ by O₂. The SO_x compounds (SO₂ + SO₃) are adsorbed on the transition metal oxides and they are difficult to desorb at low temperatures. Our FTIR spectrum of the used Fe–Mn–Zr oxides showed two strong bands centered at 1402 and 1120 cm⁻¹, indicating formation of ammonium ions and sulfate species, respectively.¹⁵ The occupation of the active sites by metal sulfates and ammonium sulfates will decrease the SCR activity.¹⁴ The effects of lower levels of SO₂ have also been studied. The results for 37.5 ppm SO₂ plus 2.5% H₂O are shown in Fig. 3. As expected, less deactivation was seen for 37.5 ppm SO₂ compared with that by 1000 ppm SO₂. Further work on the modification of the catalysts is needed to improve sulfur resistance.

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