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Low temperature selective catalytic reduction (SCR) of NO with NH_3 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 NH_3 under the applied conditions with a space velocity of 15 000 h^{-1}.

Nitrogen oxides (NO, NO_2 and N_2O) 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 ($4\,NO + 4\,NH_3 + O_2 = 4\,N_2 + 6\,H_2O$). The industrial operations are carried out on $V_2O_5 + WO_3(MoO_3)/TiO_2$ catalysts at 350–400 °C.[1–3] However, the high concentration of ash (*e.g.*, K_2O, CaO and As_2O_3) in the flue gas reduces their performance and longevity, although they are resistant to SO_2.[2,4] To solve this problem, one attractive option is to place the SCR unit downstream of the desulfurizer and electrostatic precipitators where SO_2 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] $NiSO_4/Al_2O_3$,[6] MnO_x/Al_2O_3,[7] V_2O_5/activated carbon[8] and MnO_x/TiO_2.[9] They showed various SCR activities at below 200 °C under different conditions. It is known that ammonium nitrite decomposes quickly into N_2 (majority) and NO (minority) below 100 °C.[10] The formation of ammonium nitrite from NO, O_2 and NH_3 requires oxidation of NO to NO_2 by O_2. In our previous work,[11,12] we have shown that an increase in NO oxidation to NO_2 on Fe-ZSM-5 will result in a significant improvement of the SCR activity and, moreover, the reaction rate of NH_3 with NO_2 + NO is much higher than that with NO. Therefore, it is expected that a high activity for NO conversion to NO_2 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 NO_2 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% O_2 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 $m^2\ g^{-1}$, 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 NH_3, 2% O_2, 2.5% water vapor (when used), 37.5 or 1000 ppm SO_2 (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% NH_3/He and 0.99% SO_2/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 NO_2 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 N_2 and Porapak Q column for N_2O. 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 N_2 and H_2O only and N_2O formation was not observed by GC. However, on pure MnO_x, we observed 8–35% N_2O 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.

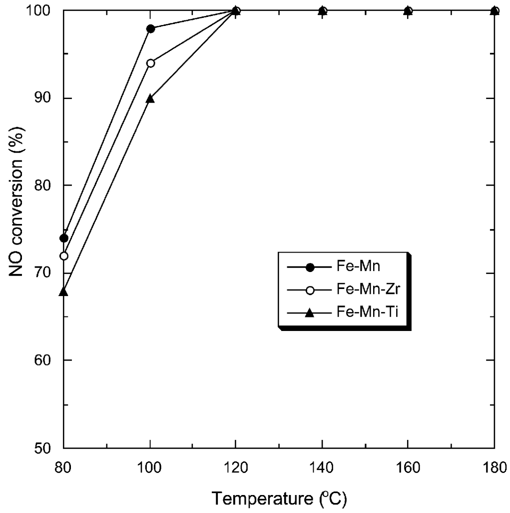

Fig. 1 SCR activities on the Fe–Mn based transition metal oxides in the absence of H_2O. *Reaction conditions*: 0.5 g catalyst, [NO] = [NH_3] = 1000 ppm, [O_2] = 2%, He = balance, total flow rate = 100 ml min^{-1} and GHSV = 15 000 h^{-1}.

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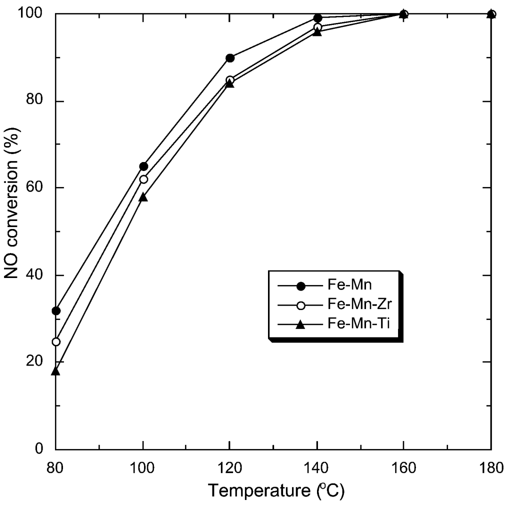

Fig. 2 SCR activities on the Fe–Mn based transition metal oxides in the presence of H_2O. *Reaction conditions*: 0.5 g catalyst, [NO] = [NH_3] = 1000 ppm, [O_2] = 2%, [H_2O] = 2.5%, He = balance, total flow rate = 100 ml min^{-1} and GHSV = 15 000 h^{-1}.

Since the combustion gases contain water vapor, we further studied the effect of H_2O on the SCR activities of the mixed oxides. As shown in Fig. 2, when 2.5% H_2O was added to the reactants, NO conversion decreased sharply at lower temperatures, *e.g.*, 80 °C. It is likely that H_2O occupies some of the active sites for the SCR reaction. When the reaction temperature was increased, the H_2O 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 H_2O. Also, the inhibition by H_2O is reversible. When H_2O 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 TiO_2, 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/TiO_2 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 NO_2 at low temperatures. Since NO_2 + NO is very active in reacting with NH_3 adsorbed species at low temperatures,[12] the formed NO_x can be reduced to nitrogen by NH_3. It is noted that there are still small concentrations of SO_2 in combustion gases even after the desulfurizer (except when using very clean fuels such as liquefied natural gas). Effects of SO_2 on the SCR activity are also important for the low temperature SCR catalyst. Our result indicated that, when 1000 ppm SO_2 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 SO_2.[7,14] In the presence of SO_2, SO_2 can be oxidized to SO_3 by O_2. The SO_x compounds (SO_2 + SO_3) 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 SO_2 have also been studied. The results for 37.5 ppm SO_2 plus 2.5% H_2O are shown in Fig. 3. As expected, less deactivation was seen for 37.5 ppm SO_2 compared with that by 1000 ppm SO_2. Further work on the modification of the catalysts is needed to improve sulfur resistance.

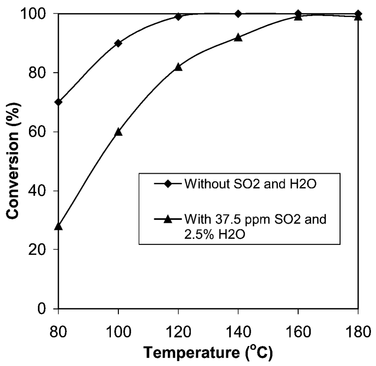

Fig. 3 SCR activities on the Fe–Mn based transition metal oxides in the presence of SO_2 + H_2O. *Reaction conditions*: 0.5 g catalyst, [NO] = [NH_3] = 1000 ppm, [O_2] = 2%, [SO_2] = 37.5 ppm and [H_2O] = 2.5% (when used), He = balance, total flow rate = 100 ml min^{-1} and GHSV = 15 000 h^{-1}.

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