# A superior catalyst for low-temperature NO reduction with NH$_3$

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**Mn-Ce mixed-oxide catalyst yields nearly 100% NO conversion at 100–150 °C at a high space velocity of 42,000 h$^{-1}$. SO$_2$ and H$_2$O (at high concentrations) have only slight effects on the activity.**

Nitrogen oxides (NO, NO$_2$, and N$_2$O) remain a major source for air pollution.[1] Nearly all NO$_x$ (95%) derives from transportation (49%) and power plants (46%).[2] The major technology for reducing nitrogen oxide emissions from stationary sources is selective catalytic reduction (SCR) of NO$_x$ (x = 1, 2) by ammonia. The general reaction is as follows:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$
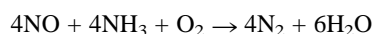
The commercial catalysts for this process are V$_2$O$_5$/TiO$_2$ (anatase) mixed with WO$_3$ or MoO$_3$.[3–6] The vanadia-based catalyst is active within a narrow temperature window of 300–400 °C, and is subjected to deactivation by SO$_2$, Thus, there has been a strong incentive to search for a highly active catalyst for low temperature SCR. Such a catalyst would be placed downstream the desulfurizer and electrostatic precipitator in the power generation system. Success in developing such a catalyst would significantly improve the economics of SCR.

Supported transition metal oxides, such as MnO/Al$_2$O$_3$,[7,8] CuO/Al$_2$O$_3$,[9] CuO/TiO$_2$,[10] Fe$_2$O$_3$/TiO$_2$,[11] V$_2$O$_5$/active carbon[12] and iron–silica aerogels[13] have been shown to be active in medium temperature SCR of NO with NH$_3$ in the presence of excess oxygen. Recently, Long and Yang[14] studied Fe–Mn based catalysts and found the Fe–Mn mixed-oxide catalyst showed 100% NO conversion at 100–180 °C for SCR of NO with NH$_3$ under the reaction conditions with a space velocity of 15,000 h$^{-1}$. Ceria (CeO$_2$) has been studied extensively in recent years because of its wide applications in many areas of chemistry.[15,16] In our previous study, we found that cerium could not only enhance the Fe-ZSM-5 catalyst but also increase the stability.[17] In this paper we present the first study on NO reduction by NH$_3$ using mixed MnO$_x$–CeO$_2$ catalysts. These results show that MnO$_x$–CeO$_2$ is a superior catalyst for NO reduction by NH$_3$ in the low temperature window of 80–150 °C with 100% N$_2$ selectivity and complete NO conversion at temperatures as low as 120 °C.

Manganese nitrate, cerium nitrate and citric acid were mixed in the desired proportions and the mole ratio of citric acid to metal components (the total mole of manganese and cerium) was 1.0. The above mixture was stirred at room temperature for 1 hour. The solution was dried at 100 °C, resulting in a porous, foam-like solid. The foam-like precursor was calcined in air at a desired temperature for 6 hours. The pure manganese oxide and ceria catalysts were prepared by the same procedure. The catalyst is denoted as MnO$_x$(z)–CeO$_2$(y). Z represents the mole ratio of Mn/(Mn+Ce) and y denotes the calcination temperature, for example, MnO$_x$(0.3)–CeO$_2$(650). The BET surface area of the mixed oxide is in the range of 50–70 m$^2$ g$^{-1}$, while that of the pure CeO$_2$ and MnO$_x$ are only lower 30 m$^2$ g$^{-1}$.

The SCR activity measurement was carried out in a fixed-bed quartz reactor. The typical reactant gas composition was as follows: 1000 ppm NO, 1000 ppm NH$_3$, 2% O$_2$, 100 ppm SO$_2$ (when used), water vapor (when used), and balance He. Water

vapor was generated by passing He through a heated gas-wash bottle containing de-ionized water. The NO and NO$_2$ concentrations were continually monitored by a chemiluminescent NO/NO$_x$ analyzer (Thermo Electron Corporation, Model 10). 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 also analyzed by a gas chromatograph (Shimadzu, 8A) at 50 °C with 5A molecular sieve column for N$_2$ and Porapak Q column for N$_2$O.

Because the reaction was carried out at low temperatures (< 200 °C), it must be confirmed that the decrease of NO was not caused by the adsorption of NO on the catalysts. In each experiment, we first purged the catalyst with the reactant gas until the NO concentration in the outlet reached the inlet concentration (1000 ppm). Based on the experiment we can calculate the nitrogen balance (inlet [NO] = outlet [NO] + [N$_2$] + [N$_2$O]). For all the experiments in this work, the nitrogen balance exceeded 95%.

Results on the NO conversion as a function of temperature are given in Fig. 1 for Ce–Mn oxide catalysts with different molar ratios of Mn/(Mn+Ce). Clearly, high catalytic activities were already achieved in the lower temperature region. At 80 °C, 82% of NO conversion was obtained at a space velocity of 42,000 h$^{-1}$ on the MnO$_x$(0.3)–CeO$_2$(650) catalyst. At higher temperatures, NO conversion increased significantly and reached nearly 100% at above 120 °C. GC analyses showed that all of the products were N$_2$ and H$_2$O. N$_2$O formation was not observed when the reaction temperature was below 150 °C. Fig. 1 also shows the effect of the ratio of Mn/(Mn+Ce) on the acitivity. The SCR activity at low temperatures decreased in the following sequence: MnO$_x$(0.3)–CeO$_2$(650) > MnO$_x$(0.4)–CeO$_2$(650) > MnO$_x$(0.5)–CeO$_2$(650) > MnO$_x$(0.2)–CeO$_2$(650) > MnO$_x$(0.1)–CeO$_2$(650). Fig. 2 shows the activities of MnO$_x$–CeO$_2$ mixed-oxide catalysts calcined at different temperatures. The result indicates that the calcination tem-
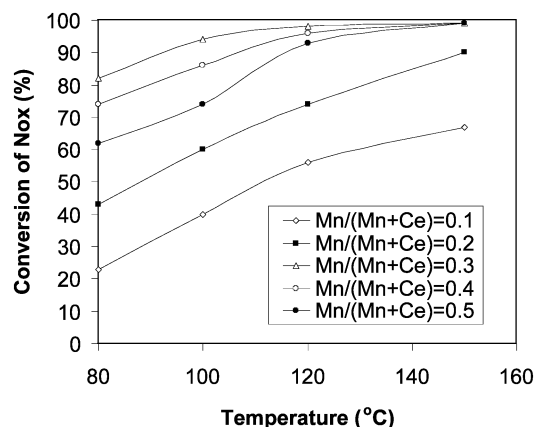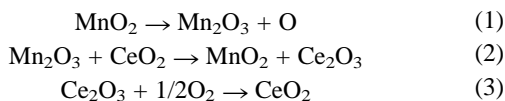


**Fig. 1** NO conversions for various MnO$_x$–CeO$_2$ mixed-oxide catalysts in the absence of SO$_2$ and H$_2$O. Reaction conditions: [NO] = [NH$_3$] = 1000 ppm, [O$_2$] = 2%, GHSV = 42,000 h$^{-1}$.

perature influences the SCR activity significantly. From Fig. 2 we can see that the catalyst calcined at 650 °C had the highest activity. The XRD patterns (not shown) do not have intense or sharp peaks for the Mn–Ce mixed oxides. Rather, they showed broad reflections due to $CeO_2$ with a cubic fluorite structure. The interaction of $CeO_2$ with $Mn_2O_3$ is not well known. Imamura et al.[19] found that the activity of a physical mixture of $Mn_2O_3$ and $CeO_2$ in wet air oxidation of ammonia was lower than that of co-precipitated $Mn_2O_3$–$CeO_2$. This observation suggested that there existed a synergistic mechanism between the manganese and cerium oxides. Ding et al[20] explained the synergistic mechanism by the following chain of reactions:

$$MnO_2 \rightarrow Mn_2O_3 + O \qquad (1)$$

$$Mn_2O_3 + CeO_2 \rightarrow MnO_2 + Ce_2O_3 \qquad (2)$$

$$Ce_2O_3 + 1/2O_2 \rightarrow CeO_2 \qquad (3)$$

They concluded that the co-existence of $MnO_2$–$Mn_2O_3$ might explain the increased activity for oxidation of ammonia. Normally, the adsorbed oxygen on manganese would be expected to participate in the oxidation reaction. The additional oxygen generated (via eqn 1) may be more active and accessible. Furthermore, oxygen transfer from $CeO_2$ to $Mn_2O_3$ may further enhance these reactions. Imamura et al.[21] also observed that the ability of Ce in increasing the valence of Mn (that is, to provide oxygen to Mn) was probably related to the well-known oxygen storage function of $CeO_2$. Although the detailed mechanism is not known, the action of Ce may well be to increase the valance of Mn and increase its oxidation ability.

Water vapor is one of the main components in flue gases and leads to catalyst deactivation. Therefore, resistance of $DeNO_x$ catalysts to deactivation by water vapor is very important for industrial application of a low temperature $DeNO_x$ processes.[18] We further studied the effect of $H_2O$ on the SCR activities of the Ce–Mn mixed-oxide catalyst. Before adding water the SCR reaction had been stabilized for one hour at 120 °C reaction temperature. When 2.5% $H_2O$ was added to the reactants, the NO conversion showed only a barely detectable decrease. Upon switching off the water vapor, the activity was rapidly restored to 100% of its original level. The inhibition by water vapor became appreciable at high water vapor concentrations, as shown in Fig. 3. When 19% $H_2O$ was added, the NO conversion decreased to about 98%. Upon removal of the water vapor supply, however, the activity was rapidly restored to its original value again.

Effect of $SO_2$ on the SCR activity is also important for the low temperature SCR catalyst though the flow gas passed through the desulfurizer. The effect of $SO_2 + H_2O$ on SCR activity of the Ce–Mn catalysts is also illustrated in Fig. 3. Our results indicated that, when 100 ppm $SO_2$ and 2.5% $H_2O$ were



Fig. 3 Effect of on-stream time on SCR activity with $H_2O + SO_2$ and without $H_2O + SO_2$ Reaction conditions: 120 °C, [NH$_3$] = [NO] = 1000 ppm, [O$_2$] = 2%, GHSV = 42,000h$^{-1}$. Catalyst: MnO$_x$(0.3)–CeO$_2$(650)

added to the reaction gas and the reaction temperature and space velocity were kept at 120 °C and 42,000 h$^{-1}$, respectively, the NO conversion on Ce–Mn oxides was decreased to 95% at 120 °C in 4 hours. This was still a very high level of activity. Moreover, the activity was restored after $SO_2 + H_2O$ was stopped.

In addition, we found that Fe and Pr can significantly enhance resistance to $SO_2$ and $H_2O$. We tested the activity of the Mn(0.3)–Pr(0.05)–$CeO_2$ (650) in the presence of 100 ppm $SO_2$ and 6% $H_2O$ for 20 hours at 150 °C. The conversion of NO decreases from 95% to 85% only, so this catalyst can be used in no sulfur or low sulfur conditions. In conclusion, a new highly active, $H_2O$ and $SO_2$ resistant catalyst has been developed for low temperature SCR of NO with $NH_3$ in excess $O_2$. Further studies are in progress for an understanding of the mechanism of the catalytic system.

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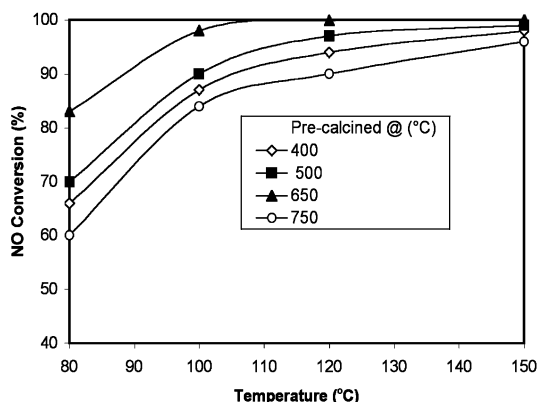21 S. Imamura, Ind. Eng. Chem. Res., 1999, 38, 1743.

Fig. 2 SCR activity of MnO$_x$(0.3)–CeO$_2$ mixed-oxide catalyst pre-calcined at different temperatures. Reaction conditions: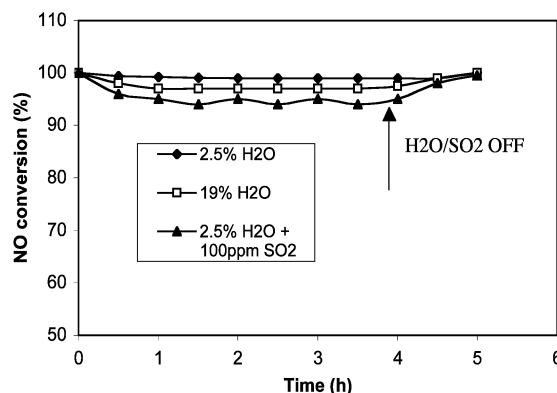 [NH$_3$] = [NO] = 1000 ppm, [O$_2$] = 2%, GHSV = 42,000h$^{-1}$.