

Low-temperature catalytic reduction of nitrogen oxides with ammonia over supported manganese oxide catalysts

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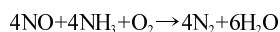
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Abstract—MnOx supported on γ -Al₂O₃, TiO₂, Y-ZrO₂ and SiO₂ was prepared by an impregnation and a deposition-precipitation method, and their catalytic activities for the low-temperature selective catalytic reduction (SCR) of NOx with NH₃ in the presence of excess O₂ were examined. The catalytic activity of the catalysts prepared by a deposition-precipitation method was higher than that of catalysts prepared by an impregnation method. The activity follows in the order: MnOx/TiO₂ ≈ MnOx/ γ -Al₂O₃ > MnOx/SiO₂ > MnOx/Y-ZrO₂. Supported MnOx catalysts prepared by a deposition-precipitation method appeared to have an amorphous manganese oxide phase and those prepared by an impregnation method exhibited a crystalline MnO₂ phase, respectively. The addition of SO₂ with H₂O in the feeding gas slightly deactivates the SCR activity of MnOx/TiO₂ catalysts.

Key words: NH₃-SCR, Supported MnOx Catalyst, Low Temperature, Deposition-precipitation, Impregnation

INTRODUCTION

The environmental concern caused by nitrogen oxides, NOx, has led to the development of efficient technologies to avoid their formation or to eliminate them. Among the developed methods, selective catalytic reduction (SCR) with NH₃ is a well-proven technique for NOx removal in stationary power stations [Bosch and Janssen, 1988]. The general reaction is as follows:



Many catalysts have been reported to be active for the above reaction [Busca et al., 1998; Parvulescu et al., 1998; Kijlsta et al., 1996]. Commercially available catalysts are based on V₂O₅/TiO₂ [Bosch and Janssen, 1988]. Because these catalysts exhibit high conversions in the temperature range of 573-673 K, the SCR should be applied before units for particle removal and desulphurization where the gas temperature decreases [Muniz et al., 2000]. However, when the flue gas has high concentrations of particles and other contaminants which are deleterious for the catalyst, proper units should be located at the upstream of the catalyst bed to resolve above problems, which causes a decrease of the exit gas temperature. Therefore, there has been much interest in developing low-temperature SCR catalysts capable of working at the downstream of the particle removal equipment and the desulphurization device without heating the flue gas [Choi et al., 2005].

Recently, it has been found that the oxidation of NO into NO₂ to increase the concentration of NO₂ can greatly enhance the catalytic activity for the reduction of NOx, especially at low temperatures. This combined catalytic system, which has a separate oxidation and

reduction function, may be suitable for the treatment of flue gases at relatively low temperatures [Kang et al., 2006; Mok et al., 2004].

For low-temperature NH₃-SCR catalysts, various transition metal (V, Cr, Mn, Fe, Co, Ni and Cu) oxides on different commercial supports such as silica and alumina have been studied. Among these catalysts, manganese oxides catalysts such as MnOx/Al₂O₃ [Singoredjo et al., 1992], MnOx/NaY [Bentrup et al., 2001] and MnOx/TiO₂ [Smirniotis et al., 2001; Qi and Yang, 2003] have been reported to be active. These supported manganese oxides catalysts were usually prepared by an impregnation or an ion-exchange method. More recently, MnOx-CeO₂ [Qi and Yang, 2004] and MnOx [Kang et al., 2006] with a high surface area were also reported to be quite active for the low-temperature NH₃-SCR.

In this work, supported manganese oxides catalysts were studied to find the effect of the preparation method such as an impregnation and a deposition-precipitation method and kinds of support such as γ -Al₂O₃, TiO₂, Y-ZrO₂, and SiO₂ on the catalytic activity for the low-temperature NH₃-SCR.

EXPERIMENTAL

1. Catalyst Preparation

Manganese oxide catalysts supported on various supports such as γ -Al₂O₃ (Sba-150, Condea), TiO₂ (P-25, Degussa), Y-ZrO₂ (TZ-8Y, Tosoh), and SiO₂ (Davisil™, Aldrich) were prepared by an impregnation (I) method or a deposition-precipitation (P) method. The impregnated catalyst was prepared by evaporating water from a slurry composed of support powders and an aqueous manganese nitrate (Mn(NO₃)₂·xH₂O, Aldrich, 98.0+%) solution. For the deposition-precipitation method, the pH of the slurry containing support powders and an aqueous manganese nitrate solution increased to be 8 at room temperature by the addition of sodium carbonate (Na₂CO₃, SHINYO, 99.0%) as a precipitant. The resulting precipitate was aged at room temperature for 1 h, filtered, and washed several times

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with distilled water. These impregnated and precipitated catalysts were dried at 393 K for 12 h and then calcined at 623 K for 4 h under static air. The amount of Mn in the final catalyst was intended to be 20 wt% for all catalysts.

2. Catalyst Characterization

Bulk crystalline structures of catalysts were determined with an X-ray diffraction (XRD) technique. XRD patterns were obtained by using Cu K α radiation with a Rigaku D/MAC-III instrument at room temperature. Surface areas were determined by N₂ adsorption using the BET method. Temperature programmed reduction (TPR) was conducted over 0.2 g sample in a 10 vol% H₂/Ar stream from 313 K to 873 K at a heating rate of 10 K/min, monitoring TCD signals.

3. Activity Measurements

Catalytic activities were measured over a fixed bed of catalysts in a tubular flow reactor of 8-mm i.d. Reactant gases were fed to the reactor by means of electronic mass flow controller (MKS). The

reactant gas typically consisted of 500 ppm NO, 500 ppm NH₃, 5 vol% O₂, and N₂. The effect of H₂O and SO₂ on NO_x conversions was examined in the presence of 10 vol% H₂O and 100 ppm SO₂ with the above reactant gas. The NO_x concentration in the inlet and outlet gas was analyzed by means of an NO/NO₂ combustion gas analyzer (Euroton).

RESULTS AND DISCUSSIONS

Fig. 1 shows the NO_x conversions over the manganese oxides catalysts supported on different supports and prepared by a different method. Generally, the catalytic activity of the catalysts prepared by a deposition-precipitation method was higher than that of catalysts prepared by an impregnation method. The activity follows in the order: Mn(P)/TiO₂ > Mn(P)/ γ -Al₂O₃ > Mn(P)/SiO₂ > Mn(P)/Y-ZrO₂ for supported manganese oxides catalysts prepared by a deposition-precipitation method and Mn(I)/TiO₂ > Mn(I)/ γ -Al₂O₃ > Mn(I)/SiO₂ > Mn(I)/Y-ZrO₂ for supported manganese oxides catalysts prepared by an impregnation method, respectively. Mn(P)/TiO₂, Mn(P)/ γ -Al₂O₃ and Mn(P)/SiO₂ catalysts show high activity at low temperatures in the range from 373 to 473 K. However, there is a noticeable decrease in NO_x conversion when the reaction temperature was over 473 K for the Mn(P)/SiO₂ catalyst.

Table 1 shows the texture properties of all the supports and catalysts examined in this work. The BET surface area of the final catalyst decreased compared with that of support itself regardless of the preparation method. Even though the BET surface area of supported manganese oxides catalysts prepared by a deposition-precipitation method was slightly smaller than that of impregnated manganese oxides catalysts, this difference was not so noticeable for each catalyst supported on the same support. Based on the activity data and the BET surface area, it can be said that no correlation can be made between them. However, the catalytic activity is strongly dependent on the support and the preparation method.

XRD was conducted to determine the crystalline structure of manganese oxides catalysts supported on different supports and prepared by a different method. As shown in Fig. 2A, there are several XRD peaks from the supported manganese oxides catalysts prepared by an impregnation method, which can be assigned to be MnO₂ and support itself. However, supported manganese oxides catalysts prepared by a deposition-precipitation method did not show any peak representing Mn-containing phase as shown in Fig. 2B. This amorphous manganese oxide phase was also observed in unsupported manganese oxides calcined at 623 K. Mn₂O₃ and Mn₃O₄ were determined to be dominant manganese oxides and small amounts

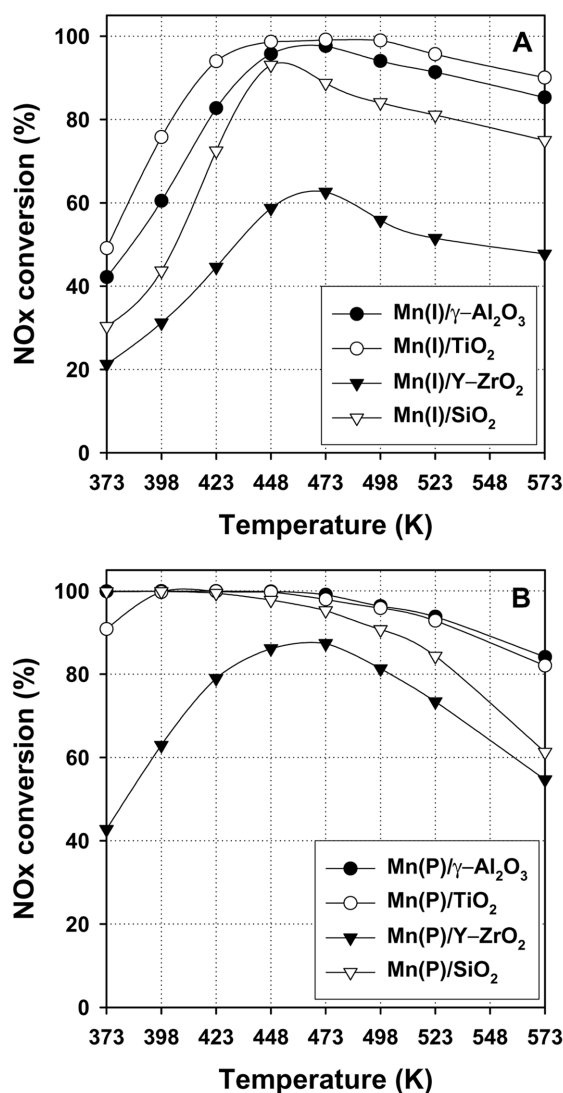


Fig. 1. NO_x conversions over various supported MnO_x catalysts calcined at 623 K. Reactants: 500 ppm NO, 500 ppm NH₃ and 5 vol% O₂ in N₂. The gas hourly space velocity (GHSV) was 40,000 h⁻¹.

Table 1. The texture properties of supports and prepared catalysts

Materials	S_{BET} (m ² /g)	V_p (cc/g)	Materials	S_{BET} (m ² /g)	V_p (cc/g)
γ -Al ₂ O ₃	153	0.89	Mn(I)/Y-ZrO ₂	9	0.46
TiO ₂	52	0.80	Mn(I)/SiO ₂	298	1.00
Y-ZrO ₂	10	0.59	Mn(P)/ γ -Al ₂ O ₃	100	0.78
SiO ₂	450	1.24	Mn(P)/TiO ₂	24	0.52
Mn(I)/ γ -Al ₂ O ₃	116	0.85	Mn(P)/Y-ZrO ₂	5	0.10
Mn(I)/TiO ₂	41	0.83	Mn(P)/SiO ₂	294	1.11

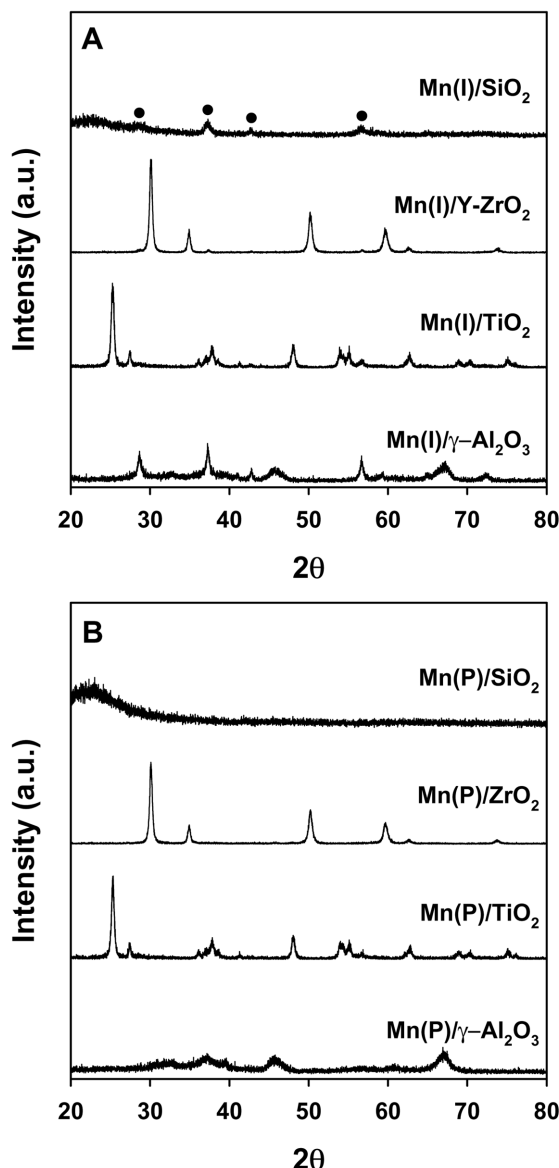


Fig. 2. XRD patterns of supported manganese oxides catalysts calcined at 623 K (• MnO_2).

of MnO_2 were also calculated from Mn K-edge XANES spectra [Kang et al., 2006]. Therefore, the catalyst with the amorphous phase shows the best SCR activity with NH_3 at low temperatures.

TPR profiles of the supported manganese oxide catalysts are illustrated in Fig. 3. All the supported catalysts show a two-step reduction. The reduction peak temperatures for impregnated manganese oxides catalysts were higher than those of manganese oxides catalysts prepared by a deposition-precipitation method, suggesting the occurrence of a stronger interaction between the manganese oxide and supports in the former system. The total amount of hydrogen consumption during the TPR experiments for all samples can be related to the stoichiometry of the manganese oxides, assuming that MnO is the final state after reduction [Kapteijn et al., 1994]. As shown in Table 2, the O/Mn values indicate the presence of a large amount of MnO_2 on impregnated manganese oxides catalysts. However, the ratio was much smaller for manganese oxides catalysts pre-

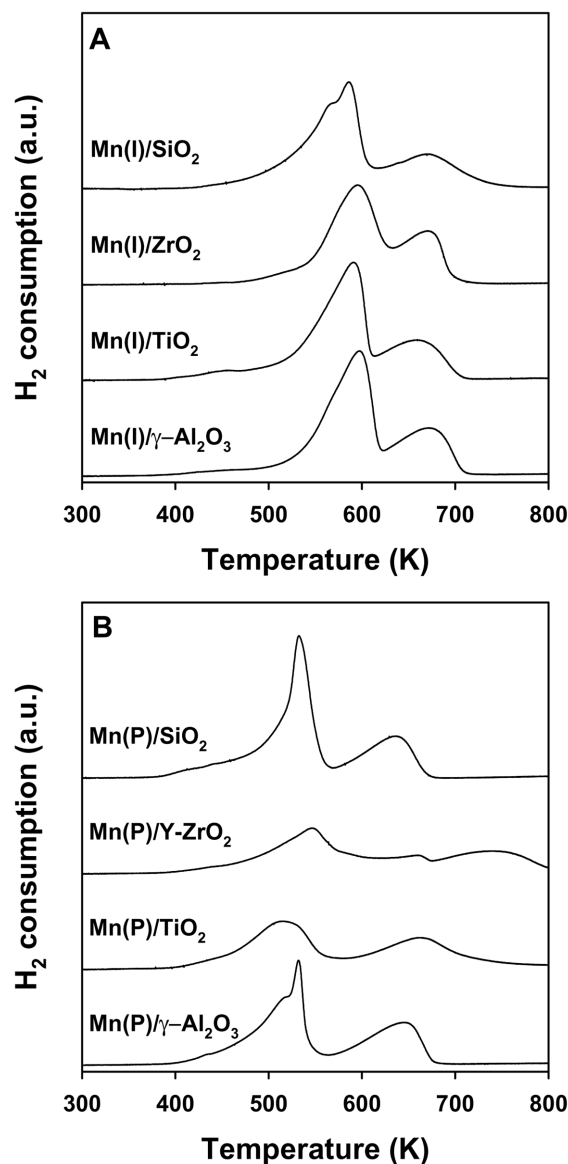


Fig. 3. TPR profiles of supported manganese oxides catalysts calcined at 623 K.

Table 2. TPR data for supported manganese oxide catalysts

Catalyst	Temperature (K)		H_2 consumption (O/Mn)
	I	II	
$\text{Mn(II)}/\gamma\text{-Al}_2\text{O}_3$	597	673	1.94
$\text{Mn(II)}/\text{TiO}_2$	591	659	1.92
$\text{Mn(II)}/\text{Y-ZrO}_2$	595	670	1.76
$\text{Mn(II)}/\text{SiO}_2$	586	671	1.86
$\text{Mn(III)}/\gamma\text{-Al}_2\text{O}_3$	532	646	1.50
$\text{Mn(III)}/\text{TiO}_2$	514	662	1.35
$\text{Mn(III)}/\text{Y-ZrO}_2$	547	736	1.32
$\text{Mn(III)}/\text{SiO}_2$	532	637	1.62

pared by a deposition-precipitation method. Therefore, supported manganese oxides catalysts prepared by a deposition-precipitation method show the presence of a large fraction of Mn_2O_3 and a small

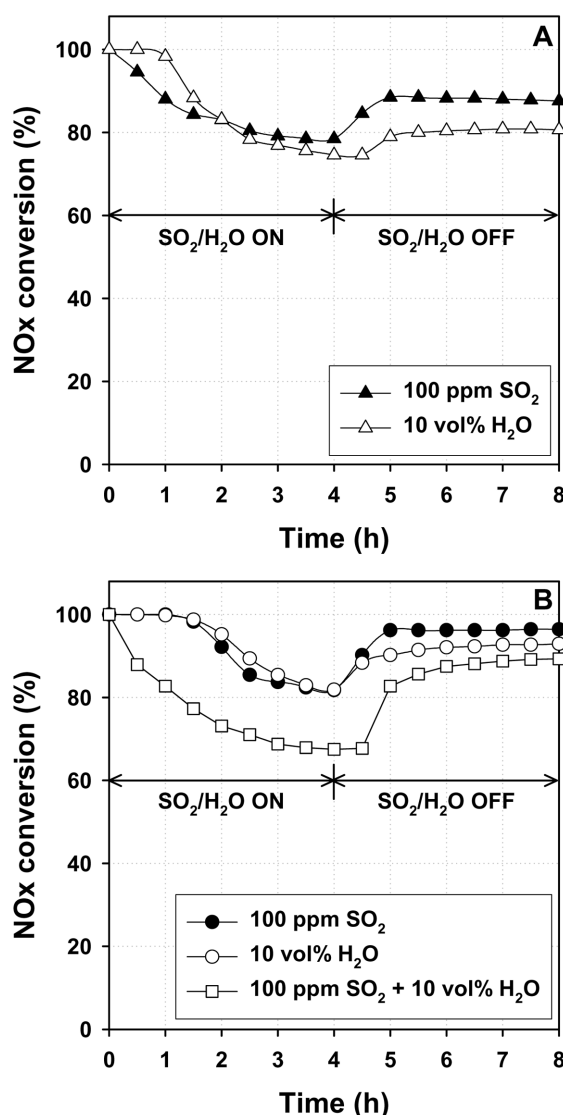


Fig. 4. Effects of H₂O and SO₂ on NO_x conversions over Mn(P)/ γ -Al₂O₃ and Mn(P)/TiO₂ catalysts at 423 K. Reactants: 500 ppm NO, 500 ppm NH₃, 5 vol% O₂ in N₂. The gas hourly space velocity (GHSV) was 40,000 h⁻¹.

fraction of Mn₃O₄ phase, which were not detected in XRD experiment.

Because a catalyst is usually deactivated mainly by water vapor and SO_x in the combustion gases, the resistance of de-NO_x catalysts to water vapor and SO_x is very important for industrial applications. Fig. 4 shows the effects of H₂O and/or SO₂ on the SCR activities over Mn(P)/ γ -Al₂O₃ and Mn(P)/TiO₂ catalysts at 423 K. Before the addition of H₂O and SO₂, the catalytic reaction was stabilized for 2 hrs at 423 K. As shown in Fig. 4A, the NO_x conversion over Mn(P)/ γ -Al₂O₃ catalyst decreased to be 75% in the presence of 100 ppm SO₂ and 78% in the presence of 10 vol% H₂O, respectively. Upon removal of H₂O or SO₂ supply, the NO_x conversion increased to be nearly 88% and 81%, respectively. For Mn(P)/TiO₂ catalyst, NO_x conversion decreased to be 82% in the presence of 100 ppm SO₂ and 82% in the presence of 10 vol% H₂O, respectively. Upon removal of H₂O or SO₂ supply, the NO_x con-

version increased to be nearly 96% and 93%, respectively. When SO₂ (100 ppm) and H₂O (10 vol%) were simultaneously added to the reactants, NO_x conversion decreased steadily and reached its steady-state value such as about 68%. Upon removal of SO₂ (100 ppm) and H₂O (10 vol%) supply, the NO_x conversion increased to be 90%. Fig. 5 shows that the deactivation rate of Mn(P)/ γ -Al₂O₃ catalyst by SO₂ was much higher than that of Mn(P)/TiO₂. This result indicates that TiO₂ further contributed to the resistance to SO₂. Therefore, we can conclude that the deactivation caused by H₂O and/or SO₂ is also significantly affected by a kind of support.

CONCLUSIONS

The NH₃-SCR activity of the supported manganese oxides catalysts prepared by a deposition-precipitation method is higher than that of impregnated catalysts. For supported manganese oxides catalysts prepared by a deposition-precipitation method, the activity decreased in the order: MnOx/TiO₂ ≈ MnOx/ γ -Al₂O₃ > MnOx/SiO₂ > MnOx/Y-ZrO₂. This high de-NO_x activity of supported manganese oxide catalyst prepared by a precipitation method is probably due to their amorphous manganese oxide phase. The addition of SO₂ with H₂O in the feeding gas slightly deactivates the SCR activity of MnOx/TiO₂ catalysts.

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