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Novel MnO_x catalysts for NO reduction at low temperature with ammonia

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Novel MnO_x catalysts for NO reduction at low temperature with NH_3 have been prepared by a simple precipitation method using sodium carbonate. The catalysts thus obtained have exhibited excellent catalytic activity in the temperature range of 348–473 K compared with other MnO_x-based catalysts, which is probably due to its high surface area as well as framework structure and composition. The high catalytic activity is maintained in the presence of 20 vol% water vapor in the feed.

KEY WORDS: NO reduction; MnO_x catalyst; low temperature; precipitation method; ammonia; H_2O; SO_2.

1. Introduction

The emission control of nitric oxides (NO, NO_2 and N_2O) from various combustion processes has been a major environmental concern related to the air quality. The selective catalytic reduction (SCR) is one of the most effective post-treatment for the abatement of NO_x emission to the atmosphere. Although a number of reducing agents can be utilized in SCR, ammonia has been adopted in general, which is called NH_3-SCR, for stationary sources such as power plants and nitric acid plants [1]. In this process, NO contained in flue gases is reduced by injected NH_3 to N_2 and H_2O:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \qquad (1)$$

Many catalysts have been reported to be active for the NH_3-SCR technology [2–4]. Commercially available catalysts are based on V_2O_5/TiO_2 [5]. 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 [6]. 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 the decrease of the exit gas temperature. Therefore, there is a great interest in the development of SCR catalysts active at low temperatures (<573 K).

A number of catalysts consisted of 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 such as MnO_x/Al_2O_3 [7], MnO_x/NaY [8], MnO_x/USY [9] and MnO_x/TiO_2 [10,11] have attracted much interest due to their high catalytic activities. These catalysts were prepared by the solution impregnation method on supports using manganese nitrate or acetate. Unsupported MnO_x catalysts suffer from very low surface areas. Recently, MnO_x–CeO_2 [12] with a high surface area was reported for the low temperature NO reduction with NH_3 using citric acid.

In this report, the novel MnO_x catalyst was prepared by a simple precipitation method using sodium carbonate and was compared with other MnO_x-based catalysts reported previously. The catalysts thus obtained have exhibited excellent catalytic activity in the temperature range of 373–473 K.

2. Experimental

2.1. Catalyst preparation

Two kinds of unsupported manganese oxides were prepared by a precipitation method with different precipitants, sodium carbonate (SC) and ammonium hydroxide (AH). Each catalyst is denoted as MnO_x–SC and MnO_x–AH, respectively. 0.5 M sodium carbonate (Na_2CO_3, SHINYO, 99.0%) aqueous solution or 0.5 M ammonium hydroxide (NH_4OH, DAEJUNG, 25.0–28.0%) solution was continuously added to 500 ml of

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0.5 M manganese nitrate ($Mn(NO_3)_2{\cdot}xH_2O$, Aldrich, 98.0 + %) aqueous solution until the pH of the solution reached 8. The resulting precipitate was aged at 298 K for 1 h, filtered, and washed several times with distilled water. The cake was dried in air at 393 K for 12 h and calcined at 623 K in static air. For comparison, MnO_x–CeO_2 was also prepared as reported previously by Qi and Yang [13].

15 wt% MnO_x/Al_2O_3 was prepared by an incipient wetness method.γ-Al_2O_3 (CONDEA, Sba-150) was used as a support and $Mn(NO_3)_2 \cdot xH_2O$ were used as the manganese precursor. The impregnated catalyst was dried in air at 393 K for 12 h and calcined at 623 K in static air.

2.2. *Catalyst characterization*

Bulk crystalline structures of catalysts were determined with an X-ray diffraction (XRD) technique. XRD patterns were obtained by using Cu Kα radiation using a Rigaku D/MAC-III instrument at room temperature. Surface areas were determined by N_2 adsorption using the BET method. The amount of adsorbed NH_3 was measured at 300 K by a pulse adsorption method using helium as a carrier gas.

2.3. *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). Overall flow rates were adjusted between 100 ml/min and 400 ml/min. Different gas hourly space velocities (GHSV) from 25,000 h^{-1} to 450,000 h^{-1} were achieved by changing the volume of catalyst bed and the overall flow rate.

The reactant gas typically consisted of 500 ppm NO, 500 ppm NH_3, 5 vol% O_2, and N_2. The effect of H_2O and SO_2 on NO_x conversions was examined in the presence of 11 vol% H_2O and 100 ppm SO_2 with the above reactant gas. The NO_x concentration in the inlet and outlet gas was analyzed by means of a NO/NO_2 combustion gas analyzer (Euroton).

3. Results and discussion

Catalytic activities for NO reduction with NH_3 with reaction temperatures over various MnO_x catalysts and a reference catalyst (MnO_x–CeO_2) are shown in figure 1. In case of 15wt% MnO_x/Al_2O_3 catalyst, the much lower space velocity (4000 h^{-1}) is used than those of other unsupported catalysts (25,000 h^{-1}), in order to compare NO_x conversions based on the same amount of manganese oxides. Figure 1 indicates that the activity order of the catalysts at 373 K is: MnO_x–SC > $MnO_x/Al_2O_3 \approx$ MnO_x–CeO_2 > MnO_x–AH. Although the MnO_x–SC and MnO_x–AH catalysts are prepared by a similar precipitation method, two catalysts show very different de-NO_x activities. The MnO_x–SC shows the highest activity in the whole temperature range (348–473 K) whereas the MnO_x–AH gives the least activity below 423 K. This result indicates that the nature of precipitants, sodium carbonate and ammonium hydroxide, influence on the properties of final precipitated products. Table 1 shows the BET surface areas of the catalysts used in the present work. The MnO_x–SC catalyst was found to have the higher surface area than other MnO_x-based catalysts, which may be a possible explanation for the highest activity of the MnO_x–SC catalyst.

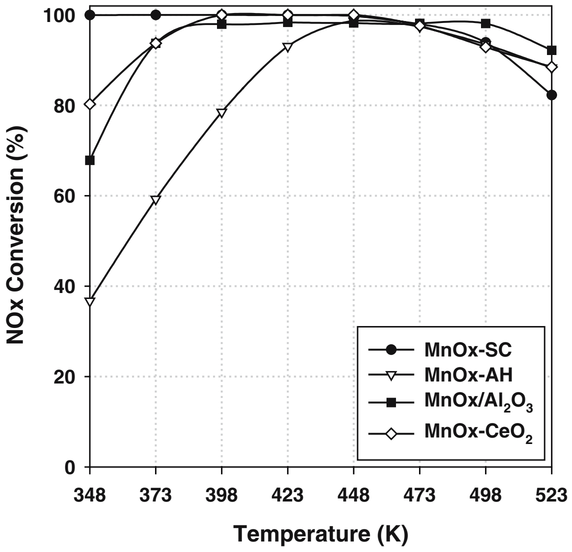

Figure 1. NO_x conversions over various MnO_x catalysts prepared by different methods at different reaction temperatures. Reactants; 500 ppm NO, 500 ppm NH_3 and 5 vol% O_2 in N_2. The gas hourly space velocity (GHSV) was 25,000 h^{-1} for all catalysts except of 15wt% MnO_x/Al_2O_3 (GHSV = 4,000 h^{-1}).

Figure 2 shows the XRD patterns of the MnO_x–SC, MnO_x–AH catalysts and various commercial Mn-based samples. As shown in figure 2a, there are several XRD peaks from the MnO_x–AH catalyst, which seems to be a mixture of Mn_2O_3 and Mn_3O_4 phases. An as-prepared MnO_x–AH sample gives sharp XRD peaks (not shown) corresponding to the Mn_3O_4 phase before the calcination at 623 K, and the phase is transformed to the mixture of Mn_2O_3 and Mn_3O_4 phases. In case of the MnO_x–SC catalyst, $MnCO_3$ phase is initially precipitated by addition of sodium carbonate as the precipitant. When the as-prepared MnO_x–SC sample is

Table 1
BET surface areas of the Mn-based catalysts

Catalysts	S_{BET} (m^2/g)	Preparation methods
MnO_x–SC	173.3	Precipitated with Na_2CO_3
MnO_x–AH	18.7	Precipitated with NH_4OH
MnO_x/Al_2O_3	124.0	Impregnated on Al_2O_3
MnO_x–CeO_2	58.7	Citric acid

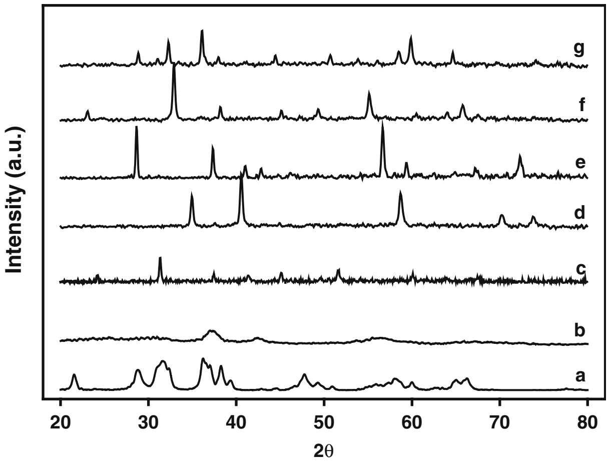

Figure 2. XRD patterns of MnO_x catalysts and different manganese oxides as references. (a) MnO_x–AH, (b) MnO_x–SC (c) $MnCO_3$, (d) MnO, (e) MnO_2, (f) Mn_2O_3, and (g) Mn_3O_4.

heated to 623 K, the XRD peaks become very broad (figure 2b) and it is not easy to identify the phase from the XRD pattern. This is probably due to the partial decomposition of as-prepared $MnCO_3$ phase and turn to an amorphous phase at this calcination temperature. This partially decomposed and amorphous structure of the MnO_x–SC catalyst may also be a reason for the excellent catalytic activity at low temperatures, in addition to the effect of high surface area. A similar result has been reported for MnO_x–CeO_2 [11], where the MnO_x–CeO_2 catalysts with different crystallinities and surface areas are prepared by changing calcination temperatures. The catalyst with the highest surface area and the lowest crystallinity showed the best SCR activity with NH_3 at low temperatures. Thermogravimetric analysis shows the weight loss (~30 wt%) of the MnO_x–SC catalyst between 500–800 K, which indicate that lots of carbon oxide species (CO_x) are remained in the catalyst even after the calcination at 623 K. There is no significant weigh loss in the MnO_x–AH catalyst. It is reasonable that the presence of CO_x species in the MnO_x–SC catalyst also affect on the de-NO_x activity at low temperature because the residual CO_x species may act as acidic sites on the catalyst surface. These acidic sites can help the basic reductant, NH_3, adsorb on the surface at low temperature, and therefore the reductant may be enriched compared with the surface of MnO_x–AH catalyst. This was also supported by the fact that 0.207 mmol $NH_3/g_{cat.}$ and 0.011 mmol $NH_3/g_{cat.}$ could be adsorbed on MnO_x–SC and MnO_x–AH, respectively.

Figure 3 shows NO_x conversion with reaction temperatures in a wide range of space velocities from 50,000 to 400,000 h^{-1} over MnO_x–SC catalyst. It is reasonable that the NO_x conversions decrease as a space velocity increases because the contact time of reactants on the catalyst surface decreases. However, it should be noted that the NO_x conversions are still quite high (about 90% conversion at 373 K) even at a very high space velocity (400,000 h^{-1}), which is very important for the practical application of the catalyst.

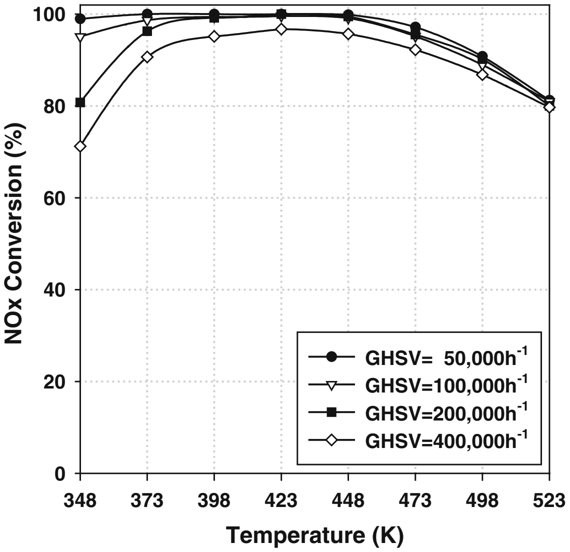

Figure 3. NO_x conversions over MnO_x–SC catalyst at different space velocities and reaction temperatures. Reactants; 500 ppm NO, 500 ppm NH_3 and 5 vol% O_2 in N_2.

Because the 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. Figure 4 shows the effects of H_2O and SO_2 on the SCR activities of the present MnO_x–SC catalyst at 398 K. Before the addition of H_2O and SO_2, the catalytic reaction has been stabilized for 2 h at 393 K. When only the water vapor is introduced to the reaction system, there is no detectable decrease in NO_x conversion for 40 h even though the amount of water vapor is reached up to 20 vol% of

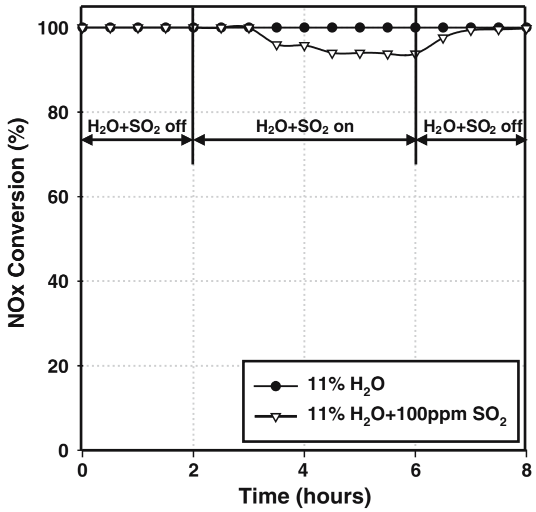

Figure 4. Effects of H_2O and SO_2 on NO_x conversions over MnO_x–SC catalyst at 398 K. Reactants; 500 ppm NO, 500 ppm NH_3, 5 vol% O_2 in N_2. The gas hourly space velocity (GHSV) was 50,000 h^{-1}.

the reaction gas. In case of feeding both SO_2 (100 ppm) and H_2O (11 vol%) to the reaction system with space velocity of 50,000 h^{-1}, the NO_x conversion over MnO_x–SC catalyst is decreased from 100% to 94%, which is still very high de-NO_x activity at 398 K. However, the activity was recovered after the supply of SO_2 was discontinued. Moreover, the activity is rapidly recovered to 100% upon removal of SO_2 and H_2O supply.

4. Conclusions

In the present work, the MnO_x catalyst, prepared by a precipitation technique using sodium carbonate as the precipitant, exhibits excellent activity for the selective catalytic reduction of NO_x with NH_3 at low temperatures even in the presence of excess oxygen and water. This high de-NO_x activity at low temperature is probably due to its high surface area, amorphous framework structure and the existence of residual carbon oxide species. The MnO_x–SC catalyst also shows the high resistance to the addition of SO_2 and H_2O in the feeding gas, and the activity is recovered to 100% after the deactivation gases are stopped.

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