

Low-Temperature Selective Catalytic Reduction of NO with NH₃ over Manganese Oxides Supported on Fly Ash-Palygorskite

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Abstract

A catalyst of manganese oxides (MnO_x) supported on fly ash-palygorskite (MnO_x/FA-PG) was prepared for low-temperature selective catalytic reduction (SCR) of nitric oxides (NO_x) by ammonia (NH₃). The influences of the preparation method, active species precursors, calcination temperature, calcination time and particle size on the SCR performance of the MnO_x/FA-PG catalyst were studied. Catalysts were characterized by Brunauer-Emmett-Teller (BET) analysis, scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray fluorescent spectrometry (XRF), and NH₃ adsorption and temperature programmed desorption (TPD) to illustrate the physico-chemical properties of catalysts. Results showed that a negligible difference in SCR activity is observed on the MnO_x/FA-PG catalyst prepared by heterogeneous deposition and wetness impregnation. Activity of the MnO_x/FA-PG catalyst prepared by wetness impregnation with Mn(NO₃)₂ as precursor was significantly superior to that of prepared with Mn(CH₃COO)₂ as precursor. Moreover, calcination temperature significantly influenced catalytic activity. Over 70% NO conversion could be achieved at 100°C for Mn₈/FA-PG catalysts calcined at 400°C for 3 h. The active component of the catalysts mainly existed in Mn⁴⁺. According to the results of NH₃ adsorption and temperature programmed desorption (TPD), adsorption capacity of NH₃ was not the decisive factor of catalytic activity and the key was the activation of adsorbed NH₃.

Keywords: Fly ash-palygorskite; Manganese oxides; Low-temperature SCR

Introduction

Over the past decades, nitrogen oxides from power plants and motor vehicles have been remained as major air pollutants. They can result in acid rain, photochemical smog, and ozone depletion [1,2]. Selective catalytic reduction (SCR) of NO_x with NH₃ in the presence of oxygen is a proven technique for the removal of NO_x from flue gases [3]. A large number of SCR catalysts have been explored, including noble metals [4,5], transition metal oxides [6,7] and zeolites [8,9]. Especially, V₂O₅-WO₃/TiO₂ based catalysts have been extensively used in the industry [10,11]. However, the operating temperature for these catalysts is usually above 300°C, and the exhaust gases usually contain a large number of fly ash and SO₂, which can easily deactivate the catalysts. Thus, the development of active SCR catalysts that can be operated at relatively low temperatures is needed.

At present, many transition metal oxides are extensively studied and proved to be highly active for low temperature SCR of NO with NH₃, among which MnO_x-supported catalysts attract the most concern [10,12-14]. Zhao et al. found that Mn_{0.06}/Al₂O₃ yields the highest NO conversion and 80% of NO conversion is obtained at 250°C and 15,000 h⁻¹ [15]. Zhang et al. reported that Mn/TiO₂ catalysts exhibit a high NO conversion of 90% at 100°C [16]. The high SCR activity for MnO_x-supported catalysts implies that there may be an intimate connection between manganese oxides and carrier. Smirniotis et al. compared TiO₂-, Al₂O₃- and SiO₂-supported MnO_x catalysts and found that the SCR performance of the supported Mn catalysts decreased in the following order: TiO₂ (anatase, high surface area), TiO₂ (rutile), TiO₂ (anatase, rutile), γ-Al₂O₃, SiO₂, TiO₂ (anatase, low surface area) [17]. The material of carrier is directly related to the SCR activity for manganese-based catalysts.

In this paper, a solid waste material, fly ash (FA), was used as support, which can cause many problems and has become an important environmental issue [18]. Due to its moderate pore volume and pore structure, as well as its high silica and alumina contents, FA is used to prepare zeolite materials. Besides, a clay mineral, palygorskite (PG)

[19,20], was added as a binder to FA. The materials were mixed well after machine extrusion to provide an inexpensive catalyst support [21]. Manganese oxide (MnO_x) was loaded as the active ingredient to produce a MnO_x-supported catalyst (MnO_x/FA-PG). This catalyst was then characterized through experiments in a fixed bed reactor to investigate the feasibility of using FA-PG as a catalyst support. Specific surface area [Brunauer-Emmett-Teller (BET)] analysis, scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray fluorescent spectrometry (XRF) were used to characterise the surface properties and crystalline structures of the catalyst. NH₃ adsorption and temperature programmed desorption (TPD) were performed to evaluate the effect of manganese species on the surface acidity of the catalyst.

Experimental

Catalyst preparation

FA was obtained from the Anqing Power Plant in Anhui Province, and natural PG was acquired from Jiashan County. Main chemical composition of the molded fly ash and palygorskite are listed in Table 1. Four particle size ranges, i.e., 5-8 mm, 2-5 mm, 0.38-0.83 mm and 0.25-0.38 mm, were chosen as the experimental samples. FA-PG was pretreated at 300°C for 3 h to remove surface water. The Mn_x/FA-PG catalysts were prepared firstly by heterogeneous precipitation and wetness impregnation of heat-pretreated FA-PG with Mn nitrate aqueous solution. The concentration of the solution was varied to yield

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| Sample | SiO ₂ | AlO ₃ | Fe ₂ O ₃ | CaO | MgO | TiO ₂ | K ₂ O | MnO | P ₂ O ₅ | SO ₃ | FeO |
|--------|------------------|------------------|--------------------------------|-------|-------|------------------|------------------|-------|-------------------------------|-----------------|------|
| FA | 48.29 | 21.64 | 3.05 | 20.33 | 1.74 | 0.98 | 1.66 | 0.04 | 0.26 | 1.87 | / |
| PG | 69.44 | 11.84 | 5.139 | 0.211 | 12.16 | 0.43 | 0.5 | 0.046 | 0.03 | / | 0.08 |

Table 1: Main chemical composition of FA and PG (%).

different Mn loading contents. The samples were dried overnight at 110°C. Then, the specific particle sizes of catalysts were calcined in O₂ stream at different temperatures and times. The catalyst samples were labeled Mn_x/FA-PG, MA-Mnx/FA-PG and Mn_x(P)/FA-PG based on loading of the active component with different precursors and preparation methods (“x”, “MA” and “P” refer to the weight percentage of Mn loading, the Mn(CH₃COO)₂ solution and the heterogeneous precipitation method, respectively).

Catalyst characterization

X-ray fluorescent spectrometry (XRF) was performed on a XRF-1800 analyses (Shimadzu, Japan) to measure the chemical composition of the catalyst. X-ray Diffraction (XRD) was performed on a D/Max2500V diffractometer (Rigaku, Japan) equipped with a monochromated Cu K α radiation source. The catalysts were scanned at 2 θ ranging from 10°-70°. Scanning electron microscopy (SEM) images of the samples were obtained by a JSM-6490LV (Hitachi, Japan) analyser.

Brunauer-Emmett-Teller (BET) surface area was measured from the N₂ adsorption and desorption isotherms at -196°C using the NOVA 2200e (Quantachrome, American) adsorption analyser. Prior to analysis, 0.08-0.1 g of catalyst was preheated at 100°C for 2 h under a N₂ atmosphere. NH₃ adsorption and temperature programmed desorption (TPD) were conducted in a quartz microreactor. Then, 100 mg of the sample was preheated in Ar at 473 K for 1 h to remove any adsorbed species. Afterward, the sample was cooled to 323 K in Ar (100 mL·min⁻¹) and 1500 ppm NH₃ balanced by Ar was adsorbed at this temperature with a total flow rate of 100 mL·min⁻¹ until no signal variation of NH₃ was detected. Subsequently, the sample was purged with 100 mL·min⁻¹ Ar until no NH₃ was detected in the outlet, and then ramped to 1073 K at a linear heating rate of 10 K·min⁻¹ in Ar (100 mL·min⁻¹). The analysis of gases was performed using an online mass spectrometer QIC2000 (Hidden, Germany).

Activity measurement

Catalyst activity was evaluated in a quartz fixed bed continuous flow reactor that operated at a pressure of 0.1 MP, and 3 g of sample was used in each test. Gas composition was 600 ppm NO, 600 ppm NH₃ and 3 vol% O₂ balanced by Ar. Total flow rate was 350 mL·min⁻¹, which corresponds to a gas hour space velocity of 4000 h⁻¹. NO concentrations in the inlet and outlet gases were measured online with a flue gas analyser (testo350-XL). Catalyst performance was estimated through NO conversion, which was calculated by the following equation:

$$X_{NO} = \frac{[NO]_{in} - [NO]_{out}}{[NO]_{in}} \times 100\% \quad (1)$$

Where $[NO]_{in}$ and $[NO]_{out}$ denote the inlet and outlet concentrations of NO, respectively.

Results and Discussion

Effect of different precursors and loadings on SCR activity

over catalysts

NO conversion of Mn_x/FA-PG catalyst prepared using Mn(NO₃)₂ as a precursor is shown in Figure 1. NO conversion increased with temperature increasing at the temperature range of 100-250°C with Mn-loading. Then, it started to decrease at temperature higher than 250°C. Besides, at the same temperature, NO removal efficiency increased with increasing Mn-loading. NO conversion for Mn₂₄/FA-PG catalyst could reach to 100% at 100°C. For FA-PG, the NO conversion was much lower in a temperature range of 100-200°C, indicating that the low temperature SCR performance of Mn-loaded catalyst was not contributed by the carrier but the MnOx itself. As shown in Figure 2, NO conversion for the MA-Mnx/FA-PG catalyst prepared using Mn(CH₃COO)₂ as precursor was higher than that of FA-PG over the entire reaction temperature, but significantly lower than that of the Mn_x/FA-PG catalyst under the same Mn-loading. It is reasonable deduced that the difference of the precursors may form different active species after calcination. Researchers also investigated the characteristics of the catalysts prepared by different precursors. However, no consensus was reached. Li et al. [22] reported that the catalyst prepared using Mn(NO₃)₂ as precursor after calcination at 400°C mainly formed MnO₂ species. Meanwhile, Mn₂O₃ species was formed when Mn(CH₃COO)₂ was used as precursor. In addition, the catalytic activity of Mn₂O₃ was higher than that of MnO₂ in the unit area. However, Wu et al. [23] considered that the catalytic activity of MnOx could be sequenced as follows: MnO₂>Mn₃O₈>Mn₂O₃>Mn₃O₄>MnO. Further explanations about the characteristics of the catalysts prepared by different precursors will illustrate in the following.

Effect of preparation method on SCR activity

From above results, catalysts prepared by Mn(NO₃)₂ as precursor had high SCR activity. Thus, the NO conversion of the Mn₈/FA-PG/300°C and Mn₈(P)/FA-PG/300°C catalysts prepared by Mn(NO₃)₂ as precursor at the entire reaction temperature range is shown in Figure 3. As shown in Figure 3, Mn₈(P)/FA-PG catalyst had higher NO conversion than Mn₈/FA-PG catalyst in the temperature range of 100-150°C. However, at the temperature higher than 200°C, NO conversion of Mn₈(P)/FA-PG was lower than that of the Mn₈/FA-PG catalyst. Besides, the preparation process for impregnation method was complex and led to the loss of raw materials during catalyst preparation. Based on the aforementioned results, the impregnation method is optimal and relatively economic.

Effect of calcination temperature and calcination time on SCR activity

Based on the preceding catalyst characterization, calcination temperature and calcination time have a significant effect on the characteristics of the catalysts. In this work, we also study the effect of calcination temperature and calcination time on SCR activity. As shown in Figure 4a, the NO conversion of the Mn_x/FA-PG catalyst first gradually increased, and then decreased slightly with increasing calcination temperature. When calcination temperature was 400°C, the highest SCR activity was obtained at a low temperature. In particular, over 70% NO conversion was got at 100°C and approximately 100% at 150°C. Hence, the Mn_x/FA-PG catalyst that calcined at 400°C had higher SCR activity. A low calcination temperature may lead to the incomplete decomposition of Mn(NO₃)₂ which is accompanied with NOx production during the reaction process. However, at a high calcination temperature, the structure of gesso-water and structure-water in PG might fold, which can lead to the collapse of passageways in FA-PG carriers; this condition is disadvantageous for

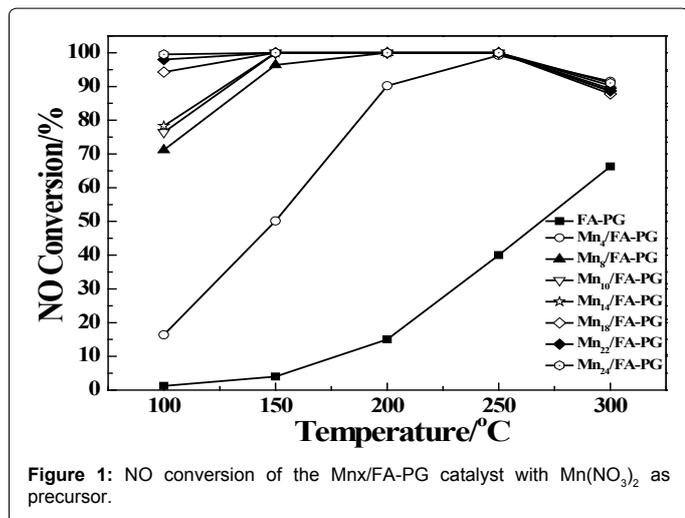


Figure 1: NO conversion of the Mn_x/FA-PG catalyst with Mn(NO₃)₂ as precursor.

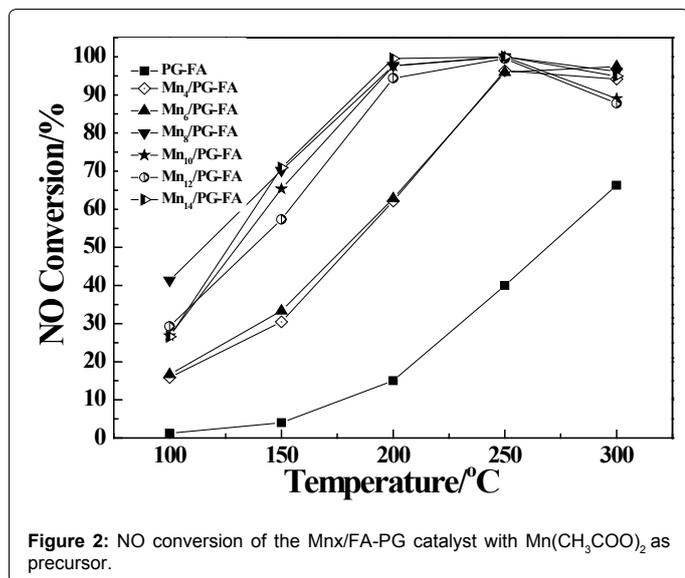


Figure 2: NO conversion of the Mn_x/FA-PG catalyst with Mn(CH₃COO)₂ as precursor.

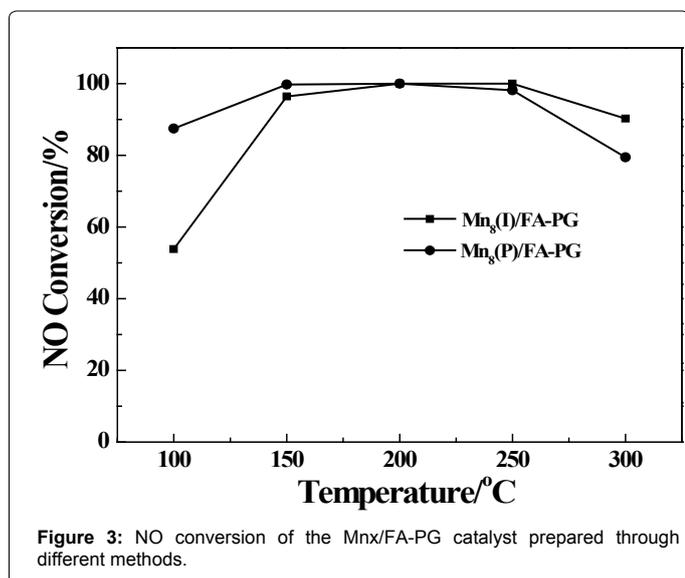


Figure 3: NO conversion of the Mn_x/FA-PG catalyst prepared through different methods.

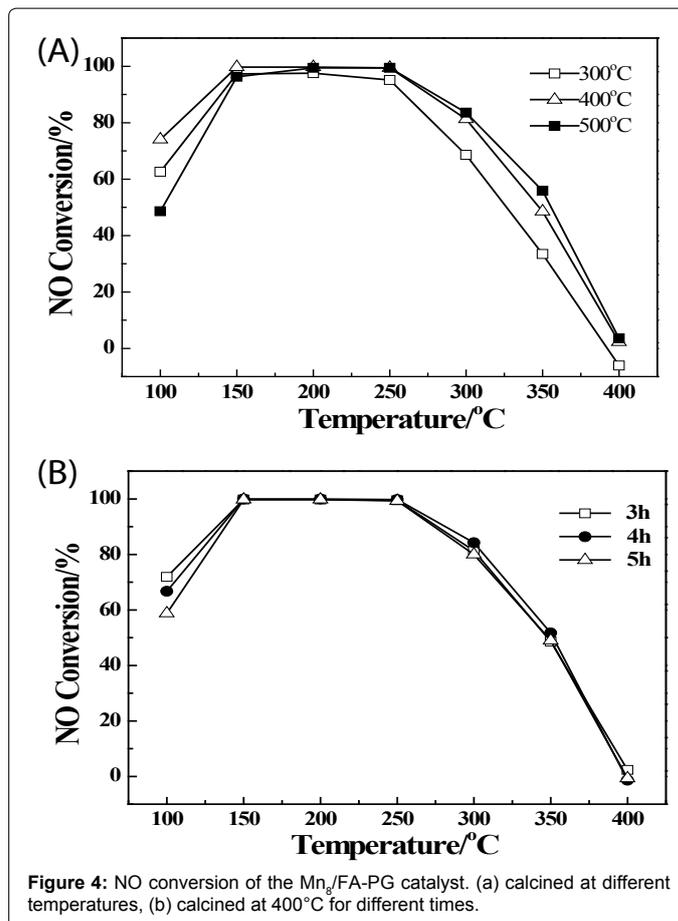


Figure 4: NO conversion of the Mn₈/FA-PG catalyst. (a) calcined at different temperatures, (b) calcined at 400°C for different times.

| Sample | Parameter | S _{BET} [m ² /g] |
|---|--------------------------------------|--------------------------------------|
| FA-PG | 0.38-0.83mm | 37.20 |
| Mn ₈ /FA-PG ^a | Impregnation | 68.70 |
| Mn ₈ (P)/FA-PG ^b | Precipitation | 72.10 |
| Mn ₈ /FA-PG | Mn(NO ₃) ₂ | 68.70 |
| MA-Mn ₈ /FA-PG ^c | Mn(CH ₃ COO) ₂ | 44.04 |
| Mn ₈ /FA-PG/300°C ^d | 300°C | 56.28 |
| Mn ₈ /FA-PG/400°C ^e | 400°C | 49.05 |
| Mn ₈ /FA-PG/500°C ^f | 500°C | 29.22 |
| Mn ₈ /FA-PG | 4.00-8.00 mm | 63.32 |
| Mn ₈ /FA-PG | 2.00-4.00 mm | 65.66 |
| Mn ₈ /FA-PG | 0.38-0.83 mm | 68.70 |
| Mn ₈ /FA-PG | 0.25-0.38 mm | 64.53 |

S_{BET}: Specific surface area

Table 2: BET surface area of catalysts. (a) Mn₈/FA-PG was prepared by impregnation method with Mn(NO₃)₂ as precursor. (b) Mn₈(P)/FA-PG was prepared via the heterogeneous precipitation method with Mn(NO₃)₂ as precursor. (c) MA-Mn₈/FA-PG prepared using Mn(CH₃COO)₂ as precursor. (d) Mn₈/FA-PG/300°C calcined at 300°C. (e) Mn₈/FA-PG/400°C calcined at 400°C. (f) Mn₈/FA-PG/500°C calcined at 500°C.

NH₃ adsorption [24]. The surface areas of Mn_x/FA-PG catalysts under different calcination temperatures are listed in Table 2. Compared with the carrier of FA-PG, the catalysts calcined at 300°C and 400°C had large BET surface areas, but the difference between them was minimal. Meanwhile, for the catalyst calcined at 500°C, the BET surface area decreased to a certain extent. A conclusion could be drawn that an extremely high calcination temperature leads to the destruction of the support structural. Besides, the NO conversion of the Mn₈/FA-PG catalyst calcined at 400°C for different times is shown in Figure 4b. As shown in Figure 4b, the NO conversion of the Mn_x/FA-PG catalyst gradually decreased with increasing calcination times. Highest SCR activity was obtained when calcined at 400°C for 3 h. Thus, catalyst of Mn₈/FA-PG mentioned below was all calcined at 400°C for 3 h.

Effect of particle size on SCR activity over catalysts

Catalyst particle size has a significant effect on SCR activity. In the preparation method described above, the Mn₈/FA-PG (4.00-8.00 mm), Mn₈/FA-PG (2.00-4.00 mm), Mn₈/FA-PG (0.38-0.83 mm) and Mn₈/FA-PG (0.25-0.38 mm) catalysts were prepared to evaluate the influence of particle size on SCR activity for Mn-based catalysts. As illustrated in Figure 5, the NO conversion of the Mn₈/FA-PG catalyst first gradually increased, and then decreased slightly with decreasing particle size. The Mn₈/FA-PG catalyst with a particle size of 0.38-0.83 mm had a highest SCR activity, which is different from the results of Xuan [25,26]. The difference can be attributed to the material of the carrier and the preparation methods. The specific surface areas of Mn₈/FA-PG catalysts under different situations are listed in Table 2. Mn₈/FA-PG catalyst with a particle size of 0.38-0.83 mm had largest surface area. According to Eley-Ridal mechanism [27], the catalyst with large surface area is more conducive to the reaction gases (NH₃ and NO_x) adsorbed on the carrier leading to the enhancement of SCR activity.

XRD analyses

The XRD patterns of the Mn_x/FA-PG catalyst prepared by wetness impregnation with Mn(NO₃)₂ and Mn(CH₃COO)₂ as precursors are shown in Figure 6. As shown in Figure 6a, all these patterns presented intense peaks of PG, kaolinite and dolomite due to the complex composition of FA-PG. However, there were no diffraction peaks of manganese oxides for Mn₈/FA-PG and MA-Mn₈/FA-PG catalysts calcined at 400°C indicating that the complex composition of FA-PG may influence the diffraction of MnOx or MnOx is uniformly dispersed on the surface of the carrier with a low percentage of active components. Thus, in this study, we particularly selected the Mn₁₂/FA-PG and MA-Mn₁₂/FA-PG catalysts for XRD analyses to illustrate the presence of manganese oxides. As shown in Figures 6d and 6e, the diffraction peaks of crystalline MnO₂ and Mn₂O₃ phases were observed in the Mn₁₂/FA-PG and MA-Mn₁₂/FA-PG catalysts respectively, suggesting that MnOx in the amorphous phase is uniformly dispersed on the surface of the carrier, which is consistent with the founding by Li [22]. This finding indicated that MnOx was mainly in the form of MnO₂ when the Mn_x/FA-PG catalyst was calcined at 400°C with Mn(NO₃)₂ as precursor. Meanwhile, the Mn(CH₃COO)₂ precursor mainly formed Mn₂O₃ species. Based on the above results in Figures 1 and 2, it is reasonable deduced that catalytic activity of MnO₂>Mn₂O₃ in the unit area. The XRD patterns of the Mn₁₂/FA-PG catalyst calcined at different temperatures are shown in Figure 7. The intensity of the diffraction peak of PG, kaolinite and dolomite for Mn-based catalyst decreased with increasing calcination temperature indicating that a high calcination temperature may destroy the primary structure of the carrier. Besides, the peaks corresponding to crystalline MnO₂ phase

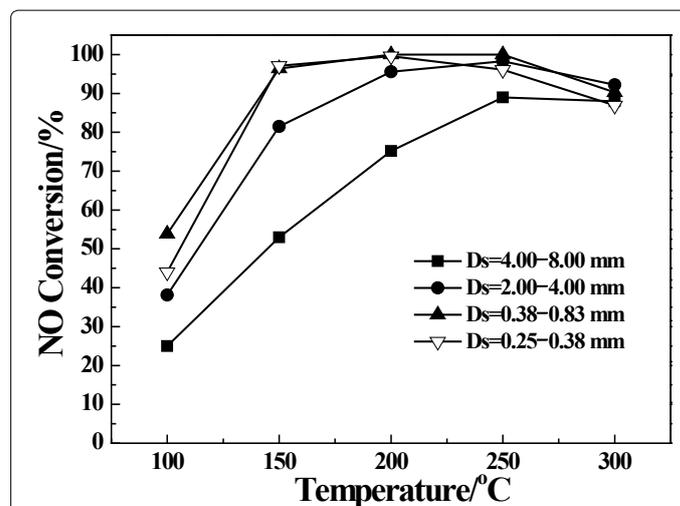


Figure 5: SCR activity of the Mn₈/FA-PG catalyst with different size of particle.

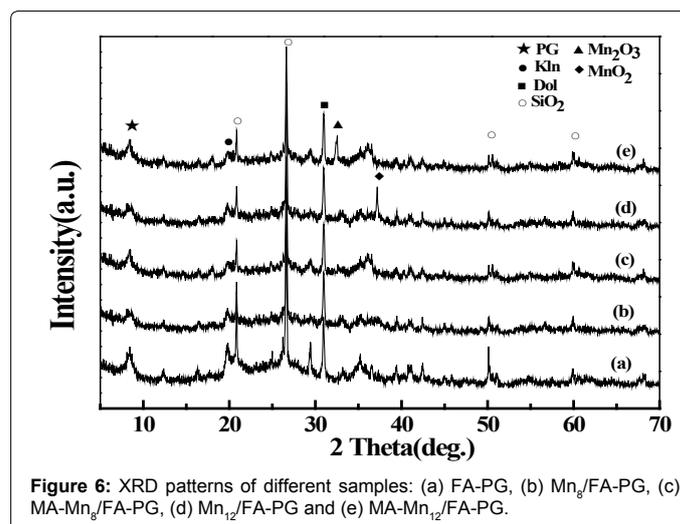


Figure 6: XRD patterns of different samples: (a) FA-PG, (b) Mn₈/FA-PG, (c) MA-Mn₈/FA-PG, (d) Mn₁₂/FA-PG and (e) MA-Mn₁₂/FA-PG.

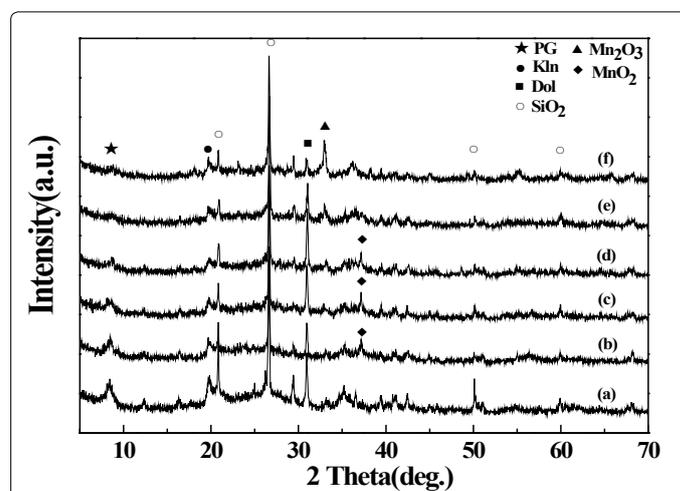


Figure 7: XRD patterns of the catalysts calcined at different temperatures: (a) Mn₁₂/FA-PG, (b) Mn₁₂/FA-PG/200°C, (c) Mn₁₂/FA-PG/300°C, (d) Mn₁₂/FA-PG/400°C, (e) Mn₁₂/FA-PG/500°C and (f) Mn₁₂/FA-PG/600°C.

diminished remarkably along with increasing calcination temperature and disappeared completely when calcination temperature reached over 400°C. When calcination temperature was 500°C, the diffraction peaks of Mn₂O₃ appeared. Moreover, the diffraction peaks of Mn₂O₃ were most prominent when calcination temperature reached to 600°C. This phenomenon is accordance with the founding by Kapteijn [28] that different calcination temperatures result in various oxidation states of manganese oxides and a high calcination temperature leads to a low valence of Mn.

SEM of the catalysts

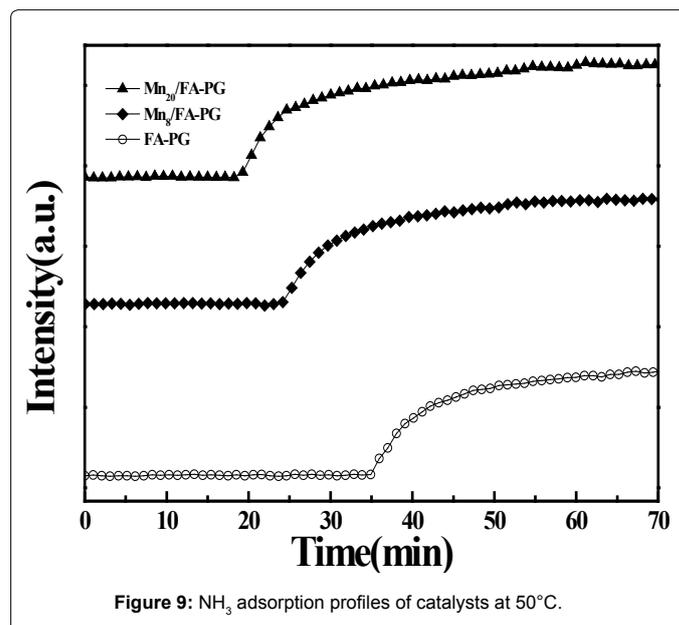
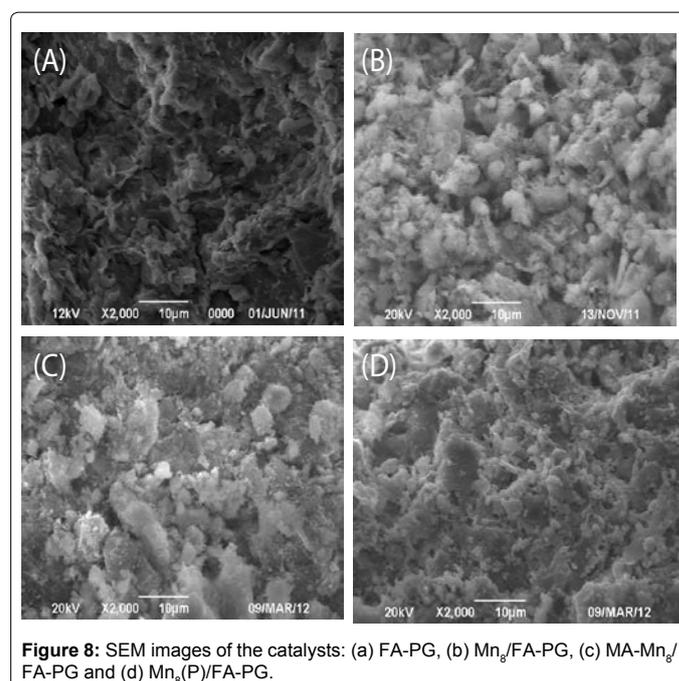
The electron microscopy images of the Mn_x/FA-PG catalyst prepared via different methods are shown in Figure 8. These images (b-d) pertaining to the Mn₈/FA-PG catalyst prepared by wetness impregnation with Mn(NO₃)₂, Mn(CH₃COO)₂ as precursors and heterogeneous precipitation method, respectively. Compared to the carrier of FA-PG, there was a certain amount of white particles existed for all of the Mn-loaded catalysts, revealing that MnO_x has dispersed on the surface of the catalyst after calcination. However, for Mn₈/FA-PG catalyst prepared with Mn(NO₃)₂ as precursor, the particles on the surface of the catalyst were obviously more and higher uniformly dispersed than that of MA-Mn₈/FA-PG catalyst prepared with Mn(CH₃COO)₂, indicating that the precursor remarkably influences the morphologies of catalysts. Moreover, for MA-Mn₈/FA-PG catalyst, there was a slight sintering phenomenon after being calcined, which is not conducive to improving catalyst activity. The SEM images of Mn₈/FA-PG and MA-Mn₈/FA-PG were agreed with the activity test in Figures 1 and 2. Besides, as shown in Figure 8d, most white globular substances (MnO_x) appeared on the surface of Mn₈/FA-PG catalyst prepared by heterogeneous deposition method illustrated that the catalyst exhibited the best SCR activity compared to the others [29].

BET analyses

The physical properties of catalysts are important in determining the adsorption-desorption phenomena of gases onto its surface and influencing the activity of catalysts. Catalyst with large surface area is more conducive to the reaction gases (NH₃ and NO_x) adsorbed on the carrier leading to the enhancement of SCR activity. Thus, the BET analyses are given and the textural properties are summarized in Table 2. Compared to the carrier of FA-PG, the surface area of catalysts increased after Mn-loaded. Mn₈(P)/FA-PG prepared by heterogeneous precipitation had larger surface area than Mn₈/FA-PG with impregnation. Combined with activity tests in Figure 3, it can be concluded that the larger surface area accounts for the improvement of SCR activity for Mn₈(P)/FA-PG. Besides, for Mn₈/FA-PG prepared with Mn(NO₃)₂ as precursor, the BET surface area was higher than that of MA-Mn₈/FA-PG prepared with Mn(CH₃COO)₂ as precursor. Similar result was obtained for Mn₈/FA-PG prepared with Mn(NO₃)₂ as precursor. For Mn_x/FA-PG catalyst with different size of particles, the catalyst with a particle size of 0.38 mm to 0.83 mm has largest surface area corresponding to the SCR activity tests in Figure 5. The specific surface areas of the Mn_x/FA-PG catalyst calcined at 300°C and 400°C both exhibited a significant increase compare to the FA-PG carrier. However, the NO conversion of the Mn_x/FA-PG decreased when calcined at 500°C because the carrier structure was destroyed when calcination temperature was too high.

NH₃ adsorption analyses

A comparative study of NH₃ adsorption for the Mn(x)/FA-PG



catalyst with different Mn loadings is presented in Figure 9. The penetration time of NH₃ was observed to decrease as Mn loading increased. This finding showed that the FA-PG carrier has a higher adsorption capacity than others. However, according to the results of BET analyses and activity test in Figure 1, the surface area of catalysts increased and the activity was improved after Mn-loaded. Thus, it can be deduced that the surface area of catalysts is not the decisive factor for NH₃ adsorption and the adsorption capacity of NH₃ not directly influence the SCR activity. Busca et al. [11] determined that the adsorption capacity of NH₃ influences catalytic activity. However, it was not the decisive factor and the key was the activation of adsorbed NH₃.

NH₃-TPD analyses of catalysts

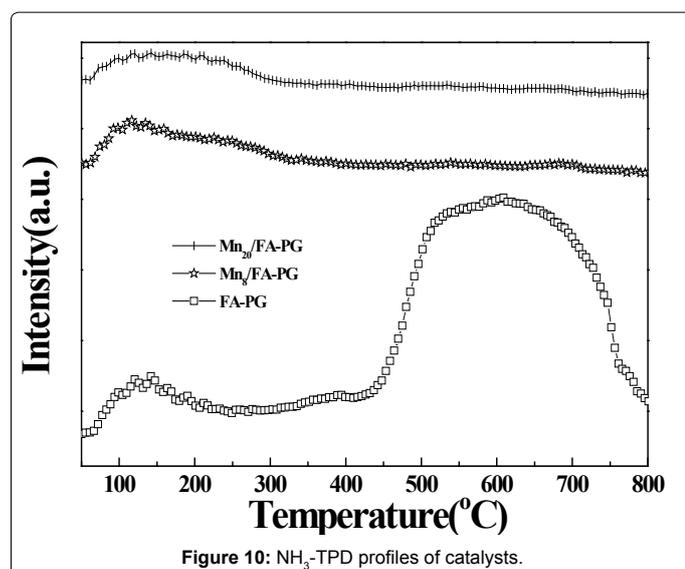


Figure 10: NH₃-TPD profiles of catalysts.

NH₃-TPD profiles of different Mn_x/FA-PG catalysts are shown in Figure 10. Three main desorption peaks with different strength were observed at 132°C, 390°C and 603°C for FA-PG in the entire temperature range indicating that the carrier of FA-PG has three obvious acid sites. However, after manganese oxides loaded on the FA-PG, only one desorption peak at 132°C was found, and the desorption peak at 390°C and 603°C were disappeared. The peak at 132°C for Mn_x/FA-PG could be assigned to the physically adsorbed of NH₃. According to the founding by Greenhalgh [30], the strength of B-acid site gradually decreased with the exchange of metal ion due to the reaction between metal ions of the precursors and OH on the support surface. Therefore, the peak at 390°C and 603°C may be caused by desorption of NH₃ that was adsorbed on the B-acid site of the carrier itself. Besides, Busca et al. [11] indicated that, the SCR performance of Mn-based catalyst is not related to the adsorption and activation of the B-acid site, but the L-acid site.

Conclusion

Mn_x/FA-PG catalyst was highly active for SCR of NO with NH₃ at a temperature range of 150-300°C. Catalysts prepared by impregnation with Mn(NO₃)₂ as precursor not only efficient but also relatively economic owing to the uniformly dispersed and high catalytic activity of MnO_x on the surface of the catalyst. NO conversion closed to 100% at 100°C under Mn-loading of 24% with particle size of 0.38 μm to 0.83 μm. Moreover, catalysts calcined at 400°C for 3 h exhibited the highest activity. Most important, the SCR performance of Mn-based catalyst was not related to the adsorption and activation of the B-acid site, but the L-acid site.

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