Preparation of Mn-Ce/TiO₂ Catalysts and its Selective Catalytic Reduction of NO at Low-temperature

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Abstract. The catalytic performance of NO removal was studied over Mn-Ce/TiO₂ catalysts prepared by rheological phase method under different preparation parameters, such as preparation method, manganese precursor, Mn/(Mn+Ce) molar ratio and calcination conditions. It was found that manganese nitrate and manganese acetate were more conducive to high denitrification efficiency than manganese chloride. The highest NO conversion of 92% is achieved at the Ce/(Mn+Ce) molar ratio of 0.15, which is much higher than that of the pure manganese constituent. The increase of calcining temperature favored the crystallization of active components and leads to the decline of catalytic activity.

1. Introduction
Nitrogen oxides (NOx), which could cause varieties of pollutions to the atmosphere, such as acid rain, photochemical smog and eutrophication of surface water, etc., are among the worst pollutions in the world nowadays. Moreover, they can also be involved in the formation of particulates in air and as a result, have significant adverse effect to ecological environment and human health. Therefore, it is urgent to control the emission of NOx to avoid further pollution. Selective Catalytic Reduction (SCR), in which reducing agents were used to transform NOx into N₂ and H₂O with the help of oxygen at the right temperature and the presence of a catalyst, has been proved as an effective technology to reach that goal.

Vanadium-based catalysts doping with WO₃ or MoO₃ are the most prevalent commercial catalysts used in manufacture factories. This kind of catalyst has to be installed upstream the particle matter collector to meet their active temperature of 300~400°C. As a result, the high concentration of dust, fly ash and other harmful impurities in the flue gas would cause such problems as deactivation, blockage or abrasion, leading to the increase of cost. Obviously, low temperature SCR technology can avoid these problems.

According to the literature [1-3], transition metal oxides, especially with manganese oxide, have better low-temperature activities than other catalyst. This is mainly due to the advantage of their non-crystal type and valence state exchange of MnOₓ over redox reaction. Many studies [4-6] found that manganese-cerium oxides had a higher SCR activity than pure manganese oxides. However, most of them were focus on powder catalyst which was difficult to apply in industry.

In this paper, the strip-shaped Mn-Ce/TiO₂ catalysts were prepared by extrusion molding. The effect of preparation parameters, such as preparation method, manganese precursor, Mn/(Mn+Ce) molar ratio, and calcination conditions were investigated. To the best of our knowledge, such research has not been reported before.
2. Experimental

2.1. Catalysts Preparation
The TiO\textsubscript{2} powder was mixed with deionized water and shaped into strips via a mini-extruder, then dried at 60 °C, and finally calcined at 800°C for 6h in a muffle furnace. Ce(NO\textsubscript{3})\textsubscript{3}•6H\textsubscript{2}O and manganese precursor, including Mn(NO\textsubscript{3})\textsubscript{2}•4H\textsubscript{2}O (50w%) solution, Mn(CH\textsubscript{3}COO)\textsubscript{2}•4H\textsubscript{2}O and MnCl\textsubscript{2}. were dissolved in deionized water. Then the mixed solution was placed on the magnetic stirrer and stirred evenly. The TiO\textsubscript{2} strips were dipped into the beaker containing the mixture. Finally the TiO\textsubscript{2} strips adsorbed completely were dried at 60°C and calcined at 500 °C for 6h in the muffle furnace.

2.2. Catalyst Characterization
Bulk crystalline structures of catalysts were performed on a German D8 advance X-ray diffraction using a Cu K\textalpha\ (\lambda=0.15406nm) X-ray source, within the scan range 10-80°. BET surface area, pore volume, and the pore size distribution were measured by nitrogen adsorption using an Autosorb-iQ physical adsorption system (Quantachrome Instruments, USA).

2.3. Catalyst activity measurement
Standard cylinders to simulate flue gas used in the experiment, the gas composition of NO (600 × 10^{-6}), NH\textsubscript{3} (600 × 10^{-6}), O\textsubscript{2} (6%) and N\textsubscript{2} as carrier gas. In all the runs, the total gas flow rate of 833ml/min and GHSV was about 1000 h\textsuperscript{-1}. The loading volume of catalyst sample is 5ml. The SCR activity measurement was carried on in a quartz tube fixed bed reactor which specifications is Φ 8 mm × 1000 mm. Using an external electric heating mode, the temperature of fixed bed was controlled by tubular resistance furnace. The NO concentration at the inlet and outlet of the reactor was analyzed by a flue gas analyzer (Testo350, Germany). During the measurements, the NO concentrations at four temperature points, 100°C, 150°C, 200°C and 250°C were measured respectively. And each test temperature point was in stable reaction for at least 10min.

3. Results and discussion

3.1. Effect of manganese precursor on the catalytic activity
Figure1 shows the denitration efficiency of the samples, which gradually increased with the temperature. The denitration efficiency curve of Mn-Ce/TiO\textsubscript{2}(MN) is similar to Mn-Ce/TiO\textsubscript{2}(MA) catalysts, which is significantly higher than Mn-Ce/TiO\textsubscript{2}(MC) catalysts in the temperature range of 80~200°C. At 200°C, the denitration efficiency of Mn-Ce/TiO\textsubscript{2}(MN) and Mn-Ce/TiO\textsubscript{2}(MA) catalysts reaches up to 90% above. By contrast, it is only 70% at 200°C for Mn-Ce/TiO\textsubscript{2}(MC) samples. Due to the difference in valence state and structure of MnO\textsubscript{x}, the denitration activity for these catalysts is also different. Kapteijn et al.\textsuperscript{[1]} investigated the activity and selectivity of pure manganese oxides for SCR of NO by ammonia and found that the activity and selectivity for N\textsubscript{2} of the unsupported manganese oxide were determined by the oxidation state and the degree of crystallinity, and that Mn\textsubscript{2}O\textsubscript{3} exhibited the highest selectivity for nitrogen while the MnO\textsubscript{2} exhibited the highest activity. The sequence of MnO\textsubscript{x} catalytic activity for unit surface area is increased as following: MnO\textsubscript{2} > Mn\textsubscript{5}O\textsubscript{8} > Mn\textsubscript{2}O\textsubscript{3} > Mn\textsubscript{3}O\textsubscript{4}.

The XRD patterns of the Mn-Ce/TiO\textsubscript{2} catalysts with different manganese precursors are shown in Figure 2. The XRD patterns for Mn-Ce/TiO\textsubscript{2} (MN) catalysts did not show intense or sharp peaks for manganese oxides or cerium oxides and only anatase phase can be observed. However, for Mn-Ce/TiO\textsubscript{2} (MA) samples, typical diffraction peaks of MnO\textsubscript{2} (JCPDS: 44-0141) were identified. And we can see the diffraction peaks of Mn\textsubscript{3}O\textsubscript{10}C\textsubscript{13} (JCPDS: 30-0821). Kang \textsuperscript{[7]} prepared MnO\textsubscript{x} by precipitation and the effects of two factors, temperature in precipitation and calcination temperature, were investigated. The resulting showed that some decomposition and amorphous also help to improve the catalytic activity of catalysts. It is consistent with our study.
Figure 1 Activity curves of Mn-Ce/TiO₂ catalysts prepared with different manganese precursors
Reaction conditions: NO=600 ppm, NH₃=600 ppm, O₂=6%, GHSV=10000 h⁻¹.
(a) manganese nitrate; (b) manganese acetate; (c) manganese chloride

Figure 2 XRD patterns of Mn-Ce/TiO₂ catalysts prepared with different manganese precursors
(a) manganese nitrate; (b) manganese acetate; (c) manganese chloride

3.2. Effect of ceria content on the catalytic activity
Results on NO conversion as a function of temperature is given in Figure3 for Mn-Ce/TiO₂ catalysts
with different molar ratios of Mn/(Mn+Ce). As we can see that the NO conversion activity is greatly
improved with the increase of Ce loading from 0 to 0.15, but when the Ce/(Mn+Ce) ratio increased
from 0.2 to 0.4, it begin to decrease. It seems that there is an optimal ceria content beyond which the
overloaded Ce would cover the active sites and thus it would be small or even negative to improve the
SCR reaction. The highest NO conversion of 92% is achieved at the Ce/(Mn+Ce) molar ratio of 0.15,
which is much higher than that of the pure manganese constituent. The catalytic activity for NO
conversion decreases in the following order: Mn(85)-Ce(15)/TiO₂> Mn(90)-Ce(10)/TiO₂> Mn(80)-
Ce(20)/TiO₂> Mn(60)/Ce(40)/TiO₂> Mn(100)/TiO₂.
Figure 3: Activity curves of Mn-Ce/TiO₂ catalysts with different molar ratios of Mn/(Mn+Ce).
Reaction conditions: NO=600 ppm, NH₃=600 ppm, O₂=6%, GHSV=10000 h⁻¹.
(a) 0%; (b) 10%; (c) 15%; (d) 20%; (e) 40%

Figure 4 shows the powder XRD patterns of the Mn-Ce/TiO₂ samples. According to the main features of the patterns, the samples can be divided into two groups: Mn-pure catalysts (with manganese oxide content of 100%) and Ce-adding catalysts (adding cerium oxide in active component). In all samples, no cerium oxide phases are detected by XRD. For pure manganese oxide sample, i.e. Mn/TiO₂ catalysts, typical diffraction peaks for Mn₂O₃ (JCPDS: 41-1442) are identified besides anatase and little rutile. As a good oxygen reservoir, ceria (CeO₂) has aroused great interest of researchers because of its oxygen storage and reducing properties. After adding Ce, the peaks of Mn oxide are disappeared, due to the synergistic effect of Mn and Ce. As described in previous research [8], the doped ceria can interact with MnOₓ and titania species and achieve the enrichment of amorphous manganese oxide active phase, and fortify the available mobile oxygen on the surface of catalyst. These aspects could be attributed to Mn-Ce/TiO₂ samples’ high denitration activity.

Figure 4: XRD patterns of Mn-Ce/TiO₂ catalysts with different molar ratios of Mn/(Mn+Ce)
(a) 0%; (b) 15%; (c) 40%
3.3. Effect of calcination temperature on the catalytic activity

The deNOx performance of the Mn-Ce/TiO₂ catalysts calcined at 500°C, 600°C, 700°C and 800°C for 6h is tested within a reaction temperature range from 100°C to 250°C under a simulate flue gas stream as shown in Figure 5. It was observed that, Mn-Ce/TiO₂ catalysts calcined at 500°C and 600°C show superior catalytic activity in the whole temperature range with NOx conversion above 90% at 150°C, and the NO conversion activity of Mn-Ce/TiO₂-500°C catalysts show some slight decrease at high test temperatures (200~250°C). With the increase of calcination temperature, the activity of catalysts is obviously reduced at low temperature especially below 150°C, indicating the possible severe structural change of Mn-Ce/TiO₂ catalysts after calcination at high temperatures. The denitratation rate of Mn-Ce/TiO₂-700°C catalysts drops to 20% at 100°C, while there is almost no active in low temperature of catalysts calcined at 800°C.

Figure 5 Activity curves of Mn-Ce/TiO₂ catalysts calcined at different temperature

Reaction conditions: NO=600 ppm, NH₃=600 ppm, O₂=6%, GHSV=10000 h⁻¹.
(a) 500°C; (b) 600°C; (c) 700°C; (d) 800°C

Figure 6 XRD patterns of Mn-Ce/TiO₂ catalysts calcined at different temperature

(a) 500°C, (b) 600°C, (c) 800°C
Typically, the calcination temperature mainly affects the oxidized state and crystallinity of MnOx. Figure 6 shows XRD patterns of Mn-Ce/TiO₂ catalysts at different temperatures, all the peaks of Mn-Ce/TiO₂ catalysts calcined at 500°C and 600°C are anatase. It indicated that TiO₂ consists of anatase as the unique phase and MnOx and CeOx were well dispersed over the support calcined at 500°C or 600°C. When the calcination temperature of catalysts were raised to 800°C, the diffraction peaks of Mn₂O₃ (JCPDS:65-7467) and CeO₂ (JCPDS:65-5923) are detected. And there were two crystal forms, anatase and rutile, coexisting in TiO₂, indicating that the crystal form transformation of TiO₂ happened.

Table 1 BET surface area, pore volume and pore diameter measurements of the catalysts calcined at different temperature

| Calcination temperature/°C | Surface Area /m²·g⁻¹ | Pore Volume /cm³·g⁻¹ | Pore Size /nm |
|----------------------------|------------------------|-----------------------|--------------|
| 500                        | 10.27                  | 0.06                  | 21.6         |
| 600                        | 5.19                   | 0.02                  | 12.1         |
| 800                        | 1.13                   | 0.01                  | 25.7         |

The BET surface areas, pore volumes, and pore sizes of the various catalysts are summarized in Table 2. From Table 2 we can see that the Mn-Ce/TiO₂ (500°C) has the largest surface area (10.27 m²/g) and the surface area of catalysts calcined at 800°C is only 1.13 m²/g. We can see that with the increasing calcination temperature, there is a continuous decrease in the BET surface area and the decrease is larger after calcination at 800°C. It can be due to various factors that the subsequent decline in the surface area upon thermal treatment at higher temperatures, such as growth of crystallite size, formation of various mixed oxide phases, and sintering.

4. Conclusions

In summary, Mn-Ce/TiO₂ catalysts for low-temperature selective catalytic reduction of NO were prepared with rheological phase method under different preparation parameters. Compared with manganese chloride, manganese nitrate and manganese acetate are more suitable as a precursor, leading to the decline of catalytic activity. With the increase of Ce loading from 0 to 0.15, the NO conversion activity is greatly improved, but when the Ce/(Mn+Ce) ratio increased from 0.2 to 0.4, it begins to decrease. With the increase of calcination temperature, the activity of catalysts is obviously reduced at low temperature especially below 150°C.

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