Effects of Ce over TiO₂ supported MnO_x-based Catalyst for NO_x Reduction by Ammonia

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Abstract. Ce modified MnO_x-based catalysts have attracted much attention due to its high activity for selective catalytic reduction of NO_x by NH₃ (NH₃-SCR) at low-temperatures. However, the most important role of Ce on the NH₃-SCR performance of MnO_x-based catalysts has not been confirmed. Herein, the typical Ce-Mn/TiO₂ catalyst was synthesized through incipient-wetness impregnation method, the positive role of Ce on Ce-Mn/TiO₂ catalyst in the NH₃-SCR process was revealed by combining different activity tests (including NO oxidation and NH₃ oxidation) and characterizations (including XRD, XPS and He-TPD-MS experiments). It was found that the introduction of Ce can promote the dispersion of MnO_x on TiO₂ support. Meanwhile, the doping of Ce in MnO_x can also increase the content of Mn⁴⁺ species. The Mn⁴⁺ species plays a crucial role in NO oxidation reaction, which can trigger the “Fast SCR” reaction and promote the conversion of NO_x. This work provides insight into the catalyst design for NH₃-SCR process at low-temperature.

1 Introduction

Nitrogen oxide (NO_x), as one of the primary atmospheric pollutants, has attracted much attention for its harm on humans and the environment. Selective catalytic reduction of NO_x by NH₃ (NH₃-SCR) has been considered to be one of the most effective deNO_x technology, and the core of this process lies in the catalyst [1]. The traditional NH₃-SCR catalyst used in the power plant is composed of V₂O₅-WO₃/TiO₂, and its suitable working temperature is between 300 °C and 400 °C [2]. However, the applicable temperature of the traditional catalyst is much higher than the flue gas temperature in cement, iron and steel, and other industries [3]. Developing low-temperature NH₃-SCR catalyst (< 200 °C) is significance.

MnO_x-based catalysts have been widely investigated for their excellent NH₃-SCR activity at low-temperature, especially after the modification of Ce element [4-6]. There are many efforts on developing effective Ce-Mn based catalysts and finding the promotion of Ce on NH₃-SCR process [7-9]. However, the most important role of Ce on improving the NH₃-SCR performance of MnO_x-based catalysts has not been confirmed.

In this work, a series of Mn/TiO₂, Ce/TiO₂ and Ce-Mn/TiO₂ catalysts were synthesized by incipient-wetness impregnation method using anatase TiO₂ as support. Ce-Mn/TiO₂ exhibits much better NH₃-SCR activity than Mn/TiO₂ and Ce/TiO₂. Combined with different activity tests (including NO oxidation and NH₃ oxidation) and characterizations (including XRD, XPS and He-TPD-MS experiments) data, the positive role of Ce element on Ce-Mn/TiO₂ catalyst in the NH₃-SCR process was revealed.

2 Experimental

2.1 Catalysts preparation

The TiO₂ (5–10 nm, anatase), 50 wt.% Mn(NO₃)₂ solution and Ce(NO₃)₃·6H₂O were purchased from Aladdin, and used without further purification. The Mn/TiO₂, Ce/TiO₂ and Ce-Mn/TiO₂ catalysts were synthesized through incipient-wetness impregnation method. After impregnating 10 h at room temperature, the samples were dried at 120 °C for 10 h, followed by calcination at 500 °C for 4 h. The molar ratio of Mn/Ti in both Mn/TiO₂ and Ce-Mn/TiO₂ catalysts are 0.14, and molar ratio of Ce/Ti in both Ce/TiO₂ and Ce-Mn/TiO₂ catalysts are 0.02.

2.2 Catalytic performance test

The reactant gases of NH₃-SCR process are listed as below: 0.06 % NO, 0.06 % NH₃, 5% O₂, and balanced by N₂. The reactant gases of NO oxidation process are listed as below: 0.06 % NO, 5% O₂, and balanced by N₂. The reactant gases of NH₃ oxidation process are listed as below: 0.06 % NH₃, 5% O₂, and balanced by N₂. The gas hourly space velocity (GHSV) of all the tests were 30000 h⁻¹. The NO and NO₂ contents were detected by an MRU OPTIMA 7 analyzer. The NO_x conversion, NO to NO₂ conversion and NO_x content in exhaust can be calculated as follows:

$$\text{NO}_x \text{ conversion} = \frac{[\text{NO} + \text{NO}_2]_{\text{in}} - [\text{NO} + \text{NO}_2]_{\text{out}}}{[\text{NO} + \text{NO}_2]_{\text{in}}} \times 100\% \quad (1)$$

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$$\text{NO to NO}_2 \text{ conversion} = \frac{[\text{NO}_2]_{\text{out}} - [\text{NO}_2]_{\text{in}}}{[\text{NO}]_{\text{in}}} \times 100\% \quad (2)$$

$$\text{NO}_x \text{ content in exhaust} = \frac{[\text{NO} + \text{NO}_2]_{\text{out}}}{[\text{NH}_3]_{\text{in}}} \times 100\% \quad (3)$$

2.3 Catalyst characterization

X-ray diffraction (XRD) was conducted on a PANalytical X'Pert PRO MPD X-ray Diffractometer. X-ray photoelectron spectroscopy (XPS) was detected by a VG ESCALABMK II spectrometer using an Al K α (1486.6 eV) photon source. Temperature-programmed desorption under He flow (He-TPD) was conducted on a Micromeritics AutoChem 2950 HP instrument, and the desorbed or composed O₂ was simultaneously detected by a mass spectrometer (MS, OMNISTar).

3 Results and discussion

3.1 Catalytic activity test

The results of the NH₃-SCR activity tests over TiO₂ support, Mn/TiO₂, Ce/TiO₂ and Ce-Mn/TiO₂ are presented in Fig. 1. Compared with Ce-TiO₂, Mn-TiO₂ catalyst showed good SCR deNO_x activity at low-temperatures, which can reach 95% NO_x conversion at 160 °C. The introduction of Ce can further significantly improve the deNO_x activity at low-temperatures, and its NO_x conversion can reach 95% at 100 °C.

Fig. 1. NH₃-SCR activity test curves.

As our previous reports [10-12], the NH₃-SCR reaction ($4\text{NH}_3 + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$) at low-temperatures can be considered as the coupling of NO oxidation ($2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$) and “Fast SCR” reaction ($2\text{NH}_3 + \text{NO} + \text{NO}_2 \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O}$), where the “Fast SCR” reaction can occur rapidly. Therefore, the NO oxidation activity of catalyst could determine its NH₃-SCR activity. To prove this point, NO oxidation activity tests were further tested. As shown in Fig. 2, the order of NO oxidation activities as follow: Ce-Mn/TiO₂ > Mn/TiO₂ > Ce/TiO₂ > TiO₂, in consistence with the order of their NH₃-SCR activities. These indicate that the introduction of Ce can increase the NO oxidation activity of Ce-Mn/TiO₂, thus leading to its high NH₃-SCR

activity at low-temperatures. Although the oxidizing ability of catalysts can promote the NO oxidation activity and NH₃-SCR activity at low-temperatures, it can also lead the NH₃ oxidation at high-temperatures. The results of NH₃ oxidation tests over the four samples are shown in Fig. 3. NH₃ began to be oxidized to NO_x at 230 °C over Mn/TiO₂ and Ce-Mn/TiO₂ samples, which can explain the NH₃-SCR deNO_x activity start to decrease since 230 °C. Therefore, the oxidizing ability of low-temperature SCR catalyst is a double-edged sword, which can increase the NO_x conversion by promoting NO oxidation at low-temperatures and decrease the NO_x conversion by promoting the NH₃ oxidation at high-temperatures.

Fig. 2. NO oxidation activity test curves.

Fig. 3. NH₃ oxidation activity test curves.

3.2 Structure characteristic of catalysts

To reveal the structure of catalysts and to construct the structure-activity relationship, XRD and XPS characteristics were conducted. The XRD patterns of the four samples are illustrated in Fig. 4. TiO₂ support is made up of anatase TiO₂ ($2\theta = 25.3^\circ, 37.0^\circ, 37.8^\circ, 38.6^\circ, 48.1^\circ, 53.9^\circ, 55.0^\circ, 62.7^\circ, 68.9^\circ$ and 70.3°) and traces of rutile TiO₂ ($2\theta = 27.5^\circ$), and there is no obvious effect on the TiO₂ crystal structure with MnO_x and CeO_x loading. For the CeO_x species, there are no characteristics peaks of CeO₂ species in the XRD patterns of Ce/TiO₂ and Ce-

Mn/TiO₂, indicating CeO_x species is well dispersed on TiO₂ support. For the MnO_x species, the characteristic peaks of MnO₂ ($2\theta = 28.7^\circ$, 42.7° and 56.8°) appear in the XRD pattern of Mn/TiO₂, but there are no peaks of MnO₂ in the pattern of Ce-Mn/TiO₂. These indicate the introduction of Ce can promote the dispersion of MnO_x. The surface element concentrations on the surface of catalysts detected by XPS are shown in Table 1. The content of Mn atom increases from 2.79% (Mn/TiO₂) to 5.85% (Ce-Mn/TiO₂) with the introduction of the Ce element, which can further prove that the dispersion of MnO_x was improved with the dope of Ce. Meanwhile, the content of Ce atom in Ce-Mn/TiO₂ (2.70%) decreases compared with that in Ce/TiO₂ (2.41%), indicating that the Ce element could be doped in the MnO_x species. Besides the dispersion of MnO_x, the effect of Ce on Mn ion valence state was also analysed. As shown in the Mn 2p XPS spectra in Fig. 5, the peaks of Mn 2p_{3/2} were deconvoluted into three peaks at 642.0 eV, 641.0 eV and 644.6 eV, corresponding to Mn⁴⁺, Mn³⁺ and Mn²⁺, respectively [4]. It can be seen that the content of Mn⁴⁺ were significantly increased with the dope of Ce element. It has been widely reported that the Mn ion with a high oxidation state (such as Mn⁴⁺) is the main active species for NO oxidation process over MnO_x-based catalysts [13–15]. Therefore, the role of Ce over Ce-Mn/TiO₂ catalyst can be assigned to two aspects: First, the introduction of Ce can promote the dispersion of MnO_x on TiO₂ support; Second, the dope of Ce in MnO_x can increase the content of Mn⁴⁺, which possesses higher NO oxidation activity.

Fig. 4. XRD patterns of TiO₂, Mn/TiO₂, Ce/TiO₂ and Ce-Mn/TiO₂ catalysts.

Table 1. Surface element content detected by XPS.

Catalysts	Surface atomic content (%)			
	Mn	Ce	Ti	O
TiO ₂	--	--	34.16	65.84
Ce/TiO ₂	--	5.41	29.71	64.88
Mn/TiO ₂	2.79	--	32.86	64.35
Ce-Mn/TiO ₂	5.85	2.70	28.05	63.40

3.3 Study on the structure-activity relationship

In the previous study [12], it has been found that a bidentate nitrate species of MnO₂NO₂ plays a crucial role over NO oxidation process, and the MnO₂NO₂ species can be decomposed to NO and O₂ in 250–400 °C. Therefore, in the temperature-programmed desorption (He-TPD) experiment of the reacted catalysts after the NO oxidation test, the amount of MnO₂NO₂ can be reflected by the amount of decomposed O₂ in 250–400 °C. For this reason, the He-TPD experiments of the reacted Mn/TiO₂ and Ce-Mn/TiO₂ after NO oxidation tests were conducted, and the corresponding O₂ MS signals are shown in Fig. 6. The peak area (250–400 °C) in the O₂ MS curve of reacted Ce-Mn/TiO₂ is about 5.6 times higher than that of reacted Mn/TiO₂. Meanwhile, according to the XPS results, the Mn⁴⁺ content in Ce-Mn/TiO₂ is about 5.1 times higher than that in Mn/TiO₂. The comparability of these two values indicates that Mn⁴⁺ plays a crucial role in MnO₂NO₂ formation, thus Mn⁴⁺ is the active site for NO oxidation process.

Fig. 5. Mn 2p XPS patterns of TiO₂, Mn/TiO₂, Ce/TiO₂ and Ce-Mn/TiO₂ catalysts.

Fig. 6. O₂ MS signals in He-TPD-MS of the reacted Mn/TiO₂ and Ce-Mn/TiO₂ after NO oxidation tests.

4 Conclusion

In this work, a series of Mn/TiO₂, Ce/TiO₂ and Ce-Mn/TiO₂ catalysts were synthesized through incipient-wetness impregnation method, and Ce-Mn/TiO₂ exhibits robust NH₃-SCR activity in low-temperature. Combined with XRD and XPS results, the positive role of Ce on Ce-Mn/TiO₂ catalyst in the NH₃-SCR process was revealed. First, the introduction of Ce can promote the dispersion of MnO_x on TiO₂ support; Second, the doping of Ce in MnO_x can also increase the content of Mn⁴⁺ species. It was found that Mn⁴⁺ species plays a crucial role in NO oxidation process, which can trigger “Fast SCR” reaction and promote NH₃-SCR process at low-temperature. This work provides new insight into the catalyst design for NH₃-SCR process at low-temperature.

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