Effects of Ce over TiO$_2$ 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 NH$_3$ (NH$_3$-SCR) at low-temperatures. However, the most important role of Ce on the NH$_3$-SCR performance of MnO$_x$-based catalysts has not been confirmed. Herein, the typical Ce-Mn/TiO$_2$ catalyst was synthesized through incipient-wetness impregnation method, the positive role of Ce on Ce-Mn/TiO$_2$ catalyst in the NH$_3$-SCR process was revealed by combining different activity tests (including NO oxidation and NH$_3$ 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 TiO$_2$ support. Meanwhile, the doping of Ce in MnO$_x$ can also increase the content of Mn$^{4+}$ species. The Mn$^{4+}$ 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 NH$_3$-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 NH$_3$ (NH$_3$-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 NH$_3$-SCR catalyst used in the power plant is composed of V$_2$O$_5$-WO$_3$/TiO$_2$, 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 NH$_3$-SCR catalyst (< 200 °C) is significance.

MnO$_x$-based catalysts have been widely investigated for their excellent NH$_3$-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 NH$_3$-SCR process [7-9]. However, the most important role of Ce on improving the NH$_3$-SCR performance of MnO$_x$-based catalysts has not been confirmed.

In this work, a series of Mn/TiO$_2$, Ce/TiO$_2$ and Ce-Mn/TiO$_2$ catalysts were synthesized by incipient-wetness impregnation method using anatase TiO$_2$ as support. Ce-Mn/TiO$_2$ exhibits much better NH$_3$-SCR activity than Mn/TiO$_2$ and Ce/TiO$_2$. Combined with different activity tests (including NO oxidation and NH$_3$ oxidation) and characterizations (including XRD, XPS and He-TPD-MS experiments) data, the positive role of Ce element on Ce-Mn/TiO$_2$ catalyst in the NH$_3$-SCR process was revealed.

2 Experimental

2.1 Catalysts preparation

The TiO$_2$ (5–10 nm, anatase), 50 wt.% Mn(NO$_3$)$_2$ solution and Ce(NO$_3$)$_3$·6H$_2$O were purchased from Aladdin, and used without further purification. The Mn/TiO$_2$, Ce/TiO$_2$ and Ce-Mn/TiO$_2$ 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/TiO$_2$ and Ce-Mn/TiO$_2$ catalysts are 0.14, and molar ratio of Ce/Ti in both Ce/TiO$_2$ and Ce-Mn/TiO$_2$ catalysts are 0.02.

2.2 Catalytic performance test

The reactant gases of NH$_3$-SCR process are listed as below: 0.06 % NO, 0.06 % NH$_3$, 5% O$_2$, and balanced by N$_2$. The reactant gases of NO oxidation process are listed as below: 0.06 % NO, 5% O$_2$, and balanced by N$_2$. The gas hourly space velocity (GHSV) of all the tests were 30000 h$^{-1}$. The NO and NO$_2$ contents were detected by an MRU OPTIMA 7 analyzer. The NO$_x$ conversion, NO to NO$_2$ 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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\[
\text{NO to NO}_2 \text{ conversion} = \left( \frac{[\text{NO}_2]_{\text{in}}}{[\text{NO}]_{\text{in}}} \right) \times 100\% \tag{2}
\]
\[
\text{NO}_x \text{ content in exhaust} = \left( \frac{[\text{NO}_x]_{\text{out}}}{[\text{NO} + \text{NO}_2]_{\text{in}}} \right) \times 100\% \tag{3}
\]

### 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\(_\alpha\) (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 O\(_2\) was simultaneous detected by a mass spectrometer (MS, OMNIStar).

### 3 Results and discussion

#### 3.1 Catalytic activity test

The results of the NH\(_3\)-SCR activity tests over TiO\(_2\) support, Mn/TiO\(_2\), Ce/TiO\(_2\), and Ce-Mn/TiO\(_2\) are presented in **Fig. 1**. Compared with Ce-TiO\(_2\), Mn-TiO\(_2\) 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.** NH\(_3\)-SCR activity test curves.

As our previous reports [10-12], the NH\(_3\)-SCR reaction (4NH\(_3\) + 4NO + O\(_2\) → 4N\(_2\) + 6H\(_2\)O) at low-temperatures can be considered as the coupling of NO oxidation (2NO + O\(_2\) → 2NO\(_2\)) and “Fast SCR” reaction (2NH\(_3\) + NO + NO\(_2\) → 2N\(_2\) + 3H\(_2\)O), where the “Fast SCR” reaction can occur rapidly. Therefore, the NO oxidation activity of catalyst could determine its NH\(_3\)-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/TiO\(_2\) > Mn/TiO\(_2\) > Ce/TiO\(_2\) > TiO\(_2\), in consistence with the order of their NH\(_3\)-SCR activities. These indicate that the introduction of Ce can increase the NO oxidation activity of Ce-Mn/TiO\(_2\), thus leading to its high NH\(_3\)-SCR activity at low-temperatures. Although the oxidizing ability of catalysts can promote the NO oxidation activity and NH\(_3\)-SCR activity at low-temperatures, it can also lead the NH\(_3\) oxidation at high-temperatures. The results of NH\(_3\) oxidation tests over the four samples are shown in **Fig. 3**. NH\(_3\) began to be oxidized to NO\(_x\) at 230 °C over Mn/TiO\(_2\) and Ce-Mn/TiO\(_2\) samples, which can explain the NH\(_3\)-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 NH\(_3\) oxidation at high-temperatures.

**Fig. 2.** NO oxidation activity test curves.

**Fig. 3.** NH\(_3\) 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**. TiO\(_2\) support is made up of anatase TiO\(_2\) (2θ = 25.3°, 37.0°, 37.8°, 38.6°, 48.1°, 53.9°, 55.0°, 62.7°, 68.9° and 70.3°) and traces of rutile TiO\(_2\) (2θ = 27.5°), and there is no obvious effect on the TiO\(_2\) crystal structure with MnO\(_x\) and CeO\(_x\) loading. For the CeO\(_x\) species, there are no characteristics peaks of CeO\(_2\) species in the XRD patterns of Ce/TiO\(_2\) and Ce-
3.3 Study on the structure-activity relationship

In the previous study [12], it has been found that a bidentate nitrate species of MnO$_2$NO$_2$ plays a crucial role over NO oxidation process, and the MnO$_2$NO$_2$ species can be decomposed to NO and O$_2$ 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 MnO$_2$NO$_2$ can be reflected by the amount of decomposed O$_2$ in 250–400 °C. For this reason, the He-TPD experiments of the reacted Mn/TiO$_2$ and Ce-Mn/TiO$_2$ after NO oxidation tests were conducted, and the corresponding O$_2$ MS signals are shown in Fig. 6. The peak area (250–400 °C) in the O$_2$ MS curve of reacted Ce-Mn/TiO$_2$ is about 5.6 times higher than that of reacted Mn/TiO$_2$. Meanwhile, according to the XPS results, the Mn$^{4+}$ content in Ce-Mn/TiO$_2$ is about 5.1 times higher than that in Mn/TiO$_2$. The comparability of these two values indicates that Mn$^{4+}$ plays a crucial role in MnO$_2$NO$_2$ formation, thus Mn$^{4+}$ is the active site for NO oxidation process.

![Fig. 5. Mn 2p XPS patterns of TiO$_2$, Mn/TiO$_2$, Ce/TiO$_2$ and Ce-Mn/TiO$_2$ catalysts.](image)

![Fig. 6. O$_2$ MS signals in He-TPD-MS of the reacted Mn/TiO$_2$ and Ce-Mn/TiO$_2$ after NO oxidation tests.](image)
4 Conclusion

In this work, a series of Mn/TiO$_2$, Ce/TiO$_2$ and Ce-Mn/TiO$_2$ catalysts were synthesized through incipient-wetness impregnation method, and Ce-Mn/TiO$_2$ exhibits robust NH$_3$-SCR activity in low-temperature. Combined with XRD and XPS results, the positive role of Ce on Ce-Mn/TiO$_2$ catalyst in the NH$_3$-SCR process was revealed. First, the introduction of Ce can promote the dispersion of MnO$_x$ on TiO$_2$ support; Second, the doping of Ce in MnO$_x$ can also increase the content of Mn$^{4+}$ species. It was found that Mn$^{4+}$ species plays a crucial role in NO oxidation process, which can trigger “Fast SCR” reaction and promote NH$_3$-SCR process at low-temperature. This work provides new insight into the catalyst design for NH$_3$-SCR process at low-temperature.

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