Catalytic Oxidation of NO over MnO$_x$–CeO$_2$ and MnO$_x$–TiO$_2$ Catalysts

Xiaolan Zeng, Xiaoyue Huo, Tianle Zhu *, Xiaowei Hong and Ye Sun

School of Space and Environment, Beihang University, Beijing 100191, China; xlzeng@buaa.edu.cn (X.Z.); xyhuo1123@163.com (X.H.); hongxiao86@126.com (X.H.); suny@buaa.edu.cn (Y.S.)

* Correspondence: zhutl@buaa.edu.cn; Tel./Fax: +86-10-8231-4215

Academic Editor: Ramesh Giri
Received: 4 October 2016; Accepted: 5 November 2016; Published: 14 November 2016

Abstract: A series of MnO$_x$–CeO$_2$ and MnO$_x$–TiO$_2$ catalysts were prepared by a homogeneous precipitation method and their catalytic activities for the NO oxidation in the absence or presence of SO$_2$ were evaluated. Results show that the optimal molar ratio of Mn/Ce and Mn/Ti are 0.7 and 0.5, respectively. The MnO$_x$–CeO$_2$ catalyst exhibits higher catalytic activity and better resistance to SO$_2$ poisoning than the MnO$_x$–TiO$_2$ catalyst. On the basis of Brunauer–Emmett–Teller (BET), X-ray diffraction (XRD), and scanning transmission electron microscope with mapping (STEM-mapping) analyses, it is seen that the MnO$_x$–CeO$_2$ catalyst possesses higher BET surface area and better dispersion of MnO$_x$ over the catalyst than MnO$_x$–TiO$_2$ catalyst. X-ray photoelectron spectroscopy (XPS) measurements reveal that MnO$_x$–CeO$_2$ catalyst provides the abundance of Mn$^{3+}$ and more surface adsorbed oxygen, and SO$_2$ might be preferentially adsorbed to the surface of CeO$_2$ to form sulfate species, which provides a protection of MnO$_x$ active sites from being poisoned. In contrast, MnO$_x$ active sites over the MnO$_x$–TiO$_2$ catalyst are easily and quickly sulfated, leading to rapid deactivation of the catalyst for NO oxidation. Furthermore, temperature programmed desorption with NO and O$_2$ (NO + O$_2$-TPD) and in situ diffuse reflectance infrared transform spectroscopy (in situ DRIFTS) characterizations results show that the MnO$_x$–CeO$_2$ catalyst displays much stronger ability to adsorb NO$_x$ than the MnO$_x$–TiO$_2$ catalyst, especially after SO$_2$ poisoning.

Keywords: MnO$_x$–CeO$_2$; MnO$_x$–TiO$_2$; catalytic oxidation; NO; SO$_2$

1. Introduction

Nitrogen oxides (NO$_x$s) emitted from stationary and mobile sources are some of the main air pollutants, which cause a variety of serious environmental problems, such as photochemical smog, acid rain, and greenhouse effect [1]. Moreover, NO$_x$s are the primary precursors of haze occurring in China. Therefore, NO$_x$ removal has become the focus of recent environmental protection. The most effective and mature technology is the selective catalytic reduction using ammonia as a reducing agent (NH$_3$-SCR). However, there still exist some problems, such as high reaction temperature, sophisticated system design, and high operation cost. Additionally, it is possible to cause secondary pollution due to the leakage of ammonia [2].

In order to solve the problems of NH$_3$-SCR, much attention has been paid to the simultaneous removal of SO$_2$ and NO$_x$s by chemical absorption. For the absorption operation, the oxidation of NO with low water-solubility to NO$_2$ is a crucial process because NO accounts for about 95% of NO$_x$s. In general, the oxidation of NO to NO$_2$ can be realized through gas phase oxidation and liquid phase oxidation. The presence of SO$_2$ is disadvantageous to NO oxidation in the liquid phase because of the high solubility and oxidizability of SO$_2$, whereas the oxidation rate of SO$_2$ is much lower than that of NO in the gas phase [3]. The gas phase oxidation is divided into homogeneous gas phase oxidation and heterogeneous gas-solid catalytic oxidation. Nowadays, catalytic oxidation of NO is potentially...
an ideal technology due to its simple operation and low cost, and considerable interest has been put into the investigation of developing catalysts for oxidizing NO into NO₂.

The catalysts for NO oxidation mainly include noble metal catalysts, transition metal catalysts, and molecular sieve catalysts. Noble metal catalysts exhibit high catalytic activity at low temperature, but are limited in industrial applications because of their high cost and poisoning problems [4–9]. Molecular sieve catalysts show certain catalytic activity but they are hydrothermally unstable and susceptible to structure collapse [10]. Transition metal oxides are cheap and also have good catalytic activity and, thus, can be appropriate catalysts for the catalytic oxidation of NO. Among the variety of transition metal catalysts, Co-based and Mn-based catalysts display the best catalytic activity for NO oxidation [11]. However, the applications of Co-based catalysts are retarded due to the toxicity of cobalt although they attract much attention [12–19]. Mn-based catalysts are considered as the promising candidates for NO oxidation to NO₂. Many Mn-based catalysts (e.g., MnOₓ/TiO₂ [20–22], Ce–Mn/TiO₂ [23], FeMnOₓ/TiO₂ [24,25]) have been studied. The results show that MnOₓ supported on TiO₂ (P25) prepared by deposition-precipitation (DP) method and chemical vapor condensation method exhibits high catalytic activity. Additionally, NO oxidation efficiency can be enhanced by modifying MnOₓ/TiO₂ with Ce and Fe. Most recently, many Mn-based catalysts (e.g., Mn–Ce–Ti [26], MnOₓ/CeO₂–ZrO₂ [27], MnO₂/TiO₂–Pal [28], Co–Mn/TiO₂ [29], Fe₂O₃@MnO₂@CNTs [30], and MnO₂@NiCoOₓOₓ [31]) have also been studied on the selective catalytic reduction of NOₓ, and they exhibit good catalytic activities. On the other hand, CeO₂, as a carrier or promoter, also has been studied extensively because of its redox properties and exceptional ability to store and release oxygen. Meanwhile, studies also show that CeO₂ possesses excellent ability to resist SO₂ poisoning [23,32].

In this study, we compared the catalytic activity and resistance to SO₂ poisoning of MnOₓ–CeO₂ and MnOₓ–TiO₂ catalysts. The fresh and SO₂ poisoned catalysts were characterized by XRD, BET, STEM-mapping, XPS, NO + O₂–TPD and in situ DRIFTS to clarify the structure-effect relationship.

2. Results and Discussion

2.1. Catalytic Activity Tests

The NO oxidation efficiencies over the MnOₓ–CeO₂–ₓ and MnOₓ–TiO₂–y catalysts are shown in Figure 1a,b, respectively. It can be seen that TiO₂ shows negligible catalytic activity during the reaction temperature range, while CeO₂ has certain catalytic activity for NO oxidation. Nonetheless, the catalytic activity of CeO₂ is lower and the activity temperature is higher, compared with those of MnOₓ–CeO₂–ₓ catalysts. Therefore, MnOₓ was the main active component for the catalytic oxidation of NO. In the presence of SO₂, the optimal molar ratio of Mn/Ce and Mn/Ti was 0.7 and 0.5, respectively. Meanwhile, the maximum NO oxidation efficiency of 72% over MnOₓ–CeO₂–0.7 catalyst is obtained at 325 °C, while that of 62% over MnOₓ–TiO₂–0.5 catalyst is obtained at 375 °C. Therefore, the MnOₓ–CeO₂–0.7 catalyst has better catalytic activity than the MnOₓ–TiO₂–0.5 catalyst.

![Figure 1](image-url)
Actually, the catalytic activities of MnO$_x$–CeO$_2$-0.7 and MnO$_x$–TiO$_2$-0.5 catalysts were also investigated in the absence of SO$_2$, and the results show that the maximum NO oxidation efficiency of MnO$_x$–CeO$_2$-0.7 and MnO$_x$–TiO$_2$-0.5 catalysts are 91% and 86% at 300 °C, as shown in Figure 2. Clearly, the presence of SO$_2$ results in a decrease of NO oxidation efficiency and an increase of the active temperature, especially for the MnO$_x$–TiO$_2$-0.5 catalyst. The MnO$_x$–CeO$_2$-0.7 catalyst displays better resistance to SO$_2$ poisoning than the MnO$_x$–TiO$_2$-0.5 catalyst.

The stability tests for NO oxidation over MnO$_x$–CeO$_2$-0.7 and MnO$_x$–TiO$_2$-0.5 catalysts were carried out under different temperatures. As shown in Figure 3a, the NO oxidation efficiency of the MnO$_x$–TiO$_2$-0.5 catalyst decreases much more rapidly than that of the MnO$_x$–CeO$_2$-0.7 catalyst. The catalytic activity of the MnO$_x$–CeO$_2$-0.7 catalyst gradually decreases at 300 °C, and maintains almost unchanged within 5 h at 350 °C while it decreases after 5 h. The stability tests without SO$_2$ over two catalysts were also carried out at 300 °C, and no activity decrease is observed in 20 h (the results are not shown here), which convinces us that the deactivation in Figure 3 is caused by the presence of SO$_2$. The on-off effect of SO$_2$ for NO oxidation over MnO$_x$–CeO$_2$-0.7 catalyst was investigated. As shown in Figure 3b, when 100 ppm SO$_2$ are added to the reactants, the NO oxidation efficiency decreases from the initial 80% to 27% after 10 h. After excluding SO$_2$ from the flue gas, the NO oxidation efficiency only recovers to 32%, which indicates that the poisoning effect of SO$_2$ is irreversible.
2.2. XRD and BET Characterizations

Figure 4 presents the XRD patterns of fresh and SO2 poisoned catalysts. For MnOx–CeO2-0.7 catalyst and SO2 poisoned MnOx–CeO2-0.7 catalyst (donated as MnOx–CeO2-0.7-S), crystalline phases of CeO2 can be clearly observed, and very weak signals of Mn2O3 are also detected, which indicates that Mn2O3 exists in a poor crystal structure. For MnOx–TiO2-0.5 catalyst and SO2 poisoned MnOx–TiO2-0.5 catalyst (donated as MnOx–TiO2-0.5-S), the stronger diffraction peaks of Mn2O3 are observed besides crystalline phases of rutile and anatase TiO2, which suggests that Mn2O3 exists in crystal structure. It is well known that the low crystallinity of MnOx is favorable for catalytic reaction [20]. Therefore, the higher activity of MnOx–CeO2-0.7 catalyst may be partly due to the well dispersion of MnOx. For all of the samples, the diffraction peaks almost do not change due to SO2 poisoning.

![XRD patterns](image)

**Figure 4.** XRD patterns of MnOx–CeO2-0.7 and MnOx–CeO2-0.7-S catalysts (a) and MnOx–TiO2-0.5 and MnOx–TiO2-0.5-S catalysts (b).

The BET surface areas of the catalysts are summarized in Table 1. It can be seen that the specific surface areas of fresh MnOx–CeO2-0.7 and MnOx–TiO2-0.5 catalysts are 96.30 and 60.21 m²·g⁻¹. Compared to catalytic performance, it is consistent with that of BET surface. Furthermore, it is worth noting that the BET specific surface areas of SO2 poisoned catalysts decrease to 67.92 (MnOx–CeO2-0.7) m²·g⁻¹ and 39.71 (MnOx–TiO2-0.5) m²·g⁻¹, which may be caused by the formation of sulfate species.

| Catalysts           | Surface Area (m²/g) |
|---------------------|---------------------|
| MnOx–CeO2-0.7       | 93.17               |
| MnOx–CeO2-0.7-S     | 67.92               |
| MnOx–TiO2-0.5       | 60.21               |
| MnOx–TiO2-0.5-S     | 39.71               |

2.3. STEM-Mapping Analysis

Figure 5 presents STEM images and their mapping analysis of fresh MnOx–CeO2-0.7 and MnOx–TiO2-0.5 catalysts. For the MnOx–CeO2-0.7 catalyst, Mn, Ce, O evenly disperses on the scanning area, which indicates excellent distribution of MnOx and CeO2. For the MnOx–TiO2-0.5 catalyst, however, many of the Mn and O atoms appear on the scanning area, while few Ti atoms are seen. Therefore, we deduce that TiO2 cannot disperse MnOx well, which can lead to low catalytic activity of the MnOx–TiO2-0.5 catalyst.
As shown in Table 2, all catalysts contain high concentration of Mn, estimated by the formula [37]:

\[
\text{Ce}^{3+} \text{ (%)} = \frac{S_{u_1} + S_{v_1}}{\sum_{i=0}^{3} (S_{u_i} + S_{v_i})} \times 100\%
\]

The Ce 3D XPS spectra can be separated into eight peaks: \(u_0\) (900.6 eV), \(u_1\) (902.4 eV), \(u_2\) (907.9 eV), \(u_3\) (916.6 eV), \(v_0\) (881.9 eV), \(v_1\) (884.4 eV), \(v_2\) (889.1 eV), and \(v_3\) (898.1 eV) [36]. The bands labeled as \(u_1\) and \(v_1\) are attributed to Ce\(^{3+}\) species, and the other six peaks are assigned to Ce\(^{4+}\) species. The ratio of Ce\(^{3+}\)/Ce\(^{3+} + \text{Ce}^{4+}\) can be estimated by the formula [37]:

2.4. XPS Analysis

XPS analysis was performed to identify the surface component and chemical states of fresh and SO\(_2\) poisoned catalysts. Surface atomic concentration and ratio are summarized in Table 2, and XPS spectra of Mn 2p, O 1s, Ce 3d, and Ti 2p of all catalysts are displayed in Figure 6. Through deconvolution of the spectra, two main peaks due to Mn 2p\(^{3/2}\) and Mn 2p\(^{1/2}\) are observed. The Mn 2p\(^{3/2}\) profiles are fitted with the Mn\(^{2+}\), Mn\(^{3+}\), and Mn\(^{4+}\), characterized by the binding energy at about 641.1 eV, 642.5 eV, and 645.1 eV [33], respectively. Previous studies [20,22,34] have shown that Mn\(^{2+}\) has a higher catalytic activity than MnO\(_2\) for NO oxidation. Cimino et al. [35] attributed the higher activity of Mn\(^{3+}\) than Mn\(^{4+}\) for CO catalytic oxidation to the weaker Mn\(^{3+}\)–O bond. Similarly, it can be deduced that the weaker Mn\(^{3+}\)–O bonds will also favor the catalytic oxidation of NO since the Mn\(^{3+}\)–O bond is easily broken, thus, promoting the generation and release of the NO\(_2\) oxidation product. As shown in Table 2, all catalysts contain high concentration of Mn\(^{3+}\). Corresponding to the high catalytic activity of catalyst, it, combining with XRD analysis results, can be also speculated that Mn\(^{3+}\) has higher catalytic activity than Mn\(^{2+}\) and Mn\(^{4+}\) for NO oxidation. The Ce 3D XPS spectra can be separated into eight peaks: \(u_0\) (900.6 eV), \(u_1\) (902.4 eV), \(u_2\) (907.9 eV), \(u_3\) (916.6 eV), \(v_0\) (881.9 eV), \(v_1\) (884.4 eV), \(v_2\) (889.1 eV), and \(v_3\) (898.1 eV) [36]. The bands labeled as \(u_1\) and \(v_1\) are attributed to Ce\(^{3+}\) species, and the other six peaks are assigned to Ce\(^{4+}\) species. The ratio of Ce\(^{3+}\)/Ce\(^{3+} + \text{Ce}^{4+}\) can be estimated by the formula [37]:

\[
\text{Ce}^{3+} \text{ (%)} = \frac{S_{u_1} + S_{v_1}}{\sum_{i=0}^{3} (S_{u_i} + S_{v_i})} \times 100\%
\]
It is well known that Ce\(^{3+}\) species can make charge imbalance and create oxygen vacancies via the shift from Ce\(^{3+}\) to Ce\(^{4+}\), which leads to the increase of surface adsorbed oxygen (Ce\(^{3+} \rightarrow \text{Ce}^{4+} + e^−, \text{O}_2 + e^- \rightarrow \text{O}_2^−\)) [38]. For the catalytic oxidation of NO, surface adsorbed oxygen plays a significant role because of its mobility and redox performance [39]. As listed in Table 2, the Ce\(^{3+}\) concentration can reach about 41.6%. Figure 6c displays the O 1s XPS spectra of all samples, two distinct bands are obtained. The one peak O_\(α\) in the range of 528–530 eV belongs to lattice oxygen and the other peak O_\(β\) with binding energy of 530–532 eV corresponds to weakly surface adsorbed oxygen [18]. From Table 2, it can be seen that the O_\(α\) concentration over MnO\(_x\)–CeO\(_2\)–0.7 catalyst is higher than that over MnO\(_x\)–TiO\(_2\)–0.5 catalyst, which is attributed to the presence of Ce\(^{3+}\) species.

On the other hand, the Mn concentration of the MnO\(_x\)–CeO\(_2\)–0.7-S catalyst is almost the same to that of the fresh MnO\(_x\)–CeO\(_2\)–0.7 catalyst, while the Mn concentration of MnO\(_x\)–TiO\(_2\)–0.5 catalyst and the Ce concentration of MnO\(_x\)–CeO\(_2\)–0.7 catalyst decrease from 13.6% to 9.4% and from 26.4% to 19.7%, respectively, because of SO\(_2\) poisoning, which is attributed that the MnO\(_x\) over MnO\(_x\)–TiO\(_2\)–0.5 catalyst and CeO\(_2\) over MnO\(_x\)–CeO\(_2\)–0.7-S catalyst are partly covered with sulfate species [36]. Meanwhile, the ratio of Ce\(^{3+}\)/(Ce\(^{3+}\) + Ce\(^{4+}\)) of the MnO\(_x\)–CeO\(_2\)–0.7 catalyst also decreases from 41.6% to 25.2%, which indicates that cerium(IV) sulfate may be formed on the catalyst surface [40]. Therefore, we can deduce that SO\(_2\) might be preferentially adsorbed to the surface of CeO\(_2\) to form sulfate species, lessening the sulfation of MnO\(_x\) active sites. It was also reported by Jin and co-workers [32] that the presence of CeO\(_2\) might partially prevent MnO\(_x\) active sites from being sulfated. Waqif [41] investigated the adsorption of SO\(_2\) on CeO\(_2\)–Al\(_2\)O\(_3\), and concluded that ceria was a basic material for SO\(_2\) adsorption. Figure 4d shows the Ti 2p XPS spectra, four peaks are formed, referred to as Ti\(^{3+}\) at 458.3 eV, 464.1 eV, and Ti\(^{4+}\) at 459.8 eV, 466.1 eV, respectively [23]. Though the Ti\(^{3+}\) concentration is pretty high, it still cannot improve the resistance to SO\(_2\) poisoning.

**Table 2.** Surface atomic distributions of the catalysts by XPS.

| Catalysts | Atomic Concentration (%) | Surface Atomic Ratio (%) |
|-----------|---------------------------|--------------------------|
| Mn | Ce or Ti | O | Mn\(^{3+}\)/Mn\(^{2+}\) + Mn\(^{4+}\) | Ce\(^{3+}\)/(Ce\(^{3+}\) + Ce\(^{4+}\)) or Ti\(^{3+}\)/(Ti\(^{3+}\) + Ti\(^{4+}\)) | O_\(α\)/O_\(α\) + O_\(β\) |
| MnO\(_x\)–CeO\(_2\)–0.7 | 5.6 | 26.4 | 68.0 | 46.42 | 41.46 | 33.4 |
| MnO\(_x\)–CeO\(_2\)–0.7-S | 5.4 | 19.7 | 70.6 | - | 25.2 | 50.3 |
| MnO\(_x\)–TiO\(_2\)–0.5 | 13.6 | 18.6 | 67.6 | 47.31 | 87.9 | 25.6 |
| MnO\(_x\)–TiO\(_2\)–0.5-S | 9.4 | 13.3 | 74.4 | - | 87.1 | 55.8 |

![Figure 6. Cont.](image-url)
which is probably one of the reasons that the MnO\textsubscript{x} catalyst has better activity than the MnO\textsubscript{x}–TiO\textsubscript{2}–0.5 catalyst in the absence of SO\textsubscript{2}.

2.5. NO + O\textsubscript{2}-TPD and In Situ DRIFTS Analyses

The adsorption behavior of the catalyst is considered a crucial step in a catalytic oxidation reaction. Therefore, NO + O\textsubscript{2}-TPD experiments were conducted to explore the NO\textsubscript{x} adsorption ability over MnO\textsubscript{x}–CeO\textsubscript{2}–0.7 and MnO\textsubscript{x}–TiO\textsubscript{2}–0.5 catalysts. As shown in Figure 7a,b, the NO and NO\textsubscript{2} curves over MnO\textsubscript{x}–CeO\textsubscript{2}–0.7 and MnO\textsubscript{x}–TiO\textsubscript{2}–0.5 catalysts are observed. For the MnO\textsubscript{x}–CeO\textsubscript{2}–0.7 catalyst, the desorption peak at about 240 °C is assigned to nitrosyl species [42], the desorption peak in the temperature range of 350–450 °C can be ascribed to the decomposition of strong adsorption species such as nitrate on catalyst surface [43]. For the MnO\textsubscript{x}–TiO\textsubscript{2}–0.5 catalyst, three major desorption peaks at 80, 180, and 320 °C are observed, which may be attributed to desorption of molecularly-adsorbed NO and NO\textsubscript{2}, nitrosyl species and desorption of nitrate species, respectively [42,44,45]. It is obvious that the total amount of NO\textsubscript{x} desorbed from MnO\textsubscript{x}–CeO\textsubscript{2}–0.7 catalyst is remarkably larger than that of the MnO\textsubscript{x}–TiO\textsubscript{2}–0.5 catalyst, indicating stronger adsorption and oxidation abilities on the surface of the MnO\textsubscript{x}–CeO\textsubscript{2}–0.7 catalyst.

In order to understand the NO\textsubscript{x} adsorption behaviors and SO\textsubscript{2} poisoning process, in situ DRIFTS measurements over MnO\textsubscript{x}–CeO\textsubscript{2}–0.7 and MnO\textsubscript{x}–TiO\textsubscript{2}–0.5 catalysts were carried out at 350 °C. Figure 7c,d shows the NO–O\textsubscript{2} co-adsorption accompanied by SO\textsubscript{2} adsorption. After introducing NO + O\textsubscript{2}, for the MnO\textsubscript{x}–CeO\textsubscript{2}–0.7 catalyst, the bands at 1593, 1566, 1540, 1242, and 1212 cm\textsuperscript{-1} are detected. All of the bands’ intensities gradually increase with the adsorption time until reaching their highest intensities and remain stable after about 40 min. The bands at 1566, 1540, and 1212–1242 cm\textsuperscript{-1} are assigned to bidentate nitrate, monodentate nitrate, and bridge nitrate, respectively [46]. A very weak band at 1593 cm\textsuperscript{-1} is due to the adsorption of NO\textsubscript{2} [47]. For the MnO\textsubscript{x}–TiO\textsubscript{2}–0.5 catalyst, the bands attributed to monodentate nitrate (1235 cm\textsuperscript{-1}), bidentate nitrate (1548 cm\textsuperscript{-1}), and bridge nitrate (1608 cm\textsuperscript{-1}) are observed [44]. The change trend of these bands’ intensities is similar to those over the MnO\textsubscript{x}–CeO\textsubscript{2}–0.7 catalyst. However, it is obvious that all of the adsorption bands’ intensities of the MnO\textsubscript{x}–TiO\textsubscript{2}–0.5 catalyst are significantly lower than those of the MnO\textsubscript{x}–CeO\textsubscript{2}–0.7 catalyst, which is probably one of the reasons that the MnO\textsubscript{x}–CeO\textsubscript{2}–0.7 catalyst has better activity than the MnO\textsubscript{x}–TiO\textsubscript{2}–0.5 catalyst in the absence of SO\textsubscript{2}.

Figure 6. XPS spectra of the catalysts. (a) Mn 2p; (b) Ce 3d; (c) O 1s; and (d) Ti 2p.
prove that the catalytic activity and resistance to SO₂ poisoning of MnOₓ–CeO₂ catalysts are better than MnOₓ–TiO₂ catalysts. Moreover, the formation of sulfate species is irreversible and sulfate species occupied the sites for NO oxidation permanently. Through the above analysis, it is consistent with XPS analysis. Moreover, the formation of sulfate species is irreversible and sulfate species almost vanishes after 60 min for the MnOₓ–CeO₂-0.7 catalyst. Whereas MnOₓ active sites are sulfated so seriously that the MnOₓ–CeO₂-0.7 catalyst has no ability to adsorb NOₓ, leading to low catalytic activity. The results confirm that SO₂ has little influence on NOₓ adsorption over the MnOₓ–CeO₂-0.7 catalyst. However, the bands’ intensities at 1608 cm⁻¹ and 1548 cm⁻¹ drop rapidly with time and the peak of monodentrate nitrate almost vanishes after 60 min for the MnOₓ–TiO₂-0.5 catalyst. The results confirm that SO₂ has little influence on NOₓ adsorption over the MnOₓ–CeO₂-0.7 catalyst, while there is strongly competitive adsorption between SO₂ and NOₓ over the MnOₓ–TiO₂-0.5 catalyst in a certain reaction time. Tang et al. [49] reported the mechanism of catalytic oxidation of NO over Mn-based catalysts that NO firstly adsorbed on Mn sites to form nitrosyls, and then were oxidized to nitrates, which decomposed to the final product, NO₂.

In the following, 100 ppm SO₂ was added to the reaction system. It can be seen from Figure 7c that a new band at 1346 cm⁻¹ appears over the MnOₓ–CeO₂-0.7 catalyst and the intensity grows with time. Similarly, the new peaks at 1346 cm⁻¹ and 1152 cm⁻¹ are also observed over the MnOₓ–TiO₂-0.5 catalyst and their intensities rise rapidly with the reaction time. The band at 1346 cm⁻¹ is due to the ν(S=O) vibration of surface sulfate species, and the band at 1152 cm⁻¹ can be ascribed to sulfate species [48]. Moreover, it can be noted that all the adsorption bands’ intensities almost remain unchanged within 10 min and the bands’ intensities of monodentrate and bidentrate nitrate slightly decrease for the MnOₓ–CeO₂-0.7 catalyst. However, the bands’ intensities at 1608 cm⁻¹ and 1548 cm⁻¹ drop rapidly with time and the peak of monodentrate nitrate almost vanishes after 60 min for the MnOₓ–TiO₂-0.5 catalyst. The results confirm that SO₂ has little influence on NOₓ adsorption over the MnOₓ–CeO₂-0.7 catalyst, while there is strongly competitive adsorption between SO₂ and NOₓ over the MnOₓ–TiO₂-0.5 catalyst in a certain reaction time. Tang et al. [49] reported the mechanism of catalytic oxidation of NO over Mn-based catalysts that NO firstly adsorbed on Mn sites to form nitrosyls, and then were oxidized to nitrates, which decomposed to the final product, NO₂.

According to the DRIFTS results and the mechanism, we further deduce that SO₂ preferentially combines with CeO₂ to form sulfate species, and MnOₓ active sites are exposed to the surface to adsorb NOₓ over the MnOₓ–CeO₂-0.7 catalyst. Whereas MnOₓ active sites are sulfated so seriously that the MnOₓ–TiO₂-0.5 catalyst has no ability to adsorb NOₓ, leading to low catalytic activity. The results are consistent with XPS analysis. Moreover, the formation of sulfate species is irreversible and sulfate species occupied the sites for NO oxidation permanently. Through the above analysis, it is sufficient to prove that the catalytic activity and resistance to SO₂ poisoning of MnOₓ–CeO₂ catalysts are better than MnOₓ–TiO₂ catalysts.

**Figure 7.** NO + O₂-TPD profiles of the MnOₓ–CeO₂-0.7 catalyst (a) and the MnOₓ–TiO₂-0.5 catalyst (b); in situ DRIFTS spectra of MnOₓ–CeO₂-0.7 catalyst (c); and MnOₓ–TiO₂-0.5 catalyst (d) at 350 °C.
3. Materials and Methods

3.1. Catalyst Preparation

A series of MnO\textsubscript{x}–CeO\textsubscript{y–x} and MnO\textsubscript{x}–TiO\textsubscript{y–y} catalysts, where x and y are the molar ratio of Mn/Ce and Mn/Ti, respectively, were prepared by homogeneous precipitation method. Take MnO\textsubscript{x}–CeO\textsubscript{y} catalysts, where for example, 13.02 g Ce(NO\textsubscript{3})\textsubscript{3}·6H\textsubscript{2}O and 7.15 g Mn(NO\textsubscript{3})\textsubscript{2} (50% solution) were firstly added to 100 mL deionized water and stirred for 2 h. Excessive urea aqueous solution was added into the mixed solution under stirring. Then, the mixed solution was stirred for 12 h at 90 °C. In order to make Mn precipitate completely, an appropriate amount of ammonia solution were added into the mixed solution until the pH value was 9.5. The precipitate was collected by filtration and washed with deionized water, followed by drying at 110 °C overnight and subsequently calcination at 500 °C for 4 h in the air atmosphere. MnO\textsubscript{x}–TiO\textsubscript{y} catalysts were prepared by similar process with MnO\textsubscript{x}–CeO\textsubscript{y–x} catalysts. The difference is that tetrabutyl titanate was firstly dissolved in ethanol. Finally, the catalysts were crushed and sieved to 40–60 mesh for activity test.

3.2. Catalytic Activity Measurement

The catalytic activity was evaluated in a quartz U-tube fixed-bed flow reactor (i.d. 13 mm) from 450–250 °C. The test data was recorded after the reaction for 40 min at each temperature. The reaction gas consisted of 400 ppm NO, 10% O\textsubscript{2}, 1% H\textsubscript{2}O, 100 ppm SO\textsubscript{2} (when used), and balanced with N\textsubscript{2}. The total flow rate was fixed at 2 L/min, which is corresponded to a gas hourly space velocity (GHSV) of 40,000 h\textsuperscript{−1}. The concentrations of NO, NO\textsubscript{2}, O\textsubscript{2}, and SO\textsubscript{2} were analyzed by a flue gas analyzer (Testo 350, Testo AG, Schwarzwald, Germany). The NO oxidation efficiency was calculated by the following equation:

\[
\text{NO oxidation (\%) = } \frac{[\text{NO}]_{\text{inlet}} - [\text{NO}]_{\text{outlet}}}{[\text{NO}]_{\text{inlet}}} \times 100\%
\]

3.3. Catalyst Characterization

The XRD patterns were recorded by powder X-ray diffractometer (XRD-600) with Cu Kα radiation (\(\lambda = 1.54 \text{ Å}\)). The samples were scanned at 2θ ranging from 10° to 80° with a scan speed of 6° min\textsuperscript{−1}. BET Surface areas of the catalysts were determined by N\textsubscript{2} adsorption-desorption isotherms at −196 °C using specific surface area and porosity analyzer (NOVA 2200, Quantachrome, Boynton Beach, FL, USA). The samples were degassed under vacuum at 300 °C for 4 h. The STEM-mapping analysis was performed using a transmission electron microscope (JEM-2100F, JEOL, Tokyo, Japan) to observe distribution of metal oxides. The surface chemical states of catalysts were tested by X-ray photoelectron spectras (PHI Quantron SXMTM, ULVAC-PHI, Kanagawa, Japan) using an Al Kα X-ray source (1486.7 eV) at 15 kV and 25 W with the binding energy calibrated by C 1s at 284.8 eV.

In situ DRIFTS investigations were performed in a quartz reactor with a FTIR spectrometer (MultiGasTM 2030 HS). Prior to the tests, the samples (200 mg) were pretreated in 10% O\textsubscript{2}/N\textsubscript{2} (500 mL/min) at 500 °C for 0.5 h followed by cooling down to 350 °C. The catalysts were exposed to 400 ppm NO, 10% O\textsubscript{2}, N\textsubscript{2} at 350 °C for 40 min, and then cooled down to 50 °C rapidly with N\textsubscript{2} purging. Subsequently, the catalysts were again heated from 50–600 °C with a rate of 10 °C/min in N\textsubscript{2}.

In situ DRIFTS investigations were performed using a Nicolet 6700 spectrometer at 4 cm\textsuperscript{−1} resolution with 64 co-added scans. Prior to adsorption experiments, the catalysts were pretreated at 500 °C for 0.5 h in N\textsubscript{2} (100 mL·min\textsuperscript{−1}) to eliminate the physisorbed water and other impurities. Then the samples were cooled down to 350 °C. After the background was subtracted, the samples were firstly exposed to certain reaction gas mixtures containing 400 ppm NO, 10% O\textsubscript{2}, 1% H\textsubscript{2}O, and balanced with N\textsubscript{2} (total flow 100 mL·min\textsuperscript{−1}) for 40 min. Subsequently, the catalysts were treated under 400 ppm NO, 10% O\textsubscript{2}, 1% H\textsubscript{2}O, 100 ppm SO\textsubscript{2}, and balanced with N\textsubscript{2} for 60 min, and the in situ DRIFTS spectra were recorded in the range of 4000–900 cm\textsuperscript{−1}.
4. Conclusions

In this work, catalytic oxidation of NO over MnO$_x$–CeO$_2$ and MnO$_x$–TiO$_2$ catalysts were studied in the absence or presence of SO$_2$. The optimal molar ratio of Mn/Ce and Mn/Ti are 0.7 and 0.5, respectively. MnO$_x$–CeO$_2$ catalyst gives the highest NO oxidation efficiency of 72% at 325 °C and the NO oxidation efficiency maintained unchanged in 5 h in the presence of 100 ppm SO$_2$ at 350 °C, while MnO$_x$–TiO$_2$ catalyst only yields 62% NO oxidation efficiency at 375 °C, and exhibits poor catalytic activity below 325 °C. MnO$_x$–CeO$_2$ catalysts exhibit better catalytic activity and resistance to SO$_2$ poisoning than that of MnO$_x$–TiO$_2$ catalysts, which is attributed that MnO$_x$–CeO$_2$ catalyst possesses higher surface area, better dispersion of MnO and stronger NO$_2$ adsorption oxidation ability, offers the abundance of Mn$^{2+}$ and more surface adsorbed oxygen, and SO$_2$ might be preferentially adsorbed to the surface of CeO$_2$ to form sulfate species, lessening the sulfation of MnO$_x$ sites.

Acknowledgments: This work has been financially supported by the National Natural Science Foundation of China (21377009).

Author Contributions: Tianle Zhu conceived and designed the experiments; Xiaolan Zeng and Xiaoyue Huo performed the experiments; Xiaolan Zeng, Xiaoyue Huo, Xiaowei Hong and Ye Sun analyzed the data; Xiaolan Zeng, Xiaoyue Huo and Tianle Zhu wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Zhu, J.; Thomas, A. Perovskite-Type Mixed Oxides as Catalytic Material for NO Removal. Appl. Catal. B Environ. 2009, 92, 225–233. [CrossRef]
2. Skalska, K.; Miller, J.S.; Ledakowicz, S. Trends in NO$_x$ abatement: A review. Sci. Total Environ. 2010, 408, 3976–3989. [CrossRef] [PubMed]
3. Guo, S.; Lv, L.; Zhang, J.; Chen, X.; Tong, M.; Kang, W.; Zhou, Y.; Lu, J. Simultaneous removal of SO$_2$ and NO$_x$ with ammonia combined with gas-phase oxidation of NO using ozone. Chem. Ind. Chem. Eng. Q. 2015, 21, 305–310. [CrossRef]
4. Dawody, J.; Skoglundh, M.; Fridell, E. The effect of metal oxide additives (WO$_3$, MoO$_3$, V$_2$O$_5$, Ga$_2$O$_3$) on the oxidation of NO and SO$_2$ over Pt/Al$_2$O$_3$ and Pt/BaO/Al$_2$O$_3$ catalysts. J. Mol. Catal. A Chem. 2004, 209, 215–225. [CrossRef]
5. Crocoll, M.; Kureti, S.; Weisweiler, W. Mean field modeling of NO oxidation over Pt/Al$_2$O$_3$ catalyst under oxygen-rich conditions. J. Catal. 2005, 229, 480–489. [CrossRef]
6. Fuji, T.; Sato, R. Characterization and activity of Pd-modified TiO$_2$ catalysts for photocatalytic oxidation of NO in gas phase. J. Hazard. Mater. 2009, 164, 542–548.
7. Kameeda, M.; Iizuka, H.; Hiratsuka, T.; Shinotsuka, N.; Arai, M. Improvement of thermal stability of NO oxidation Pt/Al$_2$O$_3$ catalyst by addition of Pd. Appl. Catal. B 2009, 90, 564–569. [CrossRef]
8. Boubnov, A.; Dahl, S.; Johnson, E.; Molina, A.P.; Simonsen, S.B.; Cano, F.M.; Helveg, S.; Lemus-Yegres, L.J.; Grunwaldt, J.D. Structure–activity relationships of Pt/Al$_2$O$_3$ catalysts for CO and NO oxidation at diesel exhaust conditions. Appl. Catal. B 2012, 126, 315–325. [CrossRef]
9. Khosravi, M.; Sola, C.; Abedi, A.; Hayes, R.E.; Epling, W.S.; Votsmeier, M. Oxidation and selective catalytic reduction of NO by propene over Pt and Pt/Pd diesel oxidation catalysts. Appl. Catal. B 2014, 147, 264–274. [CrossRef]
10. Bergrgrund, M.; Ingelsten, H.H.; Skoglundh, M.; Palmqvist, A.E.C. Influence of Synthesis Conditions for ZSM-5 on the Hydrothermal Stability of Cu-ZSM-5. Catal. Lett. 2009, 130, 79–85. [CrossRef]
11. Karlsson, H.T.; Rosenberg, H.S. Flue gas denitrification. Selective catalytic oxidation of NO to NO$_2$. Ind. Eng. Chem. Process Des. Dev. 1984, 23, 808–814. [CrossRef]
12. Kantcheva, M.; Vakkasoglu, A.S. Cobalt supported on zirconia and sulfated zirconia I: FT-IR spectroscopic characterization of the NO$_2$ species formed upon NO adsorption and NO/O$_2$ coadsorption. J. Catal. 2004, 223, 352–363. [CrossRef]
13. Qiang, W.; Park, S.Y.; Jin, S.C.; Chung, J.S. Co/K$_x$Ti$_2$O$_5$ catalysts prepared by ion exchange method for NO oxidation to NO$_2$. Appl. Catal. B 2008, 79, 101–107.
14. Irfan, M.F.; Sang, D.K.; Goo, J.H. CoO@ZrO2 based catalysts for NO oxidation and NOx reduction in fast SCR process. *Appl. Catal. B* 2008, 78, 267–274. [CrossRef]

15. Wang, H.; Wang, J.; Wu, Z.; Liu, Y. NO Catalytic Oxidation Behaviors over CoOx/TiO2 Catalysts Synthesized by Sol–Gel Method. *Catal. Lett.* 2010, 134, 295–302. [CrossRef]

16. Shang, D.; Cai, W.; Zhao, W.; Bu, Y.; Zhong, Q. Catalytic Oxidation of NO to NO2 Over Co–Ce–Zr Solid Solutions: Enhanced Performance of Ce–Zr Solid Solution by Co. *Catal. Lett.* 2014, 144, 538–544. [CrossRef]

17. Shang, D.; Zhong, Q.; Cai, W. Influence of the preparation method on the catalytic activity of Co/Zr1−xCe2O5 for NO oxidation. *J. Mol. Catal. A Chem.* 2015, 399, 18–24. [CrossRef]

18. Shang, D.; Zhong, Q.; Cai, W. High Performance of NO oxidation over Ce–Co–Ti catalyst: The interaction between Ce and Co. *Appl. Surf. Sci.* 2015, 325, 211–216. [CrossRef]

19. Yu, Y.; Zhong, Q.; Cai, W.; Ding, J. Promotional effect of N-doped CeO2 composite nanoxides synthesized by deposition-precipitation method as a superior catalyst for NO oxidation. *J. Colloid Interface Sci.* 2010, 352, 143–148. [CrossRef] [PubMed]

20. Wu, Z.; Tang, N.; Ling, X.; Yue, L.; Wang, H. MnOx/TiO2 composite nanoxides synthesized by deposition-precipitation method as a superior catalyst for NO oxidation. *J. Colloid Interface Sci.* 2015, 398, 344–352. [CrossRef] [PubMed]

21. Park, E.; Chin, S.; Jeong, J.; Jurng, J. Low-temperature NO oxidation over Mn/TiO2 nanocomposite synthesized by chemical vapor condensation: Effects of Mn precursor on the surface Mn species. *Micropor. Mesopor. Mater.* 2012, 163, 96–101. [CrossRef]

22. An, Z.; Zhuo, Y.; Xu, C.; Chen, C. Influence of the TiO2 crystalline phase of MnOx/TiO2 catalysts for NO oxidation. *Chin. J. Catal.* 2014, 35, 120–126. [CrossRef] [PubMed]

23. Li, X.; Zhang, S.; Jia, Y.; Liu, X.; Zhong, Q. Selective catalytic oxidation of NO with O2 over Ce-doped MnOx catalysts. *J. Nat. Gas Chem.* 2012, 21, 17–24. [CrossRef]

24. Zhang, M.; Li, C.; Qu, L.; Fu, M.; Zeng, G.; Fan, C.; Ma, J.; Zhan, F. Catalytic oxidation of NO with O2 over FeMnOx/TiO2: Effect of iron and manganese oxides loading sequences and the catalytic mechanism study. *Appl. Surf. Sci.* 2014, 300, 58–65. [CrossRef]

25. Liu, L.; Gao, X.; Zheng, C.; Zhu, X.; Luo, Z.; Ni, M.; Cen, K.; Liu, L.; Ni, M.; Cen, K. Study of the Promotion Effect of Iron on Supported Manganese Catalysts for NO Oxidation. *Aerosol Air Qual. Res.* 2014, 14, 1038–1046. [CrossRef]

26. Liu, Z.; Zhu, J.; Li, J.; Ma, L.; Woo, S.I. Novel Mn–Ce–Ti mixed-oxide catalyst for the selective catalytic reduction of NOx with NH3. *ACS Appl. Mater. Interfaces* 2014, 6, 14500–14508. [CrossRef] [PubMed]

27. Gao, R.; Zhang, D.; Maitarad, P.; Shi, L.; Rungrotmongkol, T.; Li, H.; Zhang, J.; Cao, W. Morphology-Dependent Properties of MnOx/ZrO2–CeO2 Nanostructures for the Selective Catalytic Reduction of NO with NH3. *J. Phys. Chem. C* 2013, 117, 10502–10511. [CrossRef]

28. Luo, S.; Zhou, W.; Xie, A.; Wu, F.; Yao, C.; Li, X.; Zuo, S.; Liu, T. Effect of MnO2 polymorphs structure on the selective catalytic reduction of NOx over NH3 with TiO2-Palygorskite. *Chem. Eng. J.* 2016, 286, 291–299. [CrossRef]

29. Hu, H.; Cai, S.; Li, H.; Huang, L.; Shi, L.; Zhang, D. Mechanistic aspects of deNOx processing over TiO2 supported Co-Mn oxide catalysts: Structure-activity relationships and in situ DRIFTs analysis. *ACS Catal.* 2015, 5, 6069–6077. [CrossRef]

30. Cai, S.; Hu, H.; Li, H.; Shi, L.; Zhang, D. Design of multi-shell Fe2O3@MnOx@CNTs for the selective catalytic reduction of NO with NH3: Improvement of catalytic activity and SO tolerance. *Nanoscale* 2016, 8, 3588–3598. [CrossRef] [PubMed]

31. Liu, Y.; Xu, J.; Li, H.; Cai, S.; Hu, H.; Fang, C.; Shi, L.; Zhang, D. Rational design and in situ fabrication of MnO2@NiCo2O4 nanowire arrays on Ni foam as high-performance monolith deNOx catalysts. *J. Mater. Chem. A* 2015, 3, 11543–11553. [CrossRef]

32. Jin, R.; Yue, L.; Yan, W.; Cen, W.; Wu, Z.; Wang, H.; Weng, X. The role of cerium in the improved SO2 tolerance for NO reduction with NH3 over Mn–Ce/TiO2 catalyst at low temperature. *Appl. Catal. B* 2014, 148–149, 582–588. [CrossRef]

33. Lu, X.; Song, C.; Jia, S.; Tong, Z.; Tang, X.; Teng, Y. Low-temperature selective catalytic reduction of NOx with NH3 over cerium and manganese oxides supported on TiO2-graphene. *Chem. Eng. J.* 2015, 260, 776–784. [CrossRef]

34. Atribak, I.; Bueno-López, A.; García-García, A.; Navarro, P.; Frías, D.; Montes, M. Catalytic activity for soot combustion of birnessite and cryptomelane. *Appl. Catal. B* 2010, 93, 267–273. [CrossRef]
35. Cimino, A.; Indovina, V. Catalytic activity of Mn$^{3+}$ and Mn$^{4+}$ ions dispersed in MgO for CO oxidation. *J. Catal.* 1974, 33, 493–496. [CrossRef]
36. Xiong, Y.; Tang, C.; Yao, X.; Zhang, L.; Li, L.; Wang, X.; Deng, Y.; Gao, F.; Dong, L. Effect of metal ions doping (M = Ti$^{4+}$, Sn$^{4+}$) on the catalytic performance of MnO$_x$/CeO$_2$ catalyst for low temperature selective catalytic reduction of NO with NH$_3$. *Appl. Catal. A Gen.* 2015, 495, 206–216. [CrossRef]
37. Larsson, P.O.; Andersson, A. Complete Oxidation of CO, Ethanol, and Ethyl Acetate over Copper Oxide Supported on Titania and Ceria Modified Titania. *J. Catal.* 1998, 179, 72–89. [CrossRef]
38. Wei, C.; Qin, Z.; Wei, Z. Solvent effects on formation of Cr-doped Ce$_{0.2}$Zr$_{0.8}$O$_2$ synthesized with cinnamic acid and their catalysis in oxidation of NO. *Chem. Eng. J.* 2014, 246, 328–336.
39. Jing, L.; Xu, Z.; Sun, X.; Shang, J.; Cai, W. The surface properties and photocatalytic activities of ZnO ultrafine particles. *Appl. Surf. Sci.* 2001, 180, 308–314. [CrossRef]
40. Wu, X.D.; Li, H.R.; Liu, S.; Weng, D. Sulfur poisoning and regeneration of MnO$_x$–CeO$_2$–Al$_2$O$_3$ catalyst for soot oxidation. *J. Rare Earths* 2012, 30, 659–664. [CrossRef]
41. Wang, W.H.; Li, W.; Guo, R.T.; Chen, Q.L.; Wang, Q.S.; Pan, W.G.; Hu, G.X. A CeFeO$_x$ catalyst for catalytic oxidation of NO to NO$_2$. *J. Rare Earths* 2016, 34, 876–881. [CrossRef]
42. Zhao, B.; Ran, R.; Wu, X.; Weng, D.; Wu, X.; Huang, C. Comparative study of Mn/TiO$_2$ and Mn/ZrO$_2$ catalysts for NO oxidation. *Catal. Commun.* 2014, 56, 36–40. [CrossRef]
43. Shen, M.; Zhao, Z.; Chen, J.; Su, Y.; Wang, J.; Wang, X. Effects of calcium substitute in LaMnO$_3$ perovskites for NO catalytic oxidation. *J. Rare Earths* 2013, 31, 119–123. [CrossRef]
44. Liu, F.; He, H.; Ding, Y.; Zhang, C. Effect of manganese substitution on the structure and activity of iron titanate catalyst for the selective catalytic reduction of NO with NH$_3$. *Appl. Catal. B* 2009, 93, 3760–3769. [CrossRef]
45. And, G.Q.; Yang, R.T. Characterization and FTIR Studies of MnO$_x$–CeO$_2$ Catalyst for Low-Temperature Selective Catalytic Reduction of NO with NH$_3$. *J. Phys. Chem. B* 2004, 108, 15738–15747.
46. Jiang, B.Q.; Wu, Z.B.; Liu, Y.; Lee, S.C.; Ho, W.K. DRIFT Study of the SO$_2$ Effect on Low-Temperature SCR Reaction over Fe-Mn/TiO$_2$. *J. Phys. Chem. C* 2010, 114, 4961–4965. [CrossRef]
47. Tang, N.; Liu, Y.; Wang, H.; Wu, Z. Mechanism Study of NO Catalytic Oxidation over MnO$_x$/TiO$_2$ Catalysts. *J. Phys. Chem. C* 2011, 115, 8214–8220. [CrossRef]

**Sample Availability:** Samples of the compounds are available from the authors.

© 2016 by the authors; licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC-BY) license (http://creativecommons.org/licenses/by/4.0/).