Effect of Ceria Doping on the Catalytic Activity and SO2 Resistance of MnOx/TiO2 Catalysts for the Selective Catalytic Reduction of NO with NH3 at Low Temperatures

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ABSTRACT

With its industrial applicability and low energy consumption, a process for implementing the NH3-SCR of NO at low temperatures is urgently needed. In this study, MnOx-CeO2/TiO2 (MnCe/Ti) catalysts doped with different amounts of Ce were prepared and experimentally examined for their NH3-SCR activity between 100°C and 400°C. Adding a small amount of Ce (at the Ce/Ti mole ratio of 0.05) elevated the exposure of Mn atoms on the catalyst surface, resulting in the highest NH3-SCR activity occurring between 100°C and 200°C (with a conversion rate of above 98% for the NO at 175°C). Further increasing the Ce content, however, diminished the catalytic performance. Moreover, the NH3-SCR of NO during oxidization or reduction atmosphere confirmed that oxygen species bound to the exposed Mn atoms were released more easily and the resulting vacancies were more likely to be replenished by O2 at low temperatures. In addition, incorporating Ce enhanced the SO2 resistance of the MnCe/Ti, mainly by inhibiting the accumulation of ammonium sulfates and the preferential sulfation of the Ce dopants.

Keywords: MnOx/TiO2; Ce modification; Low-temperature SCR; deNOx; SO2 poisoning.

INTRODUCTION

Nitrogen oxides (NOx) are one of the main air contaminants from fossil fuel combustion in power plant and vehicles. Selective catalytic reduction (SCR) of NOx with NH3 has been proven to be an efficient, reliable and economical post-combustion technology to control NOx emissions from stationary sources (Andreoli et al., 2015; Jiang et al., 2017; Yao et al., 2017). Nowadays, the vanadium-based catalysts (V2O5/TiO2 or V2O5-WO3/TiO2) are widely used as commercial catalysts for NOx-SCR process whereas these catalysts work efficiently in the narrow temperature window of 300–400°C (Chang et al., 2013; Roy et al., 2009; Jiang et al., 2017; Song et al., 2017). Auxiliary devices are normally required for heating the exhaust to achieve high NOx conversions. Such approach generally consumes additional energy and increases the greenhouse gases emissions (Sultana et al., 2012).

As an alternative to VOx, MnOx catalysts have attracted more interests due to their higher catalytic activities for NH3-SCR of NOx (Qi et al., 2003, 2004; Wang et al., 2012; Fan et al., 2018), decomposition of volatile organic compounds (VOCs) (Tian et al., 2010) and persistent organic pollutants (POPs) (Yang et al., 2013) at low temperatures (< 200°C). MnOx generally owns multiple valences (Mn4+/Mn3+/Mn2+) and contains various kinds of labile oxygen, which are necessary to accomplish a catalytic redox cycle and significant factors for its excellent low-temperature catalytic activity (Yang et al., 2013; Yu et al., 2017). However, MnOx catalysts are highly susceptible to acid gases (e.g., HCl and SO2) in exhausted gas especially at low temperatures, which restricts their wide application (Wang et al., 2015; Tang et al., 2007). Cerium oxide (CeO2) is frequently selected as a promoter (Long et al., 2000; Qiu et al., 2015) or an active component (Ma et al., 2015) of SCR catalysts for the unique redox couple Ce4+/Ce3+, which allows a flexible shift between CeO2 and Ce2O3 and promise the catalyst with great oxygen storage/release capacity under oxidizing or reducing conditions (Li et al., 2014; Jiang et al., 2018). To further improve the thermal stability, anti-poisoning ability and SCR activity of MnOx, many researchers modified MnOx catalyst with Ce (Wu et al., 2009; Lee et al., 2012; Jin et al., 2014; Li et al.,
by coupling the variable oxidation states of MnO, with Ce greatly improves the catalytic performance by coupling the variable oxidation states of MnO, with the fast redox cycle of CeO$_2$ (Lee et al., 2012; Andreoli et al., 2015). Besides, TiO$_2$ is commonly used as a catalyst supporter due to its large surface area, high thermal stability, strong mechanical strength and high sulfur resistance (Ettireddy et al., 2007). Therefore, TiO$_2$-supported Mn-Ce mixed oxide catalysts have been intensely studied with extraordinarily high activity for NO$_x$ removal (Lee et al., 2012; Nam et al., 2017).

In this work, MnCe/Ti catalysts with different doping contents of Ce were prepared by sol-gel method. The relationship between the catalyst property and activity was investigated with the help of activity evaluation combined with catalytic characterizations. Moreover, the deactivation and regeneration of the catalysts without or with O$_2$ were carried out to reveal the oxygen storage/release capability of the catalysts. Furthermore, the SO$_2$ resistance of MnCe/Ti catalysts was also evaluated. This study provides basic data and guidelines for future development of low-temperature SCR catalyst.

MATERIALS AND METHODS

Catalyst Preparation and Characterization

The tested MnCe/Ti catalysts were prepared by sol-gel method. Firstly, tetrabutyl titanate (0.2 mol), acetic acid (30 mL) were mixed in ethanol (30 mL) and the mixture was stirred and then dripped into the mixed solution of manganese nitrate, cerium nitrate, nitric acid (5 mL) and deionized water (15 mL) to obtain the yellow homogeneous sol. Then the sol transformed into gel and dried at 105°C for 8 h to get xerogel. The obtained xerogel was crushed to 40–60 mesh, and calcined at 500°C with a heating rate of 10°C min$^{-1}$ for 4 h in air. For comparison, MnO$_2$/TiO$_2$ (Mn/Ti) sample without Ce was synthesized by the same procedure. The catalysts were then characterized using powder X-ray diffraction analysis (XRD, XRD-6100; Shimadzu), N$_2$-physisorption with Brunauer-Emmet-Teller analysis (BET; ASAP-2020; Micromeritics), X-ray photoelectron spectroscopy (XPS; ESCALAB 250; Thermo Fisher Scientific), hydrogen temperature-programmed reduction (H$_2$-TPR; Auto Chem II 2920) and ammonia temperature-programmed desorption (NH$_3$-TPD; Auto Chem II 2920). The notation and physicochemical properties of the catalysts are listed in Table 1.

Table 1. The structure properties of Mn/Ti and MnCe/Ti catalysts.

<table>
<thead>
<tr>
<th>Notation</th>
<th>Component molar ratio Mn/Ti</th>
<th>S$_{\text{BET}}$a (m$^2$ g$^{-1}$)</th>
<th>V$_{\text{micro}}$a (cm$^3$ g$^{-1}$)</th>
<th>V$_{\text{tot}}$a (cm$^3$ g$^{-1}$)</th>
<th>D$a$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn$_{0.15}$/Ti</td>
<td>0.15</td>
<td>/</td>
<td>78.6</td>
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<td>0.146</td>
</tr>
<tr>
<td>Mn$<em>{0.15}$/Ce$</em>{0.05}$/Ti</td>
<td>0.15</td>
<td>0.05</td>
<td>112.4</td>
<td>0.034</td>
<td>0.162</td>
</tr>
<tr>
<td>Mn$<em>{0.15}$/Ce$</em>{0.1}$/Ti</td>
<td>0.15</td>
<td>0.10</td>
<td>115.3</td>
<td>0.036</td>
<td>0.176</td>
</tr>
<tr>
<td>Mn$<em>{0.15}$/Ce$</em>{0.15}$/Ti</td>
<td>0.15</td>
<td>0.15</td>
<td>138.8</td>
<td>0.040</td>
<td>0.184</td>
</tr>
</tbody>
</table>

$^a$ Structure parameters of the catalysts got by N$_2$ adsorption-desorption; S$_{\text{BET}}$: BET surface area; V$_{\text{micro}}$: micropore volume; V$_{\text{tot}}$: total pore volume; D: average pore diameter.

Effect of Ce Doping on NH$_3$-SCR Activity of Mn/Ti Catalyst

A significant impact of Ce doping on Mn/Ti catalytic activity towards NH$_3$-SCR of NO is observed in Fig. 1. The highest NO conversion for Mn$_{0.15}$/Ti catalyst achieved at 200°C is merely 70%. Optimum condition occurs at Mn$_{0.15}$/Ce$_{0.05}$/Ti catalyst, above 98% of NO can be abated even at 175°C. Further increase the Ce/Ti mole ratios to 0.1 or 0.15 reduces the catalytic activity of MnCe/Ti catalysts in the low-temperature range (< 200°C). Whereas, opposite trend is obtained above 200°C. For all the catalysts, NO conversion declines at high temperatures, while the turning point is postponed with the addition of Ce. Therefore, Ce addition not only improves the low-temperature catalytic performance of Mn/Ti catalysts but also broadens their active temperature window.

NH$_3$ oxidation with O$_2$ with or without the catalysts (Fig. 1) was implemented to ensure the assumption that the decline of NO conversion at high temperatures possibly attributes to the over-oxidation of the adsorbed NH$_3$ into NO$_x$. The NH$_3$ oxidation is barely observed in absence of catalyst and the presence of Mn$_{0.15}$/Ce$_{0.05}$/Ti and Mn$_{0.15}$/Ce$_{0.1}$/Ti catalysts.
facilitate the oxidation of NH$_3$ in the temperature range between 200–400°C. The higher NO$_x$ yield from NH$_3$ oxidation on Mn$_{0.15}$Ce$_{0.05}$/Ti catalyst coincides with its lower catalytic activity at high temperatures, confirming the over-oxidation of the adsorbed NH$_3$ is the main reason for the reducing NO conversions at the temperature above 200°C.

**Effect of Ce Doping on Catalyst Characterizations**

**XRD and BET Analysis**

Several catalyst characterizations were conducted to gain insight into the multiple influences of the Ce addition on the structures and properties of the catalysts. The XRD patterns of Mn/Ti and MnCe/Ti catalysts are shown in Fig. 2. The diffraction peaks corresponding to anatase rather than rutile TiO$_2$ appear in all the tested catalysts. The MnO$_2$ at 37.2° (PDF#31-0820) and Mn$_2$O$_3$ at 55.2° (PDF#41-1422) are observed in Mn$_{0.15}$/Ti catalysts (Tang et al., 2018). No obvious reflections assigned to the fluorite structure of CeO$_2$ can be observed for MnCe/Ti catalysts, except for a small peak at around 33.3°, which is attributed to (200) lattice plane of CeO$_2$ (Mao et al., 2015; Deng et al., 2016). Other reflections of CeO$_2$ are likely to be overlapped by the diffraction peaks of anatase TiO$_2$. In addition, MnCe/Ti catalysts also involve Ce$_2$O$_3$ showing a small diffraction peak at 30.2° (PDF#23-1048). The diffraction peaks belonging to Ce$_2$O$_3$ and CeO$_2$ become more intense and shift to higher Bragg angle when Ce/Ti mole ratio increases. The former occurs because the formed Ce$_2$O$_3$ microcrystals grow and then cluster on TiO$_2$ surface with the increase of Ce/Ti mole ratio. The latter implies that the surrounding of Ce atom has been changed in combination with Mn atom. That is because the Mn atom radius (1.32 Å) is smaller than that of Ce (1.82 Å). The Mn atoms can be embedded in CeO$_2$ lattice surface (when Ce/Ti mole ratio = 0.05) or enter into CeO$_2$ lattice to replace some of the locations originally belonging to Ce atoms to form MnCe$_x$ solid solution (when Ce/Ti mole ratio = 0.1, 0.15). These interactions between Mn and Ce atoms cause the shrinkage and distortion of CeO$_2$ lattice and result in such shifts of Ce$_2$O$_3$ and CeO$_2$ diffraction peaks in MnCe/Ti catalysts. Meanwhile, the signals corresponding to Mn species disappear when Ce is added. It is reasonable to believe that the phase structure of MnO$_x$ is changed to amorphous phase after doping Ce, due either to the high dispersion of Mn species on catalyst support, or to the incorporation of partial Mn atoms to the fluorite structure of CeO$_2$ (Dai et al., 2012). Both the above effects of Ce addition may be conducive to improve the catalytic activity of MnCe/Ti catalysts for NH$_3$-SCR of NO at low temperature.

As known, the SCR reaction is normally initiated with the adsorption of NH$_3$ (Kijlstra et al., 1997), hence the adsorption capability of the catalysts is significantly important for NO abatement. It can be noticed in Table 1 that the SBET, V$_{tot}$ and $V_{micro}$ values rise with the increase of Ce/Ti mole ratios and the D values are reduced accordingly. Literatures (Mastral et al., 2000; Murillo et al., 2004) have put forward that the gaseous reactant physisorption takes place mainly in the pores with the diameter close to the molecular size of the gaseous reactant, so that the adsorption potential is higher due to the proximity of the pore walls. Therefore, larger surface area, smaller average pore diameter and more abundant micropores (closer to the molecule sizes of NH$_3$ and NO which are smaller than 0.5 nm) contribute to the higher physisorption ability of MnCe/Ti catalysts. Mn$_{0.15}$Ce$_{0.15}$/Ti catalyst with the highest physisorption ability exhibits the lowest catalytic activity at low temperature instead, implying that the physically adsorbed NH$_3$ might not be the main active species for further NO reduction. The chemisorption of NH$_3$ by surface acid sites forming activated transient state is probably available in SCR reaction (Ramis et al., 1995).
NH$_3$-TPD and H$_2$-TPR Analysis

NH$_3$-TPD experiments were carried out to evaluate the surface acid property (i.e., the amount and the strength) of the catalyst (Fig. 3(a)), which influences the chemisorption and activation of NH$_3$ (Li et al., 2014). There are two NH$_3$ desorption peaks exists in the NH$_3$-TPD profile of all catalysts at 50–500°C. The NH$_3$ species anchored on Brønsted acidic sites are less thermally stable than the ones bonded to Lewis acidic sites (Li et al., 2014; Nam et al., 2017). Hence, the peaks at around 125°C and 300°C refer to the desorptions of the NH$_3$ adsorbed on weak Brønsted acid sites and strong Lewis acid sites (Chmielarz et al., 2003), respectively. Many scholars held the opinion that the ammonium coordinated to Lewis acid sites (NH$_3$) are effective for NO reduction (Peña et al., 2004; Wu et al., 2007); ammonium ions adsorbed on Brønsted acid sites (NH$_3^+$) act as the ‘reservoir’ of the actively coordinated NH$_3$ species (i.e., NH$_3$(ads) + H$^+$ = NH$_4^+(ads)$ = NH$_3$(ads) + H$^+$) and influence the SCR reaction indirectly (Qiu et al., 2015). As seen from Fig. 3(a), the amounts of both Brønsted acid sites and Lewis acid sites of Mn/Ti catalyst are increased with the introduction of Ce. Besides, Ce addition enhances the strength of the Lewis acid sites on MnCe/Ti catalyst surface, for all the desorption peaks of the strongly adsorbed NH$_3$ species are shifted to higher temperature. The amount and strength of surface acid sites decrease following the order Mn$_{0.15}$Ce$_{0.05}$/Ti > Mn$_{0.15}$Ce$_{0.1}$/Ti > Mn$_{0.15}$Ce$_{0.15}$/Ti > Mn$_{0.15}$/Ti, which exactly matches their catalytic activities’ variation tendency below 200°C, confirming that the surface acid property of the catalyst is one of the decisive factors for low-temperature NH$_3$-SCR activity.

Three reduction peaks on the TPR profile of Mn$_{0.15}$/Ti catalyst are observed in Fig. 3(b). The first two peaks at relatively low temperatures correspond to the reduction from MnO$_2$ or Mn$_2$O$_3$ to Mn$_3$O$_4$ and the last one centered at around 600°C refers to the further reduction from Mn$_3$O$_4$ to MnO (Liang et al., 2008; Andreoli et al., 2015). With the addition of Ce, the reduction peaks of MnCe/Ti catalysts become larger and start at lower-temperature regions. The former indicates the oxygen storage capacities of the catalysts are enlarged and the latter manifests the oxygen atoms in MnCe/Ti catalysts are easier to be offered to react with H$_2$. According to the starting position of the first reduction peak, the redox ability of the catalysts decreases in the order of Mn$_{0.15}$Ce$_{0.05}$/Ti > Mn$_{0.15}$Ce$_{0.1}$/Ti > Mn$_{0.15}$Ce$_{0.15}$/Ti > Mn$_{0.15}$/Ti, which agrees well with their NO conversions below 200°C. Mn$_{0.15}$Ce$_{0.05}$/Ti catalyst has excellent redox ability because the Mn atoms are more likely to be embedded in the CeO$_2$ microcrystal surface and hence highly dispersed. As the Ce/Ti mole ratios increase, the scattered reduction peaks tend to merge into one peak as shown in Fig. 3(b), implying the incorporation of Mn atoms into the CeO$_2$ lattice. The relatively low redox ability of the Mn$_{0.15}$Ce$_{0.1}$/Ti and Mn$_{0.15}$Ce$_{0.15}$/Ti catalysts is possibly due to the incorporation of Mn atoms into the bulk CeO$_2$ that reduces the surface exposed Mn atoms in consequence.

It is noteworthy that an opposite relationship between the redox ability of catalyst and the NO conversion at high-temperature region (> 200°C) is observed (Fig. 1). It possibly attributes to the excessively high redox ability of the catalysts causes the over-oxidation of the adsorbed NH$_3$ into NOx.

Inspired from the above results, catalyst with proper redox ability is preferred particularly at high temperatures so that over-oxidation of NH$_3$ can be alleviated or even avoided.

XPS Analysis

XPS was employed to investigate the surface element concentrations and oxidation states of the catalysts. High-resolution spectra from Mn 2p, Ce 3d, and O 1s are displayed in Fig. 4. The Mn 2p spectrum (Fig. 4(a)) suggests Mn species exist in a mixture of oxidation states on all the tested catalysts. According to the fitting results of XPS spectra, the Mn 2p$_{3/2}$ signal can be deconvoluted into three characteristic
peaks, assigned to Mn$^{4+}$ (643.4 eV), Mn$^{3+}$ (641.9 eV) and Mn$^{2+}$ (640.7 eV) respectively (Yu et al., 2014). The Mn 2p$\,_{1/2}$ signal also shows corresponding peaks from the above three Mn species in the bonding energy range 870–930 eV. The u’ and v’ peaks can be assigned to Ce$^{3+}$ species, while the u”, u”, u”, v”, v”, and v’’ peaks belong to Ce$^{4+}$ species. Table 2 illustrates that the Mn$_{0.15}$Ce$_{0.05}$/Ti catalyst with the best catalytic performance has the most relative contents of surface Mn$^{4+}$ and Ce$^{3+}$ ions. It can be attributed to the addition of a small amount of Ce (Ce/Ti = 0.05) that prevents Mn atoms from entering into the bulk TiO$_2$ and leads to the high dispersion of Mn atom on catalyst surface (Dai et al., 2011; Yao et al., 2017). The highly dispersed surface Mn atoms are more likely to be oxidized to high-valence state (+4). Meanwhile, the electron transformation between Ce atom and the exposed Mn atom shifts the equilibrium “Mn$^{3+}$ + Ce$^{4+}$↔Mn$^{4+}$ + Ce$^{3+}$” (Ding et al., 1998; Qi et al., 2004; Xiong et al., 2015) to the right and increases the Mn$^{4+}$ and Ce$^{3+}$ ions on catalyst surface. The former introduces more surface reactive oxygen species and has favorable redox properties for NO conversion (labeled as O$_\alpha$) and surface lattice oxygen (labeled as O$_\beta$) (Li et al., 2011; Meng et al., 2015). Hereinto, the O$_\alpha$ referred to the oxygen free radicals (e.g., O, O– and O$_2$–) are weakly bonded to surface metal atoms and easier to be offered in oxidation-reduction reaction. Therefore, the highest concentration ratio of O$_\alpha$/(O$_\alpha$+ O$_\beta$) in Mn$_{0.15}$Ce$_{0.05}$/Ti catalyst contributes to its best low-temperature catalytic activity towards NO conversion. Besides, O$_\beta$ peak is also observed shifting to higher binding energy in Mn$_{0.15}$Ce$_{0.05}$/Ti catalyst, suggesting that adding a small amount of Ce also weakens the interaction between metal atoms and O$_\beta$, and makes the O$_\beta$ easier to be offered to oxidize reactants. Further increase the Ce/Ti mole ratios raises the total surface oxygen atomic contents from 74.7% (Mn$_{0.15}$Ce$_{0.05}$/Ti) to 76.3% (Mn$_{0.15}$Ce$_{0.05}$/Ti) and 76.4% (Mn$_{0.15}$Ce$_{0.15}$/Ti), but the O$_\alpha$/(O$_\alpha$+ O$_\beta$) values as well as the O$_\beta$ binding energies of Mn$_{0.15}$Ce$_{0.1}$/Ti and Mn$_{0.15}$Ce$_{0.15}$/Ti catalysts are dropped instead. This phenomenon indicates that Ce addition enlarges the oxygen storage capacity of the catalyst, while the mobility of the oxygen atom relates with the exposure of Mn atom. It agrees well with the result of ref. (Lee et al., 2012), the authors believed that such an exposed Mn atom shows a direct correlation with the activity of MnCe/Ti catalyst.

The above assumption that Ce addition amount influences the exposure of Mn atom can be further evidenced by
Fig. 4. (a) Mn 2p, (b) Ce 3d and (c) O 1s XPS spectra of the Mn/Ti and MnCe/Ti catalysts.
comparing the actual Mn/(Ce + Ti) and Ce/(Mn + Ti) mole ratios with their theoretical values (Table 2). Accordingly, an assumption model is proposed in Fig. 5. As for Mn0.15/Ti catalyst, the actual Mn/(Ce + Ti) mole ratio (0.13) is slightly lower than the theoretical value (0.15) due either to the Mn atoms entering the bulk TiO2 or the presence of MnO2 crystals (in line with the XRD patterns) resulting in the poor distribution of the Mn atoms (Fig. S5a). After adding a small amount of Ce (Ce/Ti = 0.05), the actual Ce/(Mn + Ti) value of Mn0.15Ce0.05/Ti catalyst (0.03) is close to the theoretical mole ratio (0.04); the actual Mn/(Ce + Ti) mole ratio of Mn0.15Ce0.05/Ti catalyst (0.17) become clearly larger than its theoretical value (0.14). It indicates that more Mn atoms are exposed and better dispersed on catalyst surface (in agreement with XRD patterns), because the highly dispersed CeO2 microcrystal prevents the Mn atoms from entering into the bulk TiO2 (Fig. S5b). As for Mn0.15Ce0.1/Ti and Mn0.15Ce0.15/Ti, their actual Ce/(Mn + Ti) values (0.06 and 0.07) are greatly lower than their theoretical values (0.09 and 0.13). Considering the radius of Ce atom (1.82 Å) is larger than that of Ti (1.45 Å), it is difficult for Ce atom getting into TiO2 lattice. So, it is reasonable to believe that the lower actual Ce/(Mn + Ti) values of Mn0.15Ce0.1/Ti and Mn0.15Ce0.15/Ti catalysts result from the agglomeration of CeO2 crystals (in line with XRD patterns) on TiO2 surface which causes the poor dispersion of CeO2. Coincidentally, both the actual Mn/(Ce + Ti) mole ratio values of Mn0.15Ce0.1/Ti and Mn0.15Ce0.15/Ti (0.07) are obviously lower than their theoretical values (0.14 and 0.13). It coincides with the conjecture that the exposed surface Mn atoms are significantly decreased due to the incorporation of Mn atom into the bulk of CeO2 crystal which agglomerates on the TiO2 surface as shown in Fig. S5c.

NH3-SCR in Oxygen-rich and Oxygen-free Atmosphere

NH3-SCR of NO under oxidizing/reducing conditions were carried out to investigate the oxygen storage/release capability of the Mn/Ti and MnCe/Ti catalysts. The experimental result shown in Fig. 6 demonstrates that NH3-SCR reaction still takes place in oxygen-free atmosphere and indicates that the reactive oxygen species in catalyst participates in NH3-SCR of NO. Ce addition can alleviate the deactivation of the catalysts in oxygen-free atmosphere effectively and the NO conversion of Mn0.15Ce0.05/Ti catalyst in oxygen-free atmosphere maintains at around 80% at 200°C for even 10 hours as shown in the inset of Fig. 6. The less deactivation in Mn0.15Ce0.05/Ti catalyst probably because there are abundant exposed Mn4+ ions on Mn0.15Ce0.05/Ti catalyst surface which can activate the adsorbed NH3(ads) (Reactions (3)–(4)); meanwhile release sufficient reactive oxygen species for NO(ads) oxidation (Reaction (5)) in oxygen-free atmosphere. However, the reoxidation of the reduced Mn atom (Reaction (6)) is blocked in oxygen-free atmosphere and thus results in the deactivation of catalysts.

$$\text{Mn}^{4+} + \text{NH}_3(\text{ads}) \rightarrow \text{Mn}^{3+} + -\text{NH}_2 + \text{H}^+ \quad (3)$$

$$\text{Mn}^{4+} + -\text{NH}_2 \rightarrow \text{Mn}^{3+} + -\text{NH} + \text{H}^+ \quad (4)$$

$$\text{Mn}^{4+} + \text{O} + \text{NO}_{(\text{ads})} \rightarrow \text{Mn}^{3+} + \text{NO}_2(\text{ads}) \quad (5)$$

<table>
<thead>
<tr>
<th>Samples</th>
<th>Mn (at %)</th>
<th>Mn4+ (%)</th>
<th>Mn3+ (%)</th>
<th>Mn2+ (%)</th>
<th>Ce (at %)</th>
<th>Ce4+ (%)</th>
<th>Ce3+ (%)</th>
<th>Ti (at %)</th>
<th>Mn/(Ce + Ti)b</th>
<th>Ce/(Mn + Ti)b</th>
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<tr>
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<td>3.7</td>
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<td>48.5</td>
<td>25.5</td>
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<td>20.8</td>
<td>0.17</td>
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<tr>
<td>Mn0.15Ce0.05/Ti</td>
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<td>41.7</td>
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<tr>
<td>Mn0.15Ce0.15/Ti</td>
<td>1.6</td>
<td>29.7</td>
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<td>22.2</td>
<td>76.4</td>
<td>25.7</td>
<td>0.22</td>
<td>20.5</td>
<td>0.07 (0.13)</td>
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</table>

a The surface element compositions of Mn, Ce and O estimated by XPS analysis.

b The actual Mn/(Ce + Ti) and Ce/(Mn + Ti) mole ratios obtained from the XPS results.

c The theoretical Mn/(Ce + Ti) and Ce/(Mn + Ti) mole ratios calculated according to the preparation processes.

Table 2. The surface atomic concentration and valence state distribution of Mn/Ti and MnCe/Ti catalysts.
As soon as O2 is reinjected into the reaction atmosphere, the NO conversions rise again in all catalysts within 10 min. That is because the oxygen vacancies can be replenished with O2 by reoxidizing the Mn atoms from +3 to +4 (Reaction (6)). In addition, the NO2(g) generated from the oxidation of NO with O2 also help reoxidize the reduced metal atom (Reaction (7)). As seen from Fig. 6, the deactivated Mn0.15Ce0.05/Ti catalyst can be completely regenerated at 200°C, while the deactivation in other catalysts seems to be irreversible under this condition. That is because the exposed Mn atoms embedded in the surface of CeO2 microcrystal contributes to a flexible redox cycle between Mn4+ and Mn3+. This phenomenon supports the result that the oxygen release/storage capability of Mn0.15Ce0.05/Ti catalyst is higher than those of the other two catalysts, which is another determining factor for its high NH3-SCR activity at low temperatures.

**NH3-SCR in SO2-containing Atmosphere**

Temperature-dependent effect of SO2 on NH3-SCR of NO over Mn0.15Ce0.05/Ti catalyst is obtained in Fig. 7(a). As observed, SO2 suppresses the SCR performance at 100–275°C. Nevertheless, still more than 75% NO conversion is provided by Mn0.15Ce0.05/Ti catalyst after SO2 poisoning at 175°C and that is even higher than the optimum value of Mn0.15/Ti catalyst obtained in SO2-free atmosphere. This result implies that Ce modification can enhance the SO2 resistance of Ce-modified Mn/Ti catalyst at low temperature, which coincides with the observations reported in previous studies (Zhu et al., 2001; Wang et al., 2015; Li et al., 2016). The improvement of Ce addition on SO2 resistance of Ce-modified Mn/Ti catalyst attributes to two main reasons. Firstly, Ce doping inhibits the depositions of ammonia sulfites and sulfates that would block the active sites and affect the oxidation properties of the catalyst (Wu et al., 2009; Jin et al., 2014; Wang et al., 2015). Secondly, surface sulfates are preferentially
formed on Ce dopants in presence of SO\textsubscript{2}, which lessens the sulfation of the main active phase (MnO\textsubscript{x}) (Jin et al., 2014; Ma et al., 2019). On the contrary, SO\textsubscript{2} presents a positive effect on NH\textsubscript{3}-SCR reaction over Mn\textsubscript{0.15}Ce\textsubscript{0.05}/Ti catalyst above 300°C, which is in good agreement with Ma et al. (2013)'s observations. That is because the depositions of ammonia sulfites and sulfates are reduced and the formation of metal sulfates (e.g., Ce\textsubscript{2}(SO\textsubscript{3})\textsubscript{3} or Ce(SO\textsubscript{4})\textsubscript{2}) is facilitated at high temperatures (Ma et al., 2013; Wang et al., 2015). The latter reduces the oxidation ability of Mn\textsubscript{0.15}Ce\textsubscript{0.05}/Ti catalyst and thereby minimizes the over-oxidation of NH\textsubscript{3}, which is the main side reaction (in Section 3.1) responsible for the reduction of SCR activity at high temperatures (Xie et al., 2004).

The transient response of SO\textsubscript{2} poisoning was also carried out on Mn\textsubscript{0.15}Ce\textsubscript{0.05}/Ti catalyst at 200°C and the result is shown in Fig. 7(b). The NO conversion declines from 96% to 65% within 20 min and then remains stable for 300 min after introducing 200 ppm SO\textsubscript{2}. As mentioned above, the sulfation is preferentially happened on Ce dopants which disrupts the Ce\textsuperscript{4+}/Ce\textsuperscript{3+} redox cycle. As such, more sulfates have been stored in ceria; less ammonia sulfites and sulfates could be further formed to cover the catalyst surface (Jin et al., 2014). Besides, Jin et al. (2014) proposed that Ce doping could reduce the thermal stability of the ammonia sulfites and sulfates on MnCe/Ti catalyst based on their theoretical calculation. For this reason, the deposition and decomposition of ammonia sulfites and sulfates on catalyst surface can easily reach a balance and hence the long-term stable SCR activity of Mn\textsubscript{0.15}Ce\textsubscript{0.05}/Ti can be achieved in presence of SO\textsubscript{2}. As soon as SO\textsubscript{2} is removed off, NO conversion can be restored to 82% but is still slightly lower than the original
one. The SCR activity can be mostly recovered after shutting SO\textsubscript{2} off, because the ammonia sulfites and sulfates can be easily removed from the Mn\textsubscript{0.15}Ce\textsubscript{0.05}/Ti surface. However, the deactivation caused by the sulfation of Ce dopants is irreversible under this condition that explains the difference between the restored and the original SCR performance. Therefore, thermal treatment at higher temperature (> 350°C) is suggested for it has the possibility to fully recover the catalyst activity after SO\textsubscript{2} poisoning (Wang et al., 2015).

CONCLUSION

Incorporating Ce significantly enhances the activity of Mn/Ti catalysts, with the maximum effect being exhibited by catalysts possessing Mn/Ti and Ce/Ti ratios of 0.15 and 0.05, respectively. The catalytic activity of the MnCe/Ti catalyst is directly correlated with the number of exposed Mn atoms, which increases with the addition of a small amount of Ce (Ce/Ti = 0.05), thus improving the oxygen storage/release capability of the catalyst. However, the presence of excessive CeO\textsubscript{2} reduces the exposure of the surface Mn due to the incorporation of the latter into the bulk CeO\textsubscript{2}, thereby decreasing the catalytic activity of the Mn\textsubscript{0.15}Ce\textsubscript{0.05}/Ti and Mn\textsubscript{0.15}Ce\textsubscript{0.15}/Ti catalysts at low temperatures. The addition of Ce can also increase the SO\textsubscript{2} resistance of Mn/Ti catalysts by (1) inhibiting the deposition of ammonia sulfites and sulfates on the catalyst surface and (2) reducing the sulfation of the main active phase (MnO\textsubscript{2}). Furthermore, SO\textsubscript{2} facilitates the SCR of Mn\textsubscript{0.15}Ce\textsubscript{0.05}/Ti catalysts above 300°C because more surface sulfates are preferentially formed on the Ce dopant, which suppresses the over-oxidation of NH\textsubscript{3} at high temperatures by reducing the oxidation ability of the catalyst.

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