Effect of ceria doping on catalytic activity and SO\textsubscript{2} resistance of MnO\textsubscript{x}/TiO\textsubscript{2} catalysts for selective catalytic reduction of NO with NH\textsubscript{3} at low temperature

Qiulin Wang\textsuperscript{1,2}, Jianjian Zhou\textsuperscript{1}, Jianchao Zhang\textsuperscript{1}, Hao Zhu\textsuperscript{1}, Yuheng Feng\textsuperscript{3,*}, Jing Jin\textsuperscript{1,2}

\textsuperscript{1} School of Energy and Power Engineering, University of Shanghai for Science and Technology, Shanghai 200093, China
\textsuperscript{2} Shanghai Key Laboratory of Multiphase Flow and Heat Transfer in Power Engineering, University of Shanghai for Science and Technology, Shanghai 200093, China
\textsuperscript{3} Thermal and Environmental Engineering Institute, Tongji University, Shanghai 200092, China

Abstract Low temperature NH\textsubscript{3}-SCR of NO is strongly needed due to its availability in industrial furnaces and energy-conserving feature. MnO\textsubscript{x}-CeO\textsubscript{2}/TiO\textsubscript{2} (MnCe/Ti) with different Ce doping contents were prepared and their catalytic activities for NH\textsubscript{3}-SCR under 100-400 \degree C were experimentally examined. The results suggest that addition a small amount of Ce (Ce/Ti mole ratio=0.05) improves the exposure of Mn atoms on catalyst surface and exhibits highest NH\textsubscript{3}-SCR activity at 100-200 \degree C, on which above 98\% of NO is abated at 175 \degree C. Further increase the Ce contents decreases the catalyst performance instead. Moreover, NH\textsubscript{3}-SCR of NO under oxidizing or reducing conditions confirms the oxygen species bounded to the exposed Mn atoms are easier to be released and the resulted oxygen vacancies are more likely to be replenished by O\textsubscript{2} at low temperature. In addition, the SO\textsubscript{2} resistance of MnCe/Ti is also enhanced by Ce modification, mainly due to the inhibition of the accumulation of ammonium sulfates and the

\*Corresponding author. Email address: fengyh@tongji.edu.cn Tel.: +86 21 65985009; Fax: +86 21 65982786
preferential sulfation of the Ce dopants.

**Keywords:** MnOₓ/TiO₂; Ce modification; Low temperature SCR; deNOₓ; SO₂ poisoning
1. Introduction

Nitrogen oxides (NO\textsubscript{x}) are one of the main air contaminants from fossil fuel combustion in power plant and vehicles. Selective catalytic reduction (SCR) of NO\textsubscript{x} with NH\textsubscript{3} has been proven to be an efficient, reliable and economical post-combustion technology to control NO\textsubscript{x} emissions from stationary sources (Andreoli \textit{et al.}, 2015; Yao \textit{et al.}, 2017; Jiang \textit{et al.}, 2017). Nowadays, the vanadium-based catalysts (V\textsubscript{2}O\textsubscript{5}/TiO\textsubscript{2} or V\textsubscript{2}O\textsubscript{5}-WO\textsubscript{3}/TiO\textsubscript{2}) are widely used as commercial catalysts for NH\textsubscript{3}-SCR process whereas these catalysts work efficiently in the narrow temperature window of 300-400 °C (Chang \textit{et al.}, 2013; Roy \textit{et al.}, 2009; Jiang \textit{et al.}, 2017; Song \textit{et al.}, 2017). Auxiliary devices are normally required for heating the exhaust to achieve high NO\textsubscript{x} conversions. Such approach generally consumes additional energy and increases the greenhouse gases emissions (Sultana \textit{et al.}, 2012).

As an alternative to VO\textsubscript{x}, MnO\textsubscript{x} catalysts have attracted more interests due to their higher catalytic activities for NH\textsubscript{3}-SCR of NO\textsubscript{x} (Wang \textit{et al.}, 2012; Fan \textit{et al.}, 2018; Qi \textit{et al.}, 2003; Qi \textit{et al.}, 2004), decomposition of volatile organic compounds (VOCs) (Tian \textit{et al.}, 2010) and persistent organic pollutant (POPs) (Yang \textit{et al.}, 2013) at low temperatures (< 200 °C). MnO\textsubscript{x} generally owns multiple valences (Mn\textsuperscript{4+}/Mn\textsuperscript{3+}/Mn\textsuperscript{2+}) 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 \textit{et al.}, 2013; Yu \textit{et al.}, 2017). However, MnO\textsubscript{x} catalysts are highly susceptible to acid gases (e.g. HCl and SO\textsubscript{2}) in exhausted gas especially at low
temperatures, which restricts their widely application (Wang et al., 2015; Tang et al., 2007).

Cerium oxide (CeO$_2$) is frequently selected as a promoter (Qiu et al., 2015; Long et al., 2000) or an active component (Ma et al., 2015) of SCR catalysts for the unique redox couple Ce$^{4+}$/Ce$^{3+}$, which allows a flexible shift between CeO$_2$ and Ce$_2$O$_3$ 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 MnO$_x$, many researchers modified MnO$_x$ catalyst with Ce (Wu et al., 2009; Jin et al., 2014; Kwon et al., 2015; Andreoli et al., 2015; Li et al., 2014; Tang et al., 2016; Lee et al., 2012). Expected results have been obtained that modification of MnO$_x$ with Ce greatly improves the catalytic performance by coupling the variable oxidation states of MnO$_x$ with the fast redox cycle of CeO$_2$ (Andreoli et al., 2015; Lee et al., 2012). 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\textsubscript{2} were carried out to reveal the oxygen storage/release capability of the catalysts. Furthermore, the SO\textsubscript{2} resistance of MnCe/Ti catalysts was also evaluated. This study provides basic data and guidelines for future development of low temperature SCR catalyst.

2. Materials and methods

2.1 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 homogenous 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\textsuperscript{-1} for 4 h in air. For comparison, MnO\textsubscript{x}/TiO\textsubscript{2} (Mn/Ti) sample without Ce was synthesized by the same procedure. The catalysts were then characterized using X-ray Diffraction Analyzer (Shimadzu, Japan), N\textsubscript{2}-Physisorption with an automated Brunauer-Emmet-Teller (BET) and pore analyzer (ASAP2020), X-ray Photoelectron Spectroscope (XPS, ESCALAB-250, Thermo Fisher Scientific), Hydrogen Temperature Programmed Reduction (H\textsubscript{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.

2.2 Catalytic activity measurement

The NH$_3$-SCR of NO was carried out in a tubular quartz furnace (inner diameter \(\times\) length = 20 mm \(\times\) 500 mm) reactor, in which the catalyst powder was vertically loaded with the aid of a quartz screen. The catalyst was heated to the desired temperatures using an electric furnace under ambient pressure. NO (300 ppm), NH$_3$ (300 ppm), SO$_2$ (200 ppm when added), O$_2$ (0% and 3%) and N$_2$ (as balance) were fed to simulated flue gas. The total gas flow passing through 2 ml catalyst was controlled at 1000 ml/min by mass flow controllers, corresponding to a gas hourly space velocity (GHSV) of 30000 h$^{-1}$. Each activity test operated after maintaining in steady condition for 1h and repeated experiments were conducted to ensure the data reliability. The inlet concentration ($C_{inlet}$), outlet concentration ($C_{outlet}$) of NO were monitored by a Flue Gas Analyzer (Optima7.0, York Instruments Co. Ltd, Germany). The outlet concentration of NO$_x$ ($C_{outlet-NOx}$) was concerned when focused on the NO$_x$ yield from the over oxidation of NH$_3$. NO conversion (%) and NO$_x$ yield (%) are defined as:

$$\text{NO conversion \%} = \frac{(C_{inlet} - C_{outlet})}{C_{inlet}} \times 100 \% \quad (1)$$

$$\text{NO$_x$ yield \%} = \frac{C_{outlet-NOx}}{C_{inlet}} \times 100 \% \quad (2)$$

3. Results and discussion
3.1 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 improves the low temperature catalytic performance of Mn/Ti catalysts and 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 absorbed NH$_3$ is the main reason for the reducing NO conversions at the temperature above 200°C.

3.2 Effect of Ce doping on catalyst characterizations
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 CeO$_2$ 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’s 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 MnCeO$_x$ solid solution (when Ce/Ti mole ratio=0.1,
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 conductive 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 I that the $S_{BET}$, $V_{tot}$ and $V_{mico}$ values rise with the increase of Ce/Ti mole ratios and the D values are reduced accordingly. Literatures (Murillo et al., 2004; Mastral et al., 2000) have put forward that the gaseous reactant adsorption 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. However, the 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 NH₃ might not be the main active species for further NO reduction. The chemisorption of NH₃ by surface acid sites forming activated transient state is probably available in SCR reaction (Ramis et al., 1995).

3.2.2 NH₃-TPD and H₂-TPR analysis

NH₃-TPD experiments were carried out to evaluate the surface acid property (i.e. the amount and the strength) of the catalyst (Fig. 3a), which influences the chemisorption and activation of NH₃ (Li et al., 2014). There are two NH₃ desorption peaks exists in the NH₃-TPD profile of all catalysts at 50-500 °C. The NH₃ 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 and 300 refer to the desorptions of the NH₃ 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 (NH₃) are effective for NO reduction (Wu et al., 2007; Peña et al., 2004); ammonium ions adsorbed on Brønsted acid sites (NH₄⁺) act as the ‘reservoir’ of the actively coordinated NH₃ species (i.e. \( \text{NH}_3(\text{g}) + \text{H}^+ = \text{NH}_4^+ (\text{ads}) + \text{H}_2 \)) and influence the SCR reaction indirectly (Qiu et al., 2015). As seen from Fig. 3a, 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  and confirms 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. 3b. 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 (Andreoli et al., 2015; Liang et al., 2008). 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 . Mn$_{0.15}$Ce$_{0.05}$/Ti catalyst has excellent redox ability because the Mn
atoms are more likely to be embeded 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. 3b, implying the incorporation of Mn atoms into the CeO$_2$ lattice. The relatively
lower 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’s 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 NO$_x$. 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.

3.2.3 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. 4a) 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$_{2/3}$ 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 650-660 eV. As for the Ce 3d
spectrum (Fig. 4b), all samples exhibit eight characteristic peaks in the range of 870-930 eV. The
u' and v' peaks can be assigned to Ce$^{3+}$ species, while the u'"", u', u'0, v'"", v"", and v'0 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 (Yao et al., 2017; Dai et al., 2011). The highly dispersed surface Mn atoms are more likely to be oxidized to high valence state (+4) which introduces more surface reactive oxygen species and has favorable redox properties for NO conversion (Yu et al., 2014; Tang et al., 2015); besides, Ce atom with low valence state (+3) has been used as an indicator for the surface defect structures (e.g. oxygen vacancies) in ceria-based materials (Tang et al., 2015). Oxygen vacancies driven by redox cycle between Ce$^{4+}$ and Ce$^{3+}$ promote the migration of the oxygen species, which is beneficial to the oxidation of NO to NO$_2$ and further enhances NO conversion through ‘fast NH$_3$-SCR’ (Xiong et al., 2015). Unexpectedly, the surface Mn$^{4+}$ and Ce$^{3+}$ ions are conversely reduced when further increase the Ce/Ti mole ratios. That’s because the crystalline structure of excessive CeO$_2$ preferentially take the Mn atom into its bulk phase and reduce the exposed Mn atom on catalyst surface. Meanwhile, the electron transformation between Mn and Ce atoms inside MnCeO$_x$ solid solution proceeds ‘Mn$^{4+}$ + Ce$^{3+}$ ↔ Mn$^{3+}$ + Ce$^{4+}$’ (Ding et al., 1998; Qi et al., 2004; Xiong et al., 2015) to the right and results in the abatement of Mn$^{4+}$ and Ce$^{3+}$ ions on the surface of
Mn$_{0.15}$Ce$_{0.1}$/Ti and Mn$_{0.15}$Ce$_{0.15}$/Ti catalysts. These also are the important reasons that explain their poorer SCR activity at low temperatures.

As shown in Fig. 4c, the O1s XPS spectra of all catalysts present two main peaks belonging to the surface chemisorbed oxygen (labeled as O$_\alpha$) and surface lattice oxygen (labeled as O$_\beta$) (Meng et al., 2015; Li et al., 2011). Hereinto, the O$_\alpha$ referred to the oxygen free radicals (e.g. O, O$^-$ and O$_2^-$) are weakly bounded 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 addition 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$_{0.1}$/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 comparing the actual Mn/(Ce+Ti) and Ce/(Mn+Ti) mole ratios with their theoretical values (Table 2). Accordingly, a assumption model is proposed in Fig.5. As for Mn$_{0.15}$/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 TiO$_2$ or the presence of MnO$_x$ crystals (in line with the XRD patterns) resulting in the poor distribution of the Mn atoms (Fig. 5a). After adding a small amount of Ce (Ce/Ti=0.05), the actual Ce/(Mn+Ti) value of Mn$_{0.15}$Ce$_{0.05}$/Ti catalyst (0.03) is close to the theoretical mole ratio (0.04); the actual Mn/(Ce+Ti) mole ratio of Mn$_{0.15}$Ce$_{0.05}$/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 CeO$_2$ microcrystal prevents the Mn atoms from entering into the bulk TiO$_2$ (Fig. 5b). As for Mn$_{0.15}$Ce$_{0.1}$/Ti and Mn$_{0.15}$Ce$_{0.15}$/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 TiO$_2$ lattice. So, it is reasonable to believe that the lower actual Ce/(Mn+Ti) values of Mn$_{0.15}$Ce$_{0.1}$/Ti and Mn$_{0.15}$Ce$_{0.15}$/Ti catalysts result from the agglomeration of CeO$_2$ crystals (in line with XRD patterns) on TiO$_2$ surface which causes the poor dispersion of CeO$_2$. Coincidentally, both the actual Mn/(Ce+Ti) mole ratio values of Mn$_{0.15}$Ce$_{0.1}$/Ti (0.08) and
Mn$_{0.15}$Ce$_{0.15}$/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 CeO$_2$ crystal which agglomerates on the TiO$_2$ surface as shown in Fig. 5c.

### 3.3 NH$_3$-SCR in oxygen-rich and oxygen-free atmosphere

NH$_3$-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 NH$_3$-SCR reaction still takes place in oxygen-free atmosphere and indicates that the reactive oxygen species in catalyst participates in NH$_3$-SCR of NO. Ce addition can alleviate the deactivation of the catalysts in oxygen-free atmosphere effectively and the NO conversion of Mn$_{0.15}$Ce$_{0.05}$/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 Mn$_{0.15}$Ce$_{0.05}$/Ti catalyst probably because there are abundant exposed Mn$^{4+}$ ions on Mn$_{0.15}$Ce$_{0.05}$/Ti catalyst surface can activate the adsorbed NH$_3$(ads) (reaction (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.

\[
\text{Mn}^{4+} + \text{NH}_3(\text{ads}) \rightarrow \text{Mn}^{3+} + \cdot \text{NH}_2 + \text{H}^+ \quad (3)
\]
As soon as O\textsubscript{2} is reinjected into the reaction atmosphere, the NO conversions rise again in all catalysts within 10 min. That’s because the oxygen vacancies can be replenished with O\textsubscript{2} by reoxidizing the Mn atoms from +3 to +4 (reaction (6)). In addition, the NO\textsubscript{2}(g) generated from the oxidation of NO with O\textsubscript{2} also help reoxidize the reduced metal atom (reaction (7)). As seen from Fig. 6, the deactivated Mn\textsubscript{0.15}Ce\textsubscript{0.05}/Ti catalyst can be completely regenerated at 200 °C, while the deactivation in other catalysts seems to be irreversible under this condition. That’s because the exposed Mn atoms embedded in the surface of CeO\textsubscript{2} microcrystal contributes to a flexible redox cycle between Mn\textsuperscript{4+} and Mn\textsuperscript{3+}. This phenomenon supports the result that the oxygen release/storage capability of Mn\textsubscript{0.15}Ce\textsubscript{0.05}/Ti catalyst is higher than those of the other two catalysts, which is another determining factor for its high NH\textsubscript{3}-SCR activity at low temperatures.

3.4 NH\textsubscript{3}-SCR in SO\textsubscript{2}-containing atmosphere

Temperature-dependent effect of SO\textsubscript{2} on NH\textsubscript{3}-SCR of NO over Mn\textsubscript{0.15}Ce\textsubscript{0.05}/Ti catalyst was obtained in Fig. 7a. As observed, SO\textsubscript{2} suppresses the SCR performance at 100-275 °C. Nevertheless, still more than 75% NO conversion is provided by Mn\textsubscript{0.15}Ce\textsubscript{0.05}/Ti catalyst after
SO\(_2\) poisoning at 175°C and that is even higher than the optimum value of Mn\(_{0.15}/\)Ti catalyst obtained in SO\(_2\)-free atmosphere. This result implies that Ce modification can enhance the SO\(_2\) resistance of MnCe/Ti catalyst at low temperature, which coincides with the observations reported in previous studies (Li et al., 2016; Wang et al., 2015; Zhu et al., 2001). The improvement of Ce addition on SO\(_2\) resistance of Ce modified Mn/Ti catalyst attributes to two main reasons. Firstly, Ce doping inhibits the depoositions of ammonia sulfites and sulfates that would block the active sites and affect the oxidation properties of the catalyst (Jin et al., 2014; Wu et al., 2009; Wang et al., 2015). Secondly, surface sulfates are preferentially formed on Ce dopants in presence of SO\(_2\), which lessens the sulfation of the main active phase (MnO\(_x\)) (Jin et al., 2014; Ma et al., 2019). On the contrary, SO\(_2\) presents a positive effect on NH\(_3\)-SCR reaction over Mn\(_{0.15}/\)Ce\(_{0.05}/\)Ti catalyst above 300°C, which is in good agreement with Ma et al.’s observations (Ma et al., 2013). That is because the depoositions of ammonia sulfites and sulfates are reduced and the formation of metal sulfates (e.g. Ce\(_2(SO_4)_3\) or Ce(SO\(_4\))\(_2\)) is facilitated at high temperatures (Ma et al., 2013; Wang et al., 2015). The latter reduces the oxidation ability of Mn\(_{0.15}/\)Ce\(_{0.05}/\)Ti catalyst and thereby minimizes the over oxidation of NH\(_3\), 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 was shown in Fig. 7b. 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. proposed that Ce doping could reduce the thermal stability of the ammonia sulfites and sulfates on MnCe/Ti catalyst based on their theoretical calculation (Jin et al., 2014). 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 (\(>350\)) is suggested for it has the possibility to fully recover the catalyst activity after SO\textsubscript{2} poisoning (Wang et al., 2015).

4. Conclusion
Ce addition effectively improves the activity of the Mn/Ti catalyst and the optimum condition is found on Mn$_{0.15}$Ce$_{0.05}$/Ti catalyst. The catalytic activity of MnCe/Ti catalyst has a direct correlation with the exposed Mn atom. The addition of a small amount of Ce (Ce/Ti=0.05) increases the exposure of Mn atom and thus improves the oxygen storage/release capability of catalysts. On the contrary, excessive CeO$_2$ decreases the exposed surface Mn atoms due to the incorporation of Mn atom into the bulk CeO$_2$ and lowers the low temperature catalytic activity of Mn$_{0.15}$Ce$_{0.1}$/Ti and Mn$_{0.15}$Ce$_{0.15}$/Ti catalysts instead. Ce addition can also improve the SO$_2$ resistance of Mn/Ti catalyst because (1) it inhibits the deposition of ammonia sulfites and sulfates on catalyst surface and (2) lessens the sulfation of main active phase (MnO$_x$). Besides, SO$_2$ is conductive to the SCR performance of Mn$_{0.15}$Ce$_{0.05}$/Ti above 300 for more surface sulfates formed preferentially on Ce dopants. It can reduce the oxidation ability of the catalyst properly and suppress the over oxidation of NH$_3$ at high temperatures.

Acknowledgements

This research is supported by Natural Science Foundation of Shanghai (17ZR1419400), National Key R&D Program of China (2018YFC1901204), National Natural Science Foundation of China (51706156 and 51976129) and Shanghai Rising-Star Program (17QC1401000).

References


resistance of catalysts for the selective catalytic reduction of NO\textsubscript{x} by NH\textsubscript{3}. Appl. Catal. B-Environ. 166-167: 37-44.


Murillo, R., García, T., Aylón, E., Callén, M.S., Navarro, M.V., López, J.M. and Mastral, A.M.


Tian, W., Fan, X.Y., Yang, H.S. and Zhang, X.B. (2010). Preparation of MnO\textsubscript{x}/TiO\textsubscript{2} composites


Yu, X.H., Li, J.M., Wei, Y.C. and Zhao, Z. (2014). Three-dimensionally ordered macroporous Mn$_x$Ce$_{1-x}$O$_{δ}$ and Pt/Mn$_{0.5}$Ce$_{0.5}$O$_{δ}$ catalysts: Synthesis and catalytic performance for soot oxidation. Ind. Eng. Chem. Res. 53(23): 9653-9664.


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

<table>
<thead>
<tr>
<th>Notation</th>
<th>Component molar ratio</th>
<th>Component molar ratio</th>
<th>S$_{BET}$ ($m^2/g$)</th>
<th>V$_{micro}$ ($cm^3/g$)</th>
<th>V$_{tot}$ ($cm^3/g$)</th>
<th>D ($nm$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn$_{0.15}$/Ti</td>
<td>0.15</td>
<td>/</td>
<td>78.6</td>
<td>0.023</td>
<td>0.146</td>
<td>7.4</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>
<td>5.8</td>
</tr>
<tr>
<td>Mn$<em>{0.15}$Ce$</em>{0.10}$/Ti</td>
<td>0.15</td>
<td>0.10</td>
<td>115.3</td>
<td>0.036</td>
<td>0.176</td>
<td>4.7</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>
<td>4.3</td>
</tr>
</tbody>
</table>

Structure parameters of the catalysts got by N$_2$ adsorption-desorption; $S_{BET}$: BET surface area; $V_{micro}$: micropore volume; $V_{tot}$: total pore volume; D: average pore diameter.

Table 2. The surface atomic concentration and valence state distribution of Mn/Ti and MnCe/Ti catalysts

<table>
<thead>
<tr>
<th>Samples</th>
<th>Mn(at %)$^a$</th>
<th>Mn valence state distribution</th>
<th>Ce(at %)$^a$</th>
<th>Ce valence state distribution</th>
<th>O(at %)$^a$</th>
<th>O$<em>{x}$/O$</em>{y}$</th>
<th>Ti(at %)$^a$</th>
<th>Mn/(Ce+Ti)$^b$</th>
<th>Ce/(Mn+Ti)</th>
<th>Mn$_{0.15}$/Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn$_{0.15}$/Ti</td>
<td>3.3</td>
<td>25.5</td>
<td>48.5</td>
<td>26.0</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>71.4</td>
<td>0.20</td>
<td>25.3</td>
</tr>
<tr>
<td>n$<em>{0.15}$Ce$</em>{0.05}$/Ti</td>
<td>3.7</td>
<td>35.7</td>
<td>41.7</td>
<td>22.5</td>
<td>0.8</td>
<td>71.3</td>
<td>28.7</td>
<td>74.7</td>
<td>0.28</td>
<td>20.8</td>
</tr>
<tr>
<td>n$<em>{0.15}$Ce$</em>{0.10}$/Ti</td>
<td>1.8</td>
<td>33.2</td>
<td>46.8</td>
<td>19.9</td>
<td>1.3</td>
<td>72.0</td>
<td>28.0</td>
<td>76.3</td>
<td>0.25</td>
<td>20.6</td>
</tr>
<tr>
<td>n$<em>{0.15}$Ce$</em>{0.15}$/Ti</td>
<td>1.6</td>
<td>29.7</td>
<td>48.1</td>
<td>22.2</td>
<td>1.5</td>
<td>74.3</td>
<td>25.7</td>
<td>76.4</td>
<td>0.22</td>
<td>20.5</td>
</tr>
</tbody>
</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.
**Figure Captions**

**Fig. 1.** NH₃-SCR activity of Mn/Ti and MnCe/Ti catalysts and NO₂ yield with or without catalyst ([NO]_{inlet}=[NH₃]_{inlet}=300 ppm, [O₂]=3%, N₂ as balance, GHSV=30000 h⁻¹)

**Fig. 2.** XRD spectra of Mn/Ti and MnCe/Ti catalysts

**Fig. 3.** NH₃-TPD spectra (a) and H₂-TPR spectra (b) of Mn/Ti and MnCe/Ti catalysts

**Fig. 4.** Mn 2p (a), Ce 3d (b) and O 1s (c) XPS spectra of the Mn/Ti and MnCe/Ti catalysts

**Fig. 5.** An assumption model for Mn/Ti (a) and MnCe/Ti (b) (c) catalysts

**Fig. 6.** NH₃-SCR activities of Mn/Ti and MnCe/Ti catalysts with or without O₂ ([NO]_{inlet}=[NH₃]_{inlet}=300ppm, [O₂]=3%, N₂ as balance, GHSV=30000h⁻¹, Temperature=200 °C)

**Fig. 7.** Effect of SO₂ on NH₃-SCR activity (a) and transient response (b) of SO₂ on Mn₀.₁₅Ce₀.₀₅/Ti catalyst ([NO]_{inlet}=[NH₃]_{inlet}=300 ppm,[O₂]=3%, SO₂=200ppm (when added), N₂ as balance, GHSV=30000 h⁻¹,Temperature=200°C)
Fig. 1. NH$_3$-SCR activity of Mn/Ti and MnCe/Ti catalysts and NO$_x$ yield with or without catalyst ([NO]$_{inlet}$=[NH$_3$]$_{inlet}$=300 ppm, [O$_2$]=3%, N$_2$ as balance, GHSV=30000 h$^{-1}$)
Fig. 2. XRD spectra of Mn/Ti and MnCe/Ti catalysts
Fig. 3. NH$_3$-TPD spectra (a) and H$_2$-TPR spectra (b) of Mn/Ti and MnCe/Ti catalysts.
**Fig. 4.** Mn 2p (a), Ce 3d (b) and O 1s (c) XPS spectra of the Mn/Ti and MnCe/Ti catalysts.
Fig. 5. An assumption model for Mn/Ti (a) and MnCe/Ti (b) (c) catalysts.
Fig. 6. NH$_3$-SCR activities of Mn/Ti and MnCe/Ti catalysts with or without O$_2$ ([NO]$_{inlet}$=[NH$_3$]$_{inlet}$=300 ppm, [O$_2$]=3%, N$_2$ as balance, GHSV=30000 h$^{-1}$, Temperature=200 °C)
Fig. 7. Effect of SO$_2$ on NH$_3$-SCR activity (a) and transient response (b) of SO$_2$ on Mn$_{0.15}$Ce$_{0.05}$/Ti catalyst ([NO]$_{\text{inlet}}$=[NH$_3$]$_{\text{inlet}}$=300 ppm,[O$_2$]=3%, SO$_2$=200 ppm (when added), N$_2$ as balance, GHSV=30000 h$^{-1}$, Temperature=200°C)