Integrated removal of NO and mercury from coal combustion flue gas using manganese oxides supported on TiO$_2$

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A catalyst composed of manganese oxides supported on titania (MnO$_x$/TiO$_2$) synthesized by a sol-gel method was selected to remove nitric oxide and mercury jointly at a relatively low temperature in simulated flue gas from coal-fired power plants. The physico-chemical characteristics of catalysts were investigated by X-ray fluorescence (XRF), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) analyses, etc. The effects of Mn loading, reaction temperature and individual flue gas components on denitration and Hg$^0$ removal were examined. The results indicated that the optimal Mn/Ti molar ratio was 0.8 and the best working temperature was 240°C for NO conversion. O$_2$ and a proper ratio of [NH$_3$]/[NO] are essential for the denitration reaction. Both NO conversion and Hg$^0$ removal efficiency could reach more than 80% when NO and Hg$^0$ were removed simultaneously using Mn0.8Ti at 240°C. Hg$^0$ removal efficiency slightly declined as the Mn content increased in the catalysts. The reaction temperature had no significant effect on Hg$^0$ removal efficiency. O$_2$ and HCl had a promotional effect on Hg$^0$ removal. SO$_2$ and NH$_3$ were observed to weaken Hg$^0$ removal because of competitive adsorption. NO first facilitated Hg$^0$ removal and then had an inhibiting effect as NO concentration increased without O$_2$, and it exhibited weak inhibition of Hg$^0$ removal efficiency in the presence of O$_2$. The oxidation of Hg$^0$ on MnO$_x$/TiO$_2$ follows the Mars–Maessen and Langmuir–Hinshelwood mechanisms.

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Introduction

Many environmental problems such as acid rain, ozone depletion and photochemical smog are related to the atmospheric pollutants NO$_x$, which are harmful to human health (Topsøe, 1997; Busca et al., 2005). The proportion of NO among the NO$_x$ is the largest (about 95%) (Smirniotis et al., 2006), and nearly half of NO in the air derives from coal combustion, which is still the main method to generate electricity in the world (Qi and Yang, 2003). In recent years, strict environmental legislations and restrictive emission standards for NO$_x$ have been introduced to control the emission of NO from coal-fired power plants (Smirniotis et al., 2006).

Along with NO$_x$, mercury is another hazardous substance emitted from coal-fired power plants. According to statistics, coal burning releases 475 tons of mercury into the atmosphere every

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year, which is nearly one fourth of global mercury emission (UNEP, 2013). As the largest mercury emission source of coal combustion, coal-fired power plants make up as much as 85% of the amount of mercury emission from coal burning (UNEP, 2013). The U.S. Environmental Protection Agency (EPA) enacted federal air toxics emission (including Hg) standards for coal-fired electricity generating units in November 2011 (Li et al., 2011a). In China, the government promulgated a decree in which mercury emission from coal-fired power plants is limited to 0.03 mg/m$^3$ in 2011 (Zhang et al., 2014).

Mercury in coal combustion flue gas exists in three different states i.e., elemental Hg (Hg$^0$), oxidized Hg (Hg$^{2+}$) and particulate-bound Hg (Hg$^{P}$) (Senior et al., 2009). Hg$^0$ and Hg$^{2+}$ can easily be removed respectively by particulate matter control devices (PMCD) and wet flue gas desulfurization (WFGD) systems (Galbreath and Zygarlicke, 2000; Wang et al., 2010). Hg$^0$ is difficult to control by existing thermal power plant air pollution control devices because of its volatility and insolubility in water (Gutiérrez-Ortiz et al., 2007; Presto and Granite, 2006). Unfortunately, Hg$^0$ makes up a considerable proportion of the forms of mercury in coal-fired flue gas (Carpi, 1997; Prestbo and Bloom, 1995). Therefore, the focus of our research is to find a way to transform Hg$^0$ to Hg$^{2+}$. Then Hg$^{2+}$ in the flue gas of coal-fired power plants can be efficiently removed by WFGD systems (Li et al., 2011a).

In recent years, Selective Catalytic Reduction (SCR) catalysts have been reported to have the ability to oxidize Hg$^0$ because of their surface lattice oxygen (Eswaran and Stenger, 2005; Kamata et al., 2008; Suarez Negreira and Wilcox, 2013). For example, Eom et al. (2007) have proven that Hg$^0$ removal efficiency over the commercial SCR catalyst (generally V$_2$O$_5$(WO$_4$)/TiO$_2$), which coal-fired power plants are using currently, can reach more than 90%. Li et al. (2011b) conclude that the CeO$_2$/TiO$_2$ catalyst exhibits good Hg$^0$ removal activity because of the strong oxygen storage capacity of Ce. Kim et al. (2010a, 2010b) report that CuCl$_2$/TiO$_2$ shows both high NO and Hg$^0$ removal efficiency. However, the reaction temperature of the above catalysts is about 350–400°C, so that they must be placed between the economizer and air preheater where they are exposed to fly ash, which diminishes the working life of the catalysts (Benson et al., 2005; Etterieddy et al., 2007; Qi and Yang, 2003). Hence, it would be beneficial to develop a catalyst whose catalytic activity for simultaneous removal of NO and Hg$^0$ is high at low temperature. A SCR reactor with this type of catalyst could be not only used to remove mercury jointly, but also be placed more downstream along the tail flue. Then the cost of Hg control would be reduced by utilizing the existing pollution control equipment of coal-fired power plants. Meanwhile, the toxic effect of fly ash on the catalysts would be decreased.

Among SCR catalysts, MnO$_x$/TiO$_2$ catalysts have been reported to exhibit prominent catalytic activity at an economical low temperature (Li et al., 2008; Kim et al., 2010a, 2010b; Li et al., 2007, 2010; Lu et al., 2014; Wu et al., 2007; Xie et al., 2012). For example, Wu et al. (2007) found that more than 90% of NO could be removed by MnO$_x$/TiO$_2$ within the reaction temperature window of 150–250°C. Xie et al. (2012) used nano-sized MnO$_x$/TiO$_2$ as catalyst and obtained high Hg$^0$ removal efficiency in the range 200–300°C. Most of these studies focused on researching either SCR denitration or Hg$^0$ removal separately with MnO$_x$/TiO$_2$ catalysts. Unlike these previous works, the current study explored the catalytic performance of MnO$_x$/TiO$_2$ for removing NO and Hg$^0$ simultaneously in simulated coal-fired flue gas, and the experiments on Hg$^0$ removal activity were all conducted on the premise of high NO conversion.

In this study, MnO$_x$/TiO$_2$ was prepared by a facile sol–gel method. The effects of reaction temperature and Mn loading on NO conversion and Hg$^0$ removal efficiency were investigated to test the catalytic activity of MnO$_x$/TiO$_2$. Hg$^0$ removal efficiency was measured when it was removed simultaneously in the optimal working conditions for denitrification in simulated flue gas. The roles of individual flue gas components on NO conversion and Hg$^0$ removal efficiency were examined as well.

1. Materials and methods

1.1. Preparation and physical characterization of catalysts

The MnO$_x$/TiO$_2$ catalysts with different manganese oxide loadings were synthesized by a facile sol–gel method. All chemicals used in the experiments were of analytic reagent grade. First, manganese nitrate was dissolved in H$_2$O, acetic acid and ethanol. Then the solution was added into tetrabutyl titanate (Ti(OC$_4$H$_9$)$_4$) that was dissolved in ethanol. The mixed solution was stirred for several hours until the solution transformed to a gel. The operations above were all conducted at room temperature. Then the gel was dried at 110°C for 12 hr and it transformed to a porous dark purple solid. The solid was crushed and sieved with a 200 mesh sifter before being calcined in air at 500°C for 5 hr. The dosage of Ti(OC$_4$H$_9$)$_4$ ethanol, acetic acid and H$_2$O was constant in the preparation processes of all catalysts, while the dosage of Mn(NO$_3$)$_2$ was determined by the designed MnO$_x$/TiO$_2$ content of the catalyst. MnO$_x$/TiO$_2$ is abbreviated to MnTi or Mn$_x$Ti (where x represents the molar ratio of the elements Mn and Ti) in the rest of this paper.

The confirmation of the chemical composition of MnTi was achieved by the X-ray fluorescence (XRF) technique. Brunauer–Emmett–Teller (BET) surface area analysis was performed using an ASAP 2020 porosimeter with N$_2$ adsorption. X-ray diffraction (XRD) measurements were carried out on an X’Pert PRO diffractometer (Cu Ka radiation) with an operating voltage of 40 kV and an emission current of 40 mA. The scanning range was from 10 to 80° (2θ) with a step size of 0.017°. X-ray photoelectron spectroscopy (XPS) analysis was carried out using a Perkin-Elmer PHI 5100 ESCA system operating at 8 × 10$^{-10}$ Torr with an Al Kα X-ray source (hv = 1486.6 eV) and pass energy of 35.75 eV.

1.2. Catalytic activity measurement

A bench-scale system consisting of a gas mixer, temperature-controlled fixed bed reactor, mercury generator, Hg online monitor and gas analyzer was constructed for this study as shown in Fig. 1. All individual flue gas components were from cylinder gases and accurately controlled by mass flow controllers. Water vapor was generated with a water vapor generator by controlling the flow of inlet water. A Hg$^0$ penetration tube (VIGI, Metronics Inc., Santa Clara, CA) was placed in a U-tube through which N$_2$ was passed to provide a constant feed of Hg$^0$ (~60 μg/m$^3$). A fixed bed reactor with a temperature controller...
was used in the experiment, and the reaction pipes were designed according to the size of the reactor. The NO and Hg\(^0\) concentrations in the gas stream were measured by a gas analyzer (OPTIMA7, YORK Instruments LTD) and Hg\(^0\) online monitor (VM3000, Mercury Instrument), respectively. Electric heating tape combined with a temperature controller was used both upstream and downstream of the fixed bed reactor to preheat the simulated flue gas and avoid any possible adsorption and condensation on the inner wall before analysis. Tail gas was treated by an active carbon trap before being released to the vent.

The experimental conditions are listed in Table 1. In Set I, the effects of Mn loading and reaction temperature on the denitration efficiency of MnTi were investigated to obtain the optimum Mn loading and reaction temperature. In Set II, the roles of O\(_2\) and NH\(_3\)/NO in the denitration reaction were studied respectively by changing the O\(_2\) and NH\(_3\) concentrations in the simulated flue gas. Set III was aimed at verifying the catalytic performance of MnTi when it was used to remove NO and Hg\(^0\) simultaneously in simulated flue gas. Set IV investigated the effects of Mn loading and reaction temperature on Hg\(^0\) removal efficiency. Set V experiments were designed to study the roles of the individual flue gas components in Hg\(^0\) oxidation reactions.

The total gas flow was constant (1 L/min) in all the experiments. The amount of catalyst used was 0.1–0.5 g. At the beginning of each test, the gas stream bypassed the reactor until the initial NO or Hg\(^0\) concentration reached stability. Then the gas flow passed through the catalyst until the NO or Hg\(^0\) concentration achieved stability once again. Stability was defined such that fluctuation of NO or Hg\(^0\) concentration was no more than 5% deviation for at least 0.5 hr. At the end of each test, the gas analyzer or Hg\(^0\) online monitor was switched to the reactor inlet to further verify the initial NO or Hg\(^0\) concentration, and then fresh catalyst was replaced to start the next test.

In this work, the NO conversion (E\(_{\text{NO}}\) (%)) and Hg\(^0\) removal efficiency (E\(_{\text{Hg}}\) (%)) are defined as Eqs. (1) and (2) respectively, which are the same as those defined for commercial SCR catalysts (Ettireddy et al., 2007; Cao et al., 2007; Pudasainee et al., 2010).

\[
E_{\text{NO}} = \frac{\text{NO}_{\text{in}} - \text{NO}_{\text{out}}}{\text{NO}_{\text{in}}} \times 100\% \quad (1)
\]

\[
E_{\text{Hg}} = \frac{\text{Hg}^0_{\text{in}} - \text{Hg}^0_{\text{out}}}{\text{Hg}^0_{\text{in}}} \times 100\% \quad (2)
\]

NO\(_{\text{in}}\) and NO\(_{\text{out}}\) represent NO concentration at the inlet and outlet of the reactor respectively, and Hg\(^0\)\(_{\text{in}}\) and Hg\(^0\)\(_{\text{out}}\) represent Hg\(^0\) concentration at the inlet and outlet of the reactor respectively.

### Table 1 – Experiment conditions.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Catalyst dosage (g)</th>
<th>Carrier gas (1 L/min)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Set I</td>
<td>Mn0.2Ti</td>
<td>0.5</td>
<td>Simulated flue gas (SFG: 4% O(_2), 12% CO(_2), 10 ppm HCl, 400 ppm SO(_2), 400 ppm NO, 400 ppm NH(_3), 4% H(_2)O)</td>
</tr>
<tr>
<td></td>
<td>Mn0.4Ti</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mn0.6Ti</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mn0.8Ti</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mn1.0Ti</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mn1.2Ti</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mn1.4Ti</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Set II</td>
<td>Mn0.8Ti</td>
<td>0.5</td>
<td>SFG (0%–6% O(_2)) SFG (160–560 ppm NH(_3))</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Set III</td>
<td>Mn0.8Ti</td>
<td>0.5</td>
<td>SFG + Hg(^0)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Set IV</td>
<td>Mn0.6Ti</td>
<td>0.5</td>
<td>SFG + Hg(^0)</td>
</tr>
<tr>
<td></td>
<td>Mn0.8Ti</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mn1.0Ti</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Set V</td>
<td>Mn0.8Ti</td>
<td>0.1</td>
<td>N(_2) + Hg(^0)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>N(_2) (+4% O(_2)) + Hg(^0) + individual flue gas components (O(_2), HCl, SO(_2), NO, NO + NH(_3))</td>
</tr>
</tbody>
</table>
represent Hg\(^+\) concentration at the inlet and outlet of the reactor respectively.

### 2. Results and discussion

#### 2.1. Characterization of the catalysts

**2.1.1. XRF analysis**

The elemental composition and content of the catalysts was examined by XRF tests, as shown in Table 2. From the table, it can be seen that the actual molar ratios of element Mn and Ti were very close to the design values. Thus the preparation of the catalysts can be considered to be accurate.

**2.1.2. XRD analysis**

The XRD patterns of MnTi catalysts with different Mn loadings are shown in Fig. 2. Characteristic peaks of anatase TiO\(_2\) are observed in all of the patterns. As the Mn content of MnTi increased, the peak intensity of TiO\(_2\) decreased gradually. This suggested the strong interaction between MnO\(_x\) and TiO\(_2\) inside the catalysts. No peaks or only weak characteristic peaks corresponding to MnO\(_x\) were observed on MnTi catalysts when the Mn content was less than 1.2, indicating that manganese oxides were well-dispersed and formed an amorphous phase on the TiO\(_2\) support (Peña et al., 2004; Wang et al., 1999; Wu et al., 2007). As the ratio of Mn/Ti increased to 1.2 or more, the peaks of MnO\(_x\) became apparent, which implied the formation of crystalline MnO\(_x\).

**2.1.3. BET analysis**

The BET surface area, pore volume and pore size of different samples are summarized in Table 3, it is apparent that the introduction of manganese oxides enlarged the surface area greatly. As Mn loading increased, the surface area and pore volume showed a trend of increasing initially. This phenomenon was attributed to MnO\(_x\) being incorporated into the TiO\(_2\) structure, providing additional nucleation sites and moderating the sintering and pore plugging of TiO\(_2\) (Kim et al., 2010a, 2010b). Mn0.6Ti and Mn0.8Ti exhibited the largest surface areas of 122 m\(^2\)/g, a value larger than that of commercial SCR catalysts (usually less than 100 m\(^2\)/g) (Senior, 2006). As the Mn content continued increasing, crystalline MnO\(_x\) formed and blocked the pores of the support so that the surface area and pore volume showed a decreasing trend.

**2.1.4. XPS analysis**

The variations of XPS spectra of Mn 2p and O 1s before and after reactions were obtained as shown in Fig. 3. Two primary peaks due to Mn 2p\(_{3/2}\) and Mn 2p\(_{1/2}\) from 635 to 660 eV could be observed in Fig. 3 (for Mn 2p). The Mn 2p\(_{3/2}\) peak is larger, in which the secondary peaks at 642.8 and 641.2 eV represent Mn\(^{4+}\) and Mn\(^{3+}\) species, respectively (Li et al., 2012; Wu et al., 2009). It could be seen that the peak of Mn\(^{4+}\) was depleted markedly when there was no O\(_2\) in the flue gas. Thus, Mn\(^{4+}\) was crucial in the catalytic process. If the flue gas contained O\(_2\), the percentage decrease of Mn\(^{4+}\) became smaller, resulting from part of the Mn\(^{3+}\) being transformed into Mn\(^{4+}\). Fig. 3 (for O 1s) indicates that two kinds of oxygen were present in the catalyst, because of the appearance of two different O 1s peaks. In the MnTi catalyst, the peak at a lower binding energy (529.8 eV) was attributed to the oxygen from TiO\(_2\), while the oxygen peak of MnO\(_x\) dropped off when

### Table 2 – Results of XRF analysis.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Element</th>
<th>Concentration (wt.%)</th>
<th>Concentration (atomic%)</th>
<th>Molar ratio of Mn/Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn0.2Ti</td>
<td>Ti</td>
<td>82.64</td>
<td>84.52</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td>17.36</td>
<td>15.48</td>
<td></td>
</tr>
<tr>
<td>Mn0.4Ti</td>
<td>Ti</td>
<td>69.19</td>
<td>72.04</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td>30.81</td>
<td>27.96</td>
<td></td>
</tr>
<tr>
<td>Mn0.6Ti</td>
<td>Ti</td>
<td>59.53</td>
<td>62.79</td>
<td>0.59</td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td>40.47</td>
<td>37.21</td>
<td></td>
</tr>
<tr>
<td>Mn0.8Ti</td>
<td>Ti</td>
<td>53.18</td>
<td>56.58</td>
<td>0.77</td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td>46.82</td>
<td>43.42</td>
<td></td>
</tr>
<tr>
<td>Mn1.0Ti</td>
<td>Ti</td>
<td>47.13</td>
<td>50.56</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td>52.87</td>
<td>49.44</td>
<td></td>
</tr>
<tr>
<td>Mn1.2Ti</td>
<td>Ti</td>
<td>42.49</td>
<td>45.87</td>
<td>1.18</td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td>57.51</td>
<td>54.13</td>
<td></td>
</tr>
<tr>
<td>Mn1.4Ti</td>
<td>Ti</td>
<td>38.96</td>
<td>42.27</td>
<td>1.37</td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td>61.04</td>
<td>57.73</td>
<td></td>
</tr>
</tbody>
</table>

**Table 3 – Surface structure properties of MnTi catalysts.**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface area (m(^2)/g)</th>
<th>Pore volume (cm(^3)/g)</th>
<th>Pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure</td>
<td>55.75</td>
<td>0.014</td>
<td>72.75</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn0.2Ti</td>
<td>89.09</td>
<td>0.070</td>
<td>39.38</td>
</tr>
<tr>
<td>Mn0.4Ti</td>
<td>105.19</td>
<td>0.198</td>
<td>60.41</td>
</tr>
<tr>
<td>Mn0.6Ti</td>
<td>122.71</td>
<td>0.276</td>
<td>70.50</td>
</tr>
<tr>
<td>Mn0.8Ti</td>
<td>122.63</td>
<td>0.245</td>
<td>62.20</td>
</tr>
<tr>
<td>Mn1.0Ti</td>
<td>96.14</td>
<td>0.164</td>
<td>56.01</td>
</tr>
<tr>
<td>Mn1.2Ti</td>
<td>67.58</td>
<td>0.118</td>
<td>85.55</td>
</tr>
<tr>
<td>Mn1.4Ti</td>
<td>54.19</td>
<td>0.140</td>
<td>86.36</td>
</tr>
</tbody>
</table>

Fig. 2 – XRD patterns of (a) pure TiO\(_2\), (b) Mn0.2Ti, (c) Mn0.4Ti, (d) Mn0.6Ti, (e) Mn0.8Ti, (f) Mn1.0Ti, (g) Mn1.2Ti, and (h) Mn1.4Ti catalysts. XRD: X-ray diffraction.
no O$_2$ was present, suggesting that the lattice oxygen in MnO$_x$ was consumed and Mn$^{4+}$ was converted into Mn$^{3+}$. O$_2$ could replenish the expended lattice oxygen, because the peak at 532.2 eV was almost unchanged in the existence of O$_2$. Namely, Mn$^{3+}$ was oxidized to Mn$^{4+}$, which was consistent with the Mn 2p results.

### 2.2. NO removal activity over MnTi catalysts

#### 2.2.1. Effect of temperature and Mn content

Fig. 4 shows the NO reduction activity over different MnTi catalysts at different reaction temperatures under simulated flue gas conditions. The general reaction is shown in Eq. (3) (Qi and Yang, 2003):

$$4\text{NO} + 4\text{NH}_3 + O_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \quad (3)$$

As the Mn content increased from 0.2 to 0.8, the denitration performance over MnTi catalysts was significantly enhanced. The catalytic efficiency was highest overall as the ratio reached 0.8. Beyond this value, further increase of Mn loading started to reduce NO conversion. The catalytic efficiencies of Mn0.6Ti, Mn0.8Ti and Mn1.0Ti were higher relative to the other catalysts. This owed to their relatively high surface area and the amorphous phase of MnO$_x$ on the support, which are both beneficial to the catalytic performance of the catalyst.

When the ratio of Mn/Ti increased to 1.2 and 1.4, the decline of NO conversion was a consequence of the transformation of MnO$_x$ from the amorphous to crystalline phase, which contributed little to the catalytic activity.
For the optimal sample Mn0.8Ti, NO conversion improved as reaction temperature increased until it reached 240°C. After that, the NO conversion rate decreased with increasing temperature, which is because NH₃ could be excessively oxidized at high temperature as shown in Eq. (4) (Bergene et al., 1996; Mayer et al., 2001):

\[ 4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O} \] (4)

2.2.2. Effect of O₂ and NH₃

The effect of O₂ concentration in simulated flue gas on NO conversion was studied and the results are shown in Fig. 5. There was a great increase of NO conversion to 80% after adding O₂ into the flue gas. The rate of increase became slower and nearly reached a plateau when the O₂ concentration was more than 2%. It should be pointed out that NO conversion could still reach 23.2% in the absence of O₂. One reason for this is that NO and NH₃ reacted with lattice oxygen on the catalyst surface (Wu et al., 2007); another explanation is that NO and NH₃ can set off a reaction weakly without O₂ following Eq. (5) (Busca et al., 1998):

\[ 6\text{NO} + 4\text{NH}_3 \rightarrow 5\text{N}_2 + 6\text{H}_2\text{O} \] (5)

As a whole, oxygen played an important role in the denitration reaction, and was considered to be the oxidation agent for the catalyst.

As the reductant added in the flue gas for NO conversion, NH₃ exists together with NO, and the amount of NH₃ is relative to the NO concentration in the SCR reaction. So different ratios of [NH₃]/[NO] were chosen to determine the effect of NH₃ on NO conversion (and also on Hg⁰ removal efficiency in the later experiments). Fig. 5 shows the effect of NH₃ on the SCR reaction. NO conversion increased quickly with increasing NH₃ concentration when the ratio of [NH₃]/[NO] was below 1.0. When [NH₃]/[NO] was more than 1.0, NO conversion tended to a constant value and was independent of [NH₃]/[NO]; this is because the acidic adsorption sites on the surface of the catalyst were limited and no more NH₃ could be adsorbed to react with NO (Wu et al., 2007). An excess of NH₃, however, may have adverse effects on Hg⁰ oxidation because of its reducibility, and it is easy to cause the leakage of NH₃, which is harmful to the air as well.

2.3. Hg⁰ removal activity over MnTi catalysts

2.3.1. Catalytic activity for removing NO and Hg⁰ simultaneously

As the primary function of a SCR catalyst is to remove NOx from the flue gas, the study of Hg⁰ removal activity must be on the premise of high denitrification efficiency. Thus in the experiment on removing NO and Hg⁰ simultaneously, Mn0.8Ti was selected to conduct an experiment at 240°C in simulated flue gas because it had the highest NO conversion according to the above results. The catalytic efficiency is shown in Fig. 6. E₉₆ was as high as 83.1% and remained stable. As Hg⁰ oxidation competed for the active sites on the catalyst with the denitrification reaction, E₉₆ showed a reduction of 4.2% compared to that obtained for removing NO separately. But the extent of the decline was small. E₉₆ could still remain at more than 80% for a long time. This might be attributed to the fact that the Hg⁰ concentration (~60 μg/m³) was extremely small in the flue gas compared to the NO concentration (400 ppm). The impact of Hg⁰ on NO conversion was slight and almost negligible.

It should be noted that the space velocity in this experiment was about 50,000/hr, which is much higher than that of actual SCR reactors used in coal-fired power plants (2000–4000 hr⁻¹) (Li et al., 2008b). Also, the composition of the simulated flue gas used in our study was in the range of those flue gases resulting from burning sub-bituminous coals, whose HCl concentration is relatively low. Both higher space velocity and lower HCl concentration in flue gas bring about lower catalytic efficiency over SCR catalysts (Granite et al., 2000; Li et al., 2008a, 2011b; Senior, 2006). Under these extremely adverse conditions, NO conversion and Hg⁰ removal efficiency of Mn0.8Ti could both reach more than 80% at 240°C. The good dispersion of MnOₓ on the support, high surface area and internal appreciable Mn⁴⁺ content of the catalyst were the reasons for the excellent catalytic activity.
2.3.2. Effect of reaction temperature and Mn content

The dependence of Hg\(^0\) removal efficiencies on Mn loading and reaction temperature was investigated under simulated flue gas conditions. Three samples of Mn\(_{0.6}\)Ti, Mn\(_{0.8}\)Ti and Mn\(_{1.0}\)Ti were selected in this experiment to respectively react at 200, 240 and 280°C because of their relatively high NO conversion. Fig. 7 shows that all of the Hg\(^0\) removal efficiencies reached more than 70%. As Mn content increased, the crystallinity of MnO\(_x\) on the support was enhanced, which was adverse for its catalytic performance (Qi and Yang, 2003; Wu et al., 2007), resulting in a slight decrease of \(E_{Hg}\). For each catalyst, Hg\(^0\) removal efficiency was high and independent of reaction temperature within a relatively broad temperature window of 200–280°C.

2.3.3. Effect of individual flue gas components

The effect of O\(_2\) on Hg\(^0\) removal efficiency. \(E_{Hg}\) could reach more than 60% in pure N\(_2\) atmosphere as shown in Fig. 8, which was due to adsorbed Hg\(^0\) reacting with lattice oxygen to form mercuric oxide (Li et al., 2008a; Granite et al., 2000). Combined with the result that 23.2% NO conversion was obtained over the MnTi catalyst in simulated flue gas without O\(_2\), it can be concluded that the MnTi catalyst has a high oxygen storage capacity. \(E_{Hg}\) increased from 63.4% to 93.9% after adding 2% O\(_2\) into the pure N\(_2\) gas flow, because gas-phase O\(_2\) could regenerate lattice oxygen, which served as the oxidant for Hg\(^0\) oxidation according to XPS analysis. No obvious increase of \(E_{Hg}\) was found when the O\(_2\) concentration further increased to 4% or 6%, indicating that 2% O\(_2\) was sufficient to replenish the lattice oxygen consumed by Hg\(^0\). Further increasing O\(_2\) concentration had no significant effect on Hg\(^0\) removal efficiency.

The effect of HCl on Hg\(^0\) removal efficiency. HCl is a determining factor for \(E_{Hg}\) because HgCl\(_2\) is the main oxidized Hg species in coal-fired flue gas (Cao et al., 2007). As Fig. 8 shows, \(E_{Hg}\) improved gradually as the HCl concentration increased from 0 to 20 ppm. HCl first reacted with lattice oxygen to form active Cl, and then adsorbed Hg\(^0\) could be oxidized by active Cl to generate the stable product HgCl\(_2\) ultimately (Presto and Granite, 2006). The consumption of the lattice oxygen by HCl during the reaction was proven by the XPS results in Fig. 3 (comparison of O1S between Fig. 3a and e). The lattice oxygen on the surface of the catalyst, however, is limited. If there is excess HCl in flue gas, the lattice oxygen will be inadequate to produce more active Cl. So \(E_{Hg}\) showed a nearly constant level when the HCl concentration further increased to 30 ppm, suggesting that Hg\(^0\) reacted only with active Cl and could not react with HCl directly. The addition of O\(_2\) into 30 ppm HCl could regenerate the lattice oxygen. Sufficient active Cl species formed so that \(E_{Hg}\) was enhanced to almost 100%.

The effect of SO\(_2\) on Hg\(^0\) removal efficiency. For MnTi catalysts, SO\(_2\) had an obvious inhibitory effect on \(E_{Hg}\) as shown in Fig. 8. \(E_{Hg}\) decreased sharply from 63.4% to less than 5% after adding 400 ppm or more SO\(_2\) into pure N\(_2\). The inhibition may be caused by two main reasons: (1) SO\(_2\) reacted with and consumed the lattice oxygen that was necessary for
Hg\textsuperscript{0} oxidation (Eswaran and Stenger, 2005; Fan et al., 2010); (2) SO\textsubscript{2} competed for adsorption sites with Hg\textsuperscript{0} on the catalyst surface (Kijlstra et al., 1998). If the inhibition resulted from the first reason, the inhibition tendency would change after adding O\textsubscript{2} into the flue gas. However, in the flue gas containing 400 ppm SO\textsubscript{2} plus 4\% O\textsubscript{2}, \textit{E}\textsubscript{Hg} was still lower than that in pure N\textsubscript{2} atmosphere, and \textit{E}\textsubscript{Hg} continued to decline as the SO\textsubscript{2} concentration increased. Therefore, the first reason was not the main cause for the depression. It was the competitive absorption between Hg\textsuperscript{0} and SO\textsubscript{2} that restrained Hg\textsuperscript{0} oxidation. At the same SO\textsubscript{2} content level, \textit{E}\textsubscript{Hg} was much higher in the presence of O\textsubscript{2} compared to that without O\textsubscript{2}. This is because SO\textsubscript{2} reacted with gas-phase O\textsubscript{2} to generate SO\textsubscript{3}, which was able to oxidize Hg\textsuperscript{0} to HgSO\textsubscript{4} (Eswaran et al., 2007).

The effect of NO on Hg\textsuperscript{0} removal efficiency. The effect of NO on \textit{E}\textsubscript{Hg} is shown in Fig. 8d. In the absence of O\textsubscript{2}, when the NO concentration increased from 0 to 400 ppm, \textit{E}\textsubscript{Hg} rose from 63.4\% to 85.6\% because NO could be oxidized by the lattice oxygen, generating some oxidizing materials such as NO\textsubscript{2} and NO\textsubscript{3} (Li et al., 2008a). Hg\textsuperscript{0} reacted with these species to form Hg(NO\textsubscript{3})\textsubscript{2} (Li et al., 2011b). In the condition of NO further increasing to 600 ppm, NO was in excess compared to Hg\textsuperscript{0} and the lattice oxygen. Excessive NO covered up active adsorption sites on the catalyst and restrained Hg\textsuperscript{0} oxidation (Qi et al., 2004), leading \textit{E}\textsubscript{Hg} to decrease to 82.4\%. After feeding 4\% O\textsubscript{2}, NO was more easily oxidized to NO\textsubscript{2}, so \textit{E}\textsubscript{Hg} showed an obvious improvement compared to that in the pure N\textsubscript{2} condition. However, it was likewise easy to form materials that have no Hg\textsuperscript{0} oxidation capacity, such as nitrite (Busca et al., 1998). \textit{E}\textsubscript{Hg}, therefore, diminished slightly as the NO concentration rose.

The effect of NH\textsubscript{3} on Hg\textsuperscript{0} removal efficiency. As Fig. 8 shown, NH\textsubscript{3} had a significant inhibiting effect on Hg\textsuperscript{0} removal efficiency. \textit{E}\textsubscript{Hg} declined to less than 10\% when the ratio of [NH\textsubscript{3}]/[NO] reached 1.0 in the absence of O\textsubscript{2}. Hg\textsuperscript{0} and NH\textsubscript{3} have been reported to exhibit intense competitive adsorption on the catalyst (Ding et al., 1998; Qi et al., 2004). Besides, NH\textsubscript{3}, together with NO, caused the denitrification reaction to occur following Eq. (3) (Eom et al., 2007; Eswaran and Stenger, 2005). The lattice oxygen that was necessary for Hg\textsuperscript{0} oxidation was expended. For these reasons, the inhibitory effect of NH\textsubscript{3} was evident. The addition of O\textsubscript{2} could supplement the lattice oxygen consumed by NH\textsubscript{3} (Li et al., 2012). Then the denitrification reaction proceeded more thoroughly, and NH\textsubscript{3} was reacted and consumed, impairing its competitive adsorption with Hg\textsuperscript{0}. As a consequence, the suppression effect of NH\textsubscript{3} on \textit{E}\textsubscript{Hg} weakened greatly when O\textsubscript{2} was present in the flue gas. This result verifies the previous conclusion in Section 2.2.2 of this paper, that the ratio of [NH\textsubscript{3}]/[NO] used in the denitrification reaction should not be too excessive.

### 2.3.4. Mechanism of Hg\textsuperscript{0} oxidation

SO\textsubscript{2} and NH\textsubscript{3} exhibit competitive absorption with Hg\textsuperscript{0} on the catalyst. As a result, the Hg\textsuperscript{0} removal efficiency was inhibited to an extreme low value. This shows that only adsorbed Hg\textsuperscript{0} can be oxidized over MnTi catalysts. According to the results above, adsorbed Hg\textsuperscript{0} reacts with surface lattice oxygen to form HgO. So the oxidation of Hg\textsuperscript{0} on MnTi catalysts follows the Mars–Maessen mechanism, which is in agreement with the study of Xie et al. (2013). Combining the mutual conversion between Mn\textsuperscript{4+} and Mn\textsuperscript{3+} during the reaction, the oxidation process is as shown in Eqs. (6) and (7). Furthermore, adsorbed Hg\textsuperscript{0} in the presence of HCl can be oxidized to HgCl\textsubscript{2}. For MnTi catalysts, the oxidant is active Cl, which is formed by adsorbed HCl reacting with lattice oxygen (Eom et al., 2007; Li et al., 2012). Hence, Hg\textsuperscript{0} oxidation on MnTi catalysts also follows the Langmuir–Hinshelwood mechanism (Eqs. (8)–(10)). The lattice oxygen consumed by Hg\textsuperscript{0} or HCl can be regenerated by O\textsubscript{2} as shown in Eq. (11).

\[
\begin{align*}
\text{Hg}^0(g) & \rightarrow \text{Hg}^2(a) & (6) \\
\text{Hg}^2(a) + \text{MnO}_2 & \rightarrow \text{HgO} + \text{Mn}_2\text{O}_3 & (7) \\
\text{HCl}(g) & \rightarrow \text{HCl}(a) & (8) \\
\text{HCl}(a) + \text{MnO}_2 & \rightarrow \text{Cl} + \text{Mn}_2\text{O}_3 + \text{H}_2\text{O} & (9) \\
\text{Mn}_2\text{O}_3 + \text{O}_2 & \rightarrow \text{Mn}_2\text{O}_4 & (11)
\end{align*}
\]

#### 3. Conclusions

MnO\textsubscript{0.8}TiO\textsubscript{2} catalysts prepared by a sol–gel method were investigated for their ability to remove NO and mercury under simulated coal combustion flue gas. Mn0.8Ti was the optimal sample for denitration and the best reaction temperature was 240°C, which is much lower than that of commercial SCR catalysts. The optimum NO conversion was 85\%. Good dispersion of MnO\textsubscript{0} on the TiO\textsubscript{2} support and the high surface area of Mn0.8Ti are likely responsible for the highly catalytic activity. Both O\textsubscript{2} and an appropriate ratio of [NH\textsubscript{3}]/[NO] are necessary for the denitrification reaction to take place smoothly. Both E\textsubscript{NO} and E\textsubscript{Hg} can be more than 80\% when NO and Hg\textsuperscript{0} were removed simultaneously at 240°C, proving that the MnTi catalyst is appropriate to be utilized for integrated removal of NO and Hg\textsuperscript{0} at a relatively low temperature. Hg\textsuperscript{0} removal efficiency slightly declined as Mn content increased. The reaction temperature had no obvious effect on Hg\textsuperscript{0} removal efficiency. O\textsubscript{2} and HCl were observed to promote Hg\textsuperscript{0} removal. Hg\textsuperscript{0} removal efficiency could reach nearly 100\% when they existed simultaneously. SO\textsubscript{2} and NH\textsubscript{3} can inhibit Hg\textsuperscript{0} removal and decrease Hg\textsuperscript{0} removal efficiency to less than 10\% because of competitive adsorption, and the inhibitory effect is alleviated after addition of O\textsubscript{2}. NO first facilitates and then depresses Hg\textsuperscript{0} removal as the NO concentration increases at 240°C, which is in agreement with the Mars–Maessen and Langmuir–Hinshelwood mechanisms. XRF: X-ray fluorescence.

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