Supporting Materials

Competition of selective catalytic reduction and non selective catalytic reduction over MnO$_x$/TiO$_2$ for NO removal: The relationship between gaseous NO concentration and N$_2$O selectivity

Shijian Yang, ab Yuwu Fu, a Yong Liao, a Shangchao Xiong, a Zan Qu, c Naiqiang Yan, c Junhua Li b

a School of Environmental and biological Engineering, Nanjing University of Science and technology, Nanjing, 210094 P. R. China

b State Key Joint Laboratory of Environment Simulation and Pollution Control (SKLESPC), School of Environment, Tsinghua University, Beijing, 100084 P. R. China

c School of Environmental Science and Engineering, Shanghai Jiao Tong University, Shanghai, 200240 P. R. China

* Corresponding author phone and fax: 86-10-62771093; E-mail: lijunhua@tsinghua.edu.cn (J. H. Li), yangshijiangsq@163.com (S. J. Yang).
1. NO-TPD and NH$_3$-TPD

Temperature programmed desorption of ammonia (NH$_3$-TPD) and temperature programmed desorption of NO (NO-TPD) were carried out on the fixed-bed quartz tube reactor.$^1$ Before the experiment, about 0.10 g of catalyst was pretreated under N$_2$ atmosphere at 300 °C for 60 min to remove adsorbed H$_2$O and other gases. After the catalyst was cooled to 50 °C, the N$_2$ flow was switched to a flow of 500 ppm NH$_3$/N$_2$ or 500 ppm NO+2% O$_2$/N$_2$ (200 ml min$^{-1}$) for 60 min. The sample was then purged by N$_2$ (200 ml min$^{-1}$) for another 60 min. At last, NH$_3$-TPD (or NO-TPD) was performed at a heating rate of 10 °C min$^{-1}$ to 600 °C under a N$_2$ flow (200 ml min$^{-1}$). The capacities of MnO$_x$/TiO$_2$ for NH$_3$ and NO adsorption were calculated from the profiles of NH$_3$-TPD and NO-TPD (shown in Fig. S1). The capacity of MnO$_x$/TiO$_2$ for NO adsorption at 50 °C was about 0.67 mmol g$^{-1}$, which was much less than that for NH$_3$ adsorption (2.1 mmol g$^{-1}$).

2. Kinetic analysis

The kinetic equations of the formation of N$_2$ and N$_2$O over MnO$_x$/TiO$_2$ through the Langmuir-Hinshelwood mechanism can be approximately described as:

$$\frac{d[N_2]}{dt} = -\frac{d[NH_4NO_2]}{dt} = k_1[NH_4NO_2]$$  \hspace{1cm} (14)

$$\frac{d[N_2O]}{dt} = -\frac{d[NH_4NO_3]}{dt} = k_2[NH_4NO_3]$$  \hspace{1cm} (15)

According to Reactions 11 and 12, the formation of NH$_4$NO$_2$ and NH$_4$NO$_3$ on MnO$_x$/TiO$_2$ can be described as:

$$\frac{d[NH_4NO_2]}{dt} = -\frac{d[NO_2^-]}{dt} = k_7[NH_3(ad)][NO_2^-]$$ \hspace{1cm} (S1)

$$\frac{d[NH_4NO_3]}{dt} = -\frac{d[NO_3^-]}{dt} = k_8[NH_3(ad)][NO_3^-]$$ \hspace{1cm} (S2)

Where, $k_7$, $k_8$, [NH$_3$(ad)], [NO$_2^-$] and [NO$_3^-$] were the kinetic constants of Reactions 11 and 12, and the concentrations of NH$_3$(ad), NO$_2^-$ and NO$_3^-$ on MnO$_x$/TiO$_2$, respectively.

According to Equations 14-15 and Equations S1-S2, the variation of NH$_4$NO$_3$ and NH$_4$NO$_2$ concentrations on MnO$_x$/TiO$_2$ can be described as follows:
As the reaction reached the steady state, the concentrations of NH$_4$NO$_3$ and NH$_4$NO$_2$ would not change. Therefore,

\[ \frac{d[\text{NH}_4\text{NO}_2]}{dt} = \frac{d[\text{NH}_3\text{NO}_2]}{dt} = 0 \]  

(S5)

According to Equations S3-S4, the concentrations of NH$_4$NO$_3$ and NH$_4$NO$_2$ on MnO$_x$/TiO$_2$ at the steady state can be described as:

\[ [\text{NH}_4\text{NO}_3] = \frac{k_3[\text{NH}_3\text{NO}_2][\text{NO}_3^-]}{k_1} \]  

(S6)

\[ [\text{NH}_4\text{NO}_2] = \frac{k_3[\text{NH}_3\text{NO}_2][\text{NO}_2^-]}{k_2} \]  

(S7)

According to Reactions 9 and 10, the formation of NO$_2^-$ and NO$_3^-$ on MnO$_x$/TiO$_2$ can be described as follows:

\[ \frac{d[\text{NO}_2]}{dt} = k_9[\text{NO}(\text{ad})][\text{Mn}^{4+}] \]  

(S8)

\[ \frac{d[\text{NO}_3^-]}{dt} = k_{10}[\text{NO}(\text{ad})][\text{Mn}^{4+}]^\beta \]  

(S9)

Where, $k_9$, $k_{10}$, $\beta$, $[\text{NO}(\text{ad})]$ and $[\text{Mn}^{4+}]$ were the kinetic constants of Reactions 9 and 10, the reaction order with respect to the concentration of Mn$^{4+}$ on MnO$_x$/TiO$_2$ and the concentrations of NO adsorbed and Mn$^{4+}$ on MnO$_x$/TiO$_2$, respectively.

Taking account of the reduction of NO$_3^-$ and NO$_2^-$ (Equations S1-S2), the variation of NO$_3^-$ and NO$_2^-$ concentrations on MnO$_x$/TiO$_2$ can be described as follows:

\[ \frac{d[\text{NO}_3^-]}{dt} = k_9[\text{NO}(\text{ad})][\text{Mn}^{4+}] - k_7[\text{NH}_3\text{NO}_2][\text{NO}_2^-] \]  

(S10)

\[ \frac{d[\text{NO}_2^-]}{dt} = k_{10}[\text{NO}(\text{ad})][\text{Mn}^{4+}]^\beta - k_8[\text{NH}_3\text{NO}_2][\text{NO}_3^-] \]  

(S11)

As the reaction reached the steady state, the concentrations of NO$_3^-$ and NO$_2^-$ would not change.
Therefore,
\[
\frac{d[\text{NO}_3^-]}{dt} = \frac{d[\text{NO}_2^-]}{dt} = 0 \quad (S12)
\]

According to Equations S10-S11, the concentrations of NO$_3^-$ and NO$_2^-$ on MnO$_x$/TiO$_2$ at the steady state can be described as follows:

\[
[\text{NO}_2^-] = \frac{k_9 [\text{NO}_{(ad)}][\text{Mn}^{4+}]}{k_7 [\text{NH}_3{(ad)}]} \quad (S13)
\]

\[
[\text{NO}_3^-] = \frac{k_{10} [\text{NO}_{(ad)}][\text{Mn}^{4+}]^\beta}{k_5 [\text{NH}_3{(ad)}]} \quad (S14)
\]

As shown in Equations S13 and S14, the concentration of adsorbed NO$_2^-$ and NO$_3^-$ would both decrease as the concentration of adsorbed NH$_3$ increased.

Thus,
\[
[\text{NH}_4\text{NO}_2] = \frac{k_9 [\text{NH}_3{(ad)}][\text{NO}_2^-]}{k_1} = \frac{k_9 [\text{NO}_{(ad)}][\text{Mn}^{4+}]}{k_1} 
\]

\[
[\text{NH}_4\text{NO}_3] = \frac{k_{10} [\text{NH}_3{(ad)}][\text{NO}_3^-]}{k_2} = \frac{k_{10} [\text{NO}_{(ad)}][\text{Mn}^{4+}]^\beta}{k_2} \quad (S15)\quad (S16)
\]

3. NH$_3$ oxidization

Fig. S2 shows NH$_3$ conversion and selectivity of the catalytic oxidization of NH$_3$ over MnO$_x$/TiO$_2$. At less than 175 °C, little NH$_3$ can be oxidized by MnO$_x$/TiO$_2$. With the further increase of reaction temperature, NH$_3$ conversion obviously increased. However, more than 50% of NH$_3$ was oxidized to N$_2$O above 200 °C. Meanwhile, NO$_x$ (including NO and NO$_2$) can not be observed in the outlet.

The mechanism of the catalytic oxidization of NH$_3$ can be approximately described as:\textsuperscript{2}

\[
\text{NH}_3{(g)} \rightarrow \text{NH}_3{(ad)} \quad (7)
\]

\[
\text{NH}_3{(ad)} + \equiv \text{Mn}^{4+} \rightarrow -\text{NH}_2 + \equiv \text{Mn}^{3+} + \text{H}^+ \quad (16)
\]

\[
-\text{NH}_2 + \equiv \text{Mn}^{4+} \rightarrow -\text{NH} + \equiv \text{Mn}^{3+} + \text{H}^+ \quad (17)
\]

\[
2\text{NH} + \frac{3}{2} \text{O}_2 \xrightleftharpoons{\text{Mn}^{4+}} \rightarrow 2\text{NO} + \text{H}_2\text{O} \quad (S17)
\]
The over-activated NH$_3$ (NH) can be further oxidized to NO by Mn$^{4+}$ on MnO$_x$/TiO$_2$ (i.e. Reaction S17), which could be the rate control step of the catalytic oxidization of NH$_3$. The formed NO from NH$_3$ oxidization can then be reduced by NH$_2$ and NH on MnO$_x$/TiO$_2$ to N$_2$ and N$_2$O, respectively. They were so-called selective catalytic oxidization of NH$_3$ and non-selectivity catalytic oxidization of NH$_3$. The concentration of NO resulted from NH$_3$ oxidization was very low, so N$_2$O selectivity of NH$_3$ oxidization was much higher than the reaction with 500 ppm of NH$_3$ and 500 ppm of NO (shown in Fig. 2).
References:


Fig. S1 NO-TPD and NH$_3$-TPD of MnO$_x$/TiO$_2$
Fig. S2 NH₃ conversion and selectivity of the catalytic oxidization of NH₃ over MnOₓ/TiO₂.

Reaction condition: [NH₃]=500 ppm, [O₂]=2%, catalyst mass=200 mg, total flow rate =200 mL min⁻¹, GHSV= 60000 cm³ g⁻¹ h⁻¹.