

# Supporting Materials

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

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## 1. NO-TPD and NH<sub>3</sub>-TPD

Temperature programmed desorption of ammonia (NH<sub>3</sub>-TPD) and temperature programmed desorption of NO (NO-TPD) were carried out on the fixed-bed quartz tube reactor.<sup>1</sup> Before the experiment, about 0.10 g of catalyst was pretreated under N<sub>2</sub> atmosphere at 300 °C for 60 min to remove adsorbed H<sub>2</sub>O and other gases. After the catalyst was cooled to 50 °C, the N<sub>2</sub> flow was switched to a flow of 500 ppm NH<sub>3</sub>/N<sub>2</sub> or 500 ppm NO+2% O<sub>2</sub>/N<sub>2</sub> (200 ml min<sup>-1</sup>) for 60 min. The sample was then purged by N<sub>2</sub> (200 ml min<sup>-1</sup>) for another 60 min. At last, NH<sub>3</sub>-TPD (or NO-TPD) was performed at a heating rate of 10 °C min<sup>-1</sup> to 600 °C under a N<sub>2</sub> flow (200 ml min<sup>-1</sup>). The capacities of MnO<sub>x</sub>/TiO<sub>2</sub> for NH<sub>3</sub> and NO adsorption were calculated from the profiles of NH<sub>3</sub>-TPD and NO-TPD (shown in Fig. S1). The capacity of MnO<sub>x</sub>/TiO<sub>2</sub> for NO adsorption at 50 °C was about 0.67 mmol g<sup>-1</sup>, which was much less than that for NH<sub>3</sub> adsorption (2.1 mmol g<sup>-1</sup>).

## 2. Kinetic analysis

The kinetic equations of the formation of N<sub>2</sub> and N<sub>2</sub>O over MnO<sub>x</sub>/TiO<sub>2</sub> through the Langmuir-Hinshelwood mechanism can be approximately described as:

$$\frac{d[\text{N}_2]}{dt} = -\frac{d[\text{NH}_4\text{NO}_2]}{dt} = k_1[\text{NH}_4\text{NO}_2] \quad (14)$$

$$\frac{d[\text{N}_2\text{O}]}{dt} = -\frac{d[\text{NH}_4\text{NO}_3]}{dt} = k_2[\text{NH}_4\text{NO}_3] \quad (15)$$

According to Reactions 11 and 12, the formation of NH<sub>4</sub>NO<sub>2</sub> and NH<sub>4</sub>NO<sub>3</sub> on MnO<sub>x</sub>/TiO<sub>2</sub> can be described as:

$$\frac{d[\text{NH}_4\text{NO}_2]}{dt} = -\frac{d[\text{NO}_2^-]}{dt} = k_7[\text{NH}_{3(\text{ad})}][\text{NO}_2^-] \quad (\text{S1})$$

$$\frac{d[\text{NH}_4\text{NO}_3]}{dt} = -\frac{d[\text{NO}_3^-]}{dt} = k_8[\text{NH}_{3(\text{ad})}][\text{NO}_3^-] \quad (\text{S2})$$

Where,  $k_7$ ,  $k_8$ ,  $[\text{NH}_{3(\text{ad})}]$ ,  $[\text{NO}_2^-]$  and  $[\text{NO}_3^-]$  were the kinetic constants of Reactions 11 and 12, and the concentrations of NH<sub>3(ad)</sub>, NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> on MnO<sub>x</sub>/TiO<sub>2</sub>, respectively.

According to Equations 14-15 and Equations S1-S2, the variation of NH<sub>4</sub>NO<sub>3</sub> and NH<sub>4</sub>NO<sub>2</sub> concentrations on MnO<sub>x</sub>/TiO<sub>2</sub> can be described as follows:

$$\frac{d[\text{NH}_4\text{NO}_2]}{dt} = k_7[\text{NH}_{3(\text{ad})}][\text{NO}_2^-] - k_1[\text{NH}_4\text{NO}_2] \quad (\text{S3})$$

$$\frac{d[\text{NH}_4\text{NO}_3]}{dt} = k_8[\text{NH}_{3(\text{ad})}][\text{NO}_3^-] - k_2[\text{NH}_4\text{NO}_3] \quad (\text{S4})$$

As the reaction reached the steady state, the concentrations of  $\text{NH}_4\text{NO}_3$  and  $\text{NH}_4\text{NO}_2$  would not change. Therefore,

$$\frac{d[\text{NH}_4\text{NO}_2]}{dt} = \frac{d[\text{NH}_4\text{NO}_3]}{dt} = 0 \quad (\text{S5})$$

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

$$[\text{NH}_4\text{NO}_2] = \frac{k_7[\text{NH}_{3(\text{ad})}][\text{NO}_2^-]}{k_1} \quad (\text{S6})$$

$$[\text{NH}_4\text{NO}_3] = \frac{k_8[\text{NH}_{3(\text{ad})}][\text{NO}_3^-]}{k_2} \quad (\text{S7})$$

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

$$\frac{d[\text{NO}_2^-]}{dt} = k_9[\text{NO}_{(\text{ad})}][\text{Mn}^{4+}] \quad (\text{S8})$$

$$\frac{d[\text{NO}_3^-]}{dt} = k_{10}[\text{NO}_{(\text{ad})}][\text{Mn}^{4+}]^\beta \quad (\text{S9})$$

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  $\text{Mn}^{4+}$  on  $\text{MnO}_x/\text{TiO}_2$  and the concentrations of  $\text{NO}$  adsorbed and  $\text{Mn}^{4+}$  on  $\text{MnO}_x/\text{TiO}_2$ , respectively.

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

$$\frac{d[\text{NO}_2^-]}{dt} = k_9[\text{NO}_{(\text{ad})}][\text{Mn}^{4+}] - k_7[\text{NH}_{3(\text{ad})}][\text{NO}_2^-] \quad (\text{S10})$$

$$\frac{d[\text{NO}_3^-]}{dt} = k_{10}[\text{NO}_{(\text{ad})}][\text{Mn}^{4+}]^\beta - k_8[\text{NH}_{3(\text{ad})}][\text{NO}_3^-] \quad (\text{S11})$$

As the reaction reached the steady state, the concentrations of  $\text{NO}_3^-$  and  $\text{NO}_2^-$  would not change.

Therefore,

$$\frac{d[\text{NO}_2^-]}{dt} = \frac{d[\text{NO}_3^-]}{dt} = 0 \quad (\text{S12})$$

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

$$[\text{NO}_2^-] = \frac{k_9[\text{NO}_{(\text{ad})}][\text{Mn}^{4+}]}{k_7[\text{NH}_{3(\text{ad})}]} \quad (\text{S13})$$

$$[\text{NO}_3^-] = \frac{k_{10}[\text{NO}_{(\text{ad})}][\text{Mn}^{4+}]^\beta}{k_8[\text{NH}_{3(\text{ad})}]} \quad (\text{S14})$$

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

Thus,

$$[\text{NH}_4\text{NO}_2] = \frac{k_7[\text{NH}_{3(\text{ad})}][\text{NO}_2^-]}{k_1} = \frac{k_9[\text{NO}_{(\text{ad})}][\text{Mn}^{4+}]}{k_1} \quad (\text{S15})$$

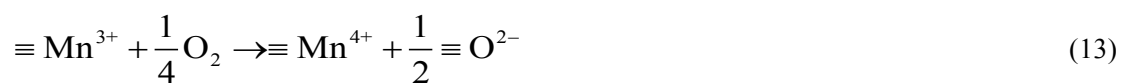
$$[\text{NH}_4\text{NO}_3] = \frac{k_8[\text{NH}_{3(\text{ad})}][\text{NO}_3^-]}{k_2} = \frac{k_{10}[\text{NO}_{(\text{ad})}][\text{Mn}^{4+}]^\beta}{k_2} \quad (\text{S16})$$

### 3. $\text{NH}_3$ oxidization

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

The mechanism of the catalytic oxidization of  $\text{NH}_3$  can be approximately described as: <sup>2</sup>

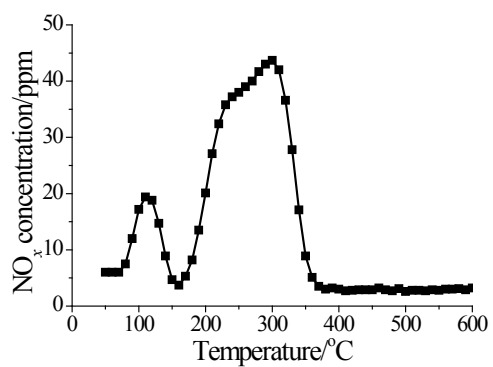




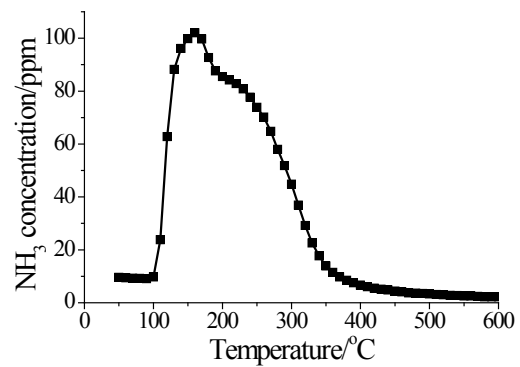
The over-activated  $\text{NH}_3$  ( $\text{NH}$ ) can be further oxidized to  $\text{NO}$  by  $\text{Mn}^{4+}$  on  $\text{MnO}_x/\text{TiO}_2$  (i.e. Reaction S17), which could be the rate control step of the catalytic oxidization of  $\text{NH}_3$ . The formed  $\text{NO}$  from  $\text{NH}_3$  oxidization can then be reduced by  $\text{NH}_2$  and  $\text{NH}$  on  $\text{MnO}_x/\text{TiO}_2$  to  $\text{N}_2$  and  $\text{N}_2\text{O}$ , respectively. They were so-called selective catalytic oxidization of  $\text{NH}_3$  and non-selectivity catalytic oxidization of  $\text{NH}_3$ <sup>3-5</sup>. The concentration of  $\text{NO}$  resulted from  $\text{NH}_3$  oxidization was very low, so  $\text{N}_2\text{O}$  selectivity of  $\text{NH}_3$  oxidization was much higher than the reaction with 500 ppm of  $\text{NH}_3$  and 500 ppm of  $\text{NO}$  (shown in Fig. 2).

## References:

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Fig. S1 NO-TPD and NH<sub>3</sub>-TPD of MnO<sub>x</sub>/TiO<sub>2</sub>

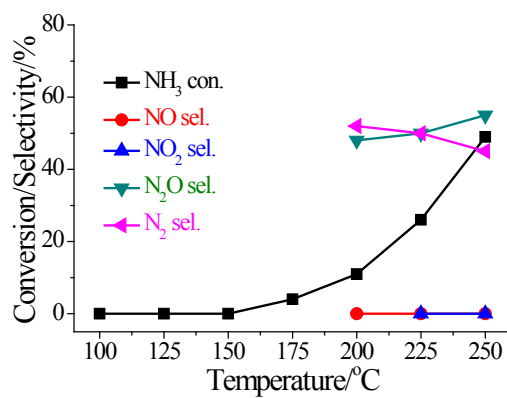


Fig. S2 NH<sub>3</sub> conversion and selectivity of the catalytic oxidation of NH<sub>3</sub> over MnO<sub>x</sub>/TiO<sub>2</sub>.

Reaction condition: [NH<sub>3</sub>]=500 ppm, [O<sub>2</sub>]=2%, catalyst mass=200 mg, total flow rate =200 mL

min<sup>-1</sup>, GHSV= 60000 cm<sup>3</sup> g<sup>-1</sup> h<sup>-1</sup>.