

Supporting Information

Global kinetic study of NO reduction by NH₃ over

V₂O₅-WO₃/TiO₂: Relationship between the SCR

performance and the key factors

Shangchao Xiong, Xin Xiao, Yong Liao, Hao dang, Wenpo Shan, Shijian Yang *

School of Environmental and Biological Engineering, Nanjing University of Science and Technology, Nanjing, 210094 P. R. China

* Corresponding author phone: 86-18-066068302; E-mail: yangshijiangsq@163.com (S. J. Yang).

The ratios of NO_x and NH₃ conversion, the amount of N₂ formed, and N₂O selectivity were calculated using the following equations:

$$\text{NO}_x \text{ conversion} = \frac{[\text{NO}_x]_{\text{in}} - [\text{NO}_x]_{\text{out}}}{[\text{NO}_x]_{\text{in}}} \quad (\text{S1})$$

$$\text{NH}_3 \text{ conversion} = \frac{[\text{NH}_3]_{\text{in}} - [\text{NH}_3]_{\text{out}}}{[\text{NH}_3]_{\text{in}}} \quad (\text{S2})$$

$$\text{N}_2 \text{ formed} = \frac{[\text{NO}_x]_{\text{in}} + [\text{NH}_3]_{\text{in}} - [\text{NO}_x]_{\text{out}} - [\text{NH}_3]_{\text{out}} - 2[\text{N}_2\text{O}]_{\text{out}}}{2} \quad (\text{S3})$$

$$\text{N}_2\text{O selectivity} = \frac{2[\text{N}_2\text{O}]_{\text{out}}}{[\text{NH}_3]_{\text{in}} + [\text{NO}_x]_{\text{in}} - [\text{NH}_3]_{\text{out}} - [\text{NO}_x]_{\text{out}}} \quad (\text{S4})$$

Where, [NH₃]_{in}, [NO_x]_{in}, [NH₃]_{out}, [NO_x]_{out} and [N₂O]_{out} were the concentrations of NH₃ and NO_x (including NO and NO₂) in the inlet, and the concentrations of NH₃, NO_x and N₂O in the outlet, respectively.

Meanwhile, the rates of NO_x conversion, NH₃ conversion, the SCR reaction, the NSCR reaction and the C-O reaction can be described as follows:

$$\delta_{\text{NO}_x} = ([\text{NO}_x]_{\text{in}} - [\text{NO}_x]_{\text{out}}) \text{GHSV} \quad (\text{S5})$$

$$\delta_{\text{NH}_3} = ([\text{NH}_3]_{\text{in}} - [\text{NH}_3]_{\text{out}}) \text{GHSV} \quad (\text{S6})$$

$$\delta_{\text{SCR}} = \frac{([\text{NO}_x]_{\text{in}} + [\text{NH}_3]_{\text{in}} - [\text{NO}_x]_{\text{out}} - [\text{NH}_3]_{\text{out}} - 2[\text{N}_2\text{O}]_{\text{out}}) \text{GHSV}}{2} \quad (\text{S7})$$

$$\delta_{\text{NSCR}} = [\text{N}_2\text{O}]_{\text{out}} \text{GHSV} \quad (\text{S8})$$

$$\delta_{\text{C-O}} = \frac{\delta_{\text{NH}_3} - \delta_{\text{NO}_x}}{2} \quad (\text{S9})$$

The variation of NH₂ on V₂O₅-WO₃/TiO₂ (hinted by Equations 18-20) can be described as:

$$-\frac{d[\text{NH}_2]}{dt} = k_4[\text{NH}_2][\text{V}^{5+}=\text{O}] + k_1[\text{NH}_2][\text{NO}_{(\text{g})}] - k_3[\text{NH}_{3(\text{ad})}][\text{V}^{5+}=\text{O}] \quad (\text{S10})$$

As the reaction reached the steady-state, NH₂ concentration on V₂O₅-WO₃/TiO₂ would not vary.

Thus,

$$[\text{NH}_2] = \frac{k_3[\text{NH}_{3(\text{ad})}][\text{V}^{5+}=\text{O}]}{k_4[\text{V}^{5+}=\text{O}] + k_1[\text{NO}_{(\text{g})}]} \quad (\text{S11})$$

Then, Equation 18 can be transformed as:

$$\left. \frac{d[N_2]}{dt} \right|_{E-R} = k_1[NH_2][NO_{(g)}] = k_1[NO_{(g)}] \frac{k_3[NH_{3(ad)}][V^{5+}=O]}{k_4[V^{5+}=O] + k_1[NO_{(g)}]} \quad (S12)$$

If little N_2O formed over $V_2O_5-WO_3/TiO_2$ (for example at 300 °C), the value of $k_4[V^{5+}=O][NH_2]$ can be regarded as nearly 0 (hinted by Equation 25). Hinted by Equation S12, N_2 formation through the Eley-Rideal mechanism would be approximately independent of gaseous NO concentration at 300 °C. Meanwhile, N_2 formation through the Langmuir-Hinshelwood mechanism was not related to gaseous NO concentration (hinted by Equation 27). They suggest that N_2 formation would not vary with the increase of gaseous NO concentration. However, Figure 7c shows that N_2 formation was promoted remarkably at 300 °C as gaseous NO concentration increased. It suggests that the rate of NH_2 formation (i.e. Equation 20) was much higher than that of NH_2 reduction (i.e. Equations 18 and 21) and $V_2O_5-WO_3/TiO_2$ was approximately saturated with the adsorption of NH_2 at the steady state.^{1, 2} Therefore, NH_2 concentration on $V_2O_5-WO_3/TiO_2$ at the steady state can be approximately regarded as a constant.

According to Reaction 17, the kinetic equation of NH_4NO_2 formation on $V_2O_5-WO_3/TiO_2$ can be described as:

$$\frac{d[V^{4+}-O-NO-NH_3]}{dt} = k_7[V^{4+}-O-NO][NH_{3(ad)}] \quad (S13)$$

Where, k_7 and $[V^{4+}-O-NO]$ were the rate constant of Reaction 17 and the concentration of NO_2^- on $V_2O_5-WO_3/TiO_2$, respectively.

According to Reaction 16, the kinetic equation of NO_2^- formation on $V_2O_5-WO_3/TiO_2$ can be described as:

$$\frac{d[V^{4+}-O-NO]}{dt} = k_8[V^{5+}=O][NO_{(ad)}] \quad (S14)$$

Where, k_8 and $[NO_{(ad)}]$ were the rate constant of Reaction 16 and the concentration of physically adsorbed NO on $V_2O_5-WO_3/TiO_2$, respectively.

Equations 27, S13 and S14 suggest that the SCR reaction (i.e. N_2 formation) over $V_2O_5-WO_3/TiO_2$ through the Langmuir-Hinshelwood mechanism was mainly related to the concentrations of NH_3 adsorbed, NO adsorbed and V^{5+} on $V_2O_5-WO_3/TiO_2$. As there were large

amounts of gaseous NO and NH₃ in the outlet during the steady state kinetic study (the conversions of NH₃ and NO were generally less than 15%), V₂O₅-WO₃/TiO₂ was almost saturated with the adsorption of NO and NH₃. It suggests that the concentrations of NO and NH₃ adsorbed on V₂O₅-WO₃/TiO₂ can be approximately regarded as constants at the steady state, and they were independent of the concentrations of gaseous NO and NH₃.³ As V⁵⁺ on V₂O₅-WO₃/TiO₂ can be rapidly replenished through Reaction 14, V⁵⁺ concentration on the surface can be regarded as a constant during NO reduction over V₂O₅-WO₃/TiO₂. As a result, the SCR reaction over V₂O₅-WO₃/TiO₂ through the Langmuir-Hinshelwood mechanism was nearly independent of gaseous NO and NH₃ concentrations.

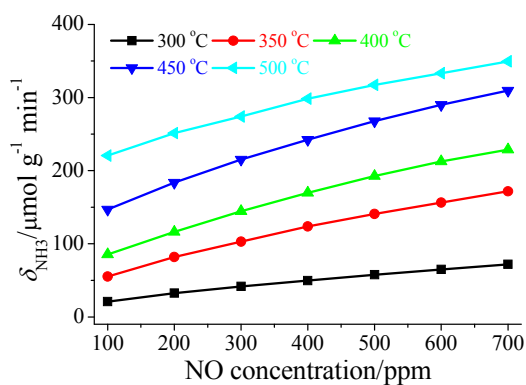
According to Equations 25, 26 and 28, the rates of NH₃ conversion and NO conversion (i.e. δ_{NH_3} and δ_{NO}) can be described as:

$$\begin{aligned}\delta_{\text{NH}_3} &= \delta_{\text{N}_2} + \delta_{\text{N}_2\text{O}} + \delta_{\text{C-O}} \\ &= k_6[\text{V}^{3+}\text{-O-NO-NH}_3] + k_1[\text{NH}_2][\text{NO}_{(\text{g})}] + \frac{k_4[\text{NH}_2][\text{V}^{5+}=\text{O}]}{k_2 + \frac{k_5}{[\text{NO}_{(\text{g})}]}} + \frac{k_4[\text{NH}_2][\text{V}^{5+}=\text{O}]}{\frac{k_2[\text{NO}_{(\text{g})}]}{k_5} + 1} \quad (\text{S15}) \\ &\approx k_{\text{SCR-LH}} + k_{\text{SCR-ER}}[\text{NO}_{(\text{g})}] + k_{\text{NSCR}} + \frac{k_4[\text{NH}_2][\text{V}^{5+}=\text{O}]}{\frac{k_2[\text{NO}_{(\text{g})}]}{k_5} + 1}\end{aligned}$$

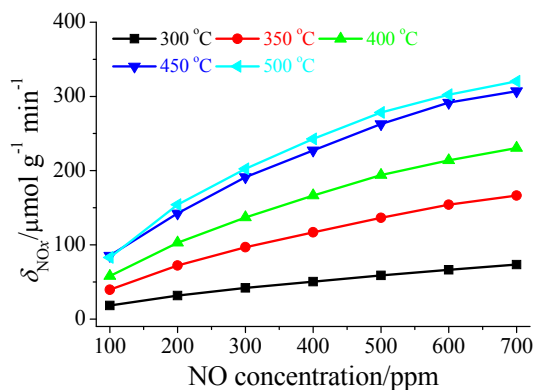
$$\begin{aligned}\delta_{\text{NO}} &= \delta_{\text{N}_2} + \delta_{\text{N}_2\text{O}} - \delta_{\text{C-O}} \\ &= k_6[\text{V}^{3+}\text{-O-NO-NH}_3] + k_1[\text{NH}_2][\text{NO}_{(\text{g})}] + \frac{k_4[\text{NH}_2][\text{V}^{5+}=\text{O}]}{k_2 + \frac{k_5}{[\text{NO}_{(\text{g})}]}} - \frac{k_4[\text{NH}_2][\text{V}^{5+}=\text{O}]}{\frac{k_2[\text{NO}_{(\text{g})}]}{k_5} + 1} \quad (\text{S16}) \\ &\approx k_{\text{SCR-LH}} + k_{\text{SCR-ER}}[\text{NO}_{(\text{g})}] + k_{\text{NSCR}} - \frac{k_4[\text{NH}_2][\text{V}^{5+}=\text{O}]}{\frac{k_2[\text{NO}_{(\text{g})}]}{k_5} + 1}\end{aligned}$$

References:

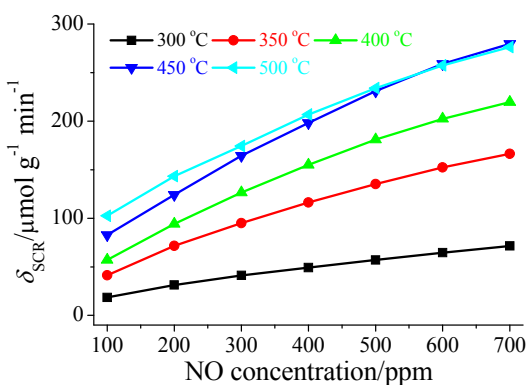
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- (3) Yang, S.; Wang, C.; Li, J.; Yan, N.; Ma, L.; Chang, H. Low temperature selective catalytic reduction of NO with NH₃ over Mn-Fe spinel: Performance, mechanism and kinetic study. *Appl. Catal. B-environ* **2011**, *110*, 71.



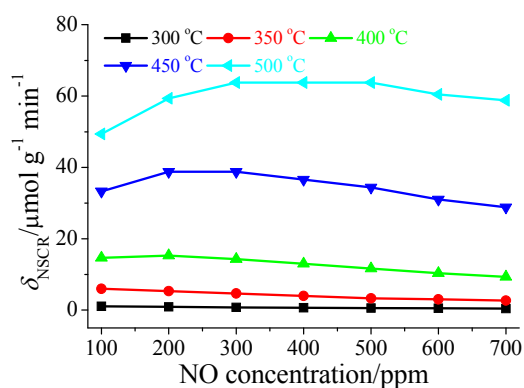
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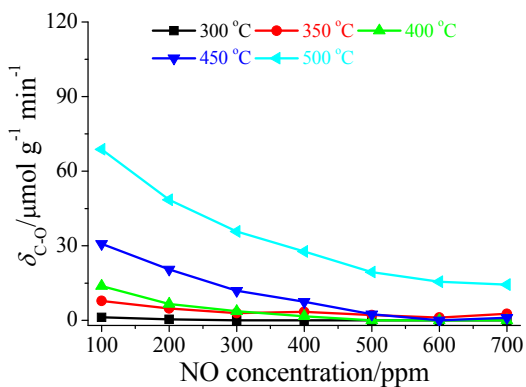
b



c



d



e

Figure S1 Dependences of δ_{NH_3} (a), δ_{NO_x} (b), δ_{SCR} (c), δ_{NSCR} (d), and $\delta_{\text{C-O}}$ (e) on gaseous NO concentration during NO reduction over 1% $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$. Reaction conditions: $[\text{NH}_3]=500$ ppm, $[\text{NO}]=100\text{-}700$ ppm, $[\text{O}_2]=2\%$, catalyst mass=3-20 mg, total flow rate=400 mL min⁻¹ and GHSV=1.2×10⁶-8.0×10⁶ cm³ g⁻¹ h⁻¹.

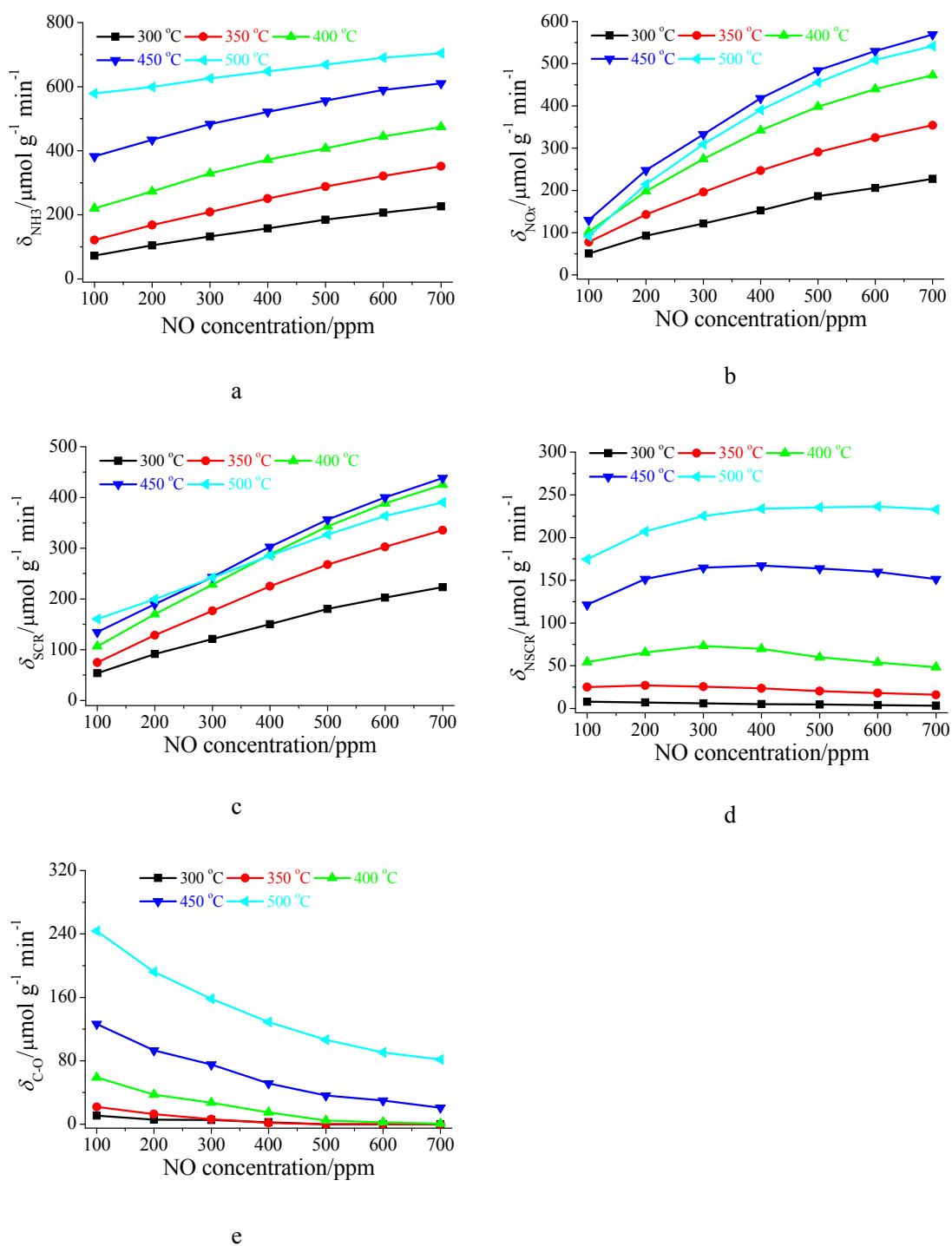


Figure S2 Dependences of δ_{NH_3} (a), δ_{NO_x} (b), δ_{SCR} (c), δ_{NSCR} (d), and $\delta_{\text{C-O}}$ (e) on gaseous NO concentration during NO reduction over 3% V₂O₅-WO₃/TiO₂. Reaction conditions: $[\text{NH}_3]=500$ ppm, $[\text{NO}]=100-700$ ppm, $[\text{O}_2]=2\%$, catalyst mass=2-5 mg, total flow rate=400 mL min⁻¹ and GHSV=4.8×10⁶-1.2×10⁷ cm³ g⁻¹ h⁻¹.

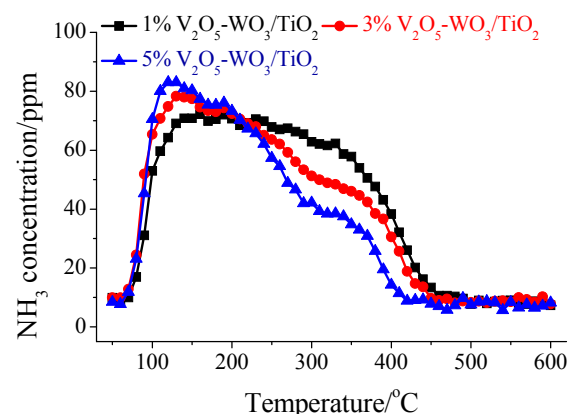


Figure S3 NH₃-TPD profiles of V₂O₅-WO₃/TiO₂