

## **Sulfation effect of Ce/TiO<sub>2</sub> catalyst for selective catalytic reduction of NO<sub>x</sub> with NH<sub>3</sub>: Mechanism and kinetic study**

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### ***Supporting Information(SI)***

13 pages: 7 figures and 1 table

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## 1. Caption to Tables / Figures

### 1.1 Catalytic performance

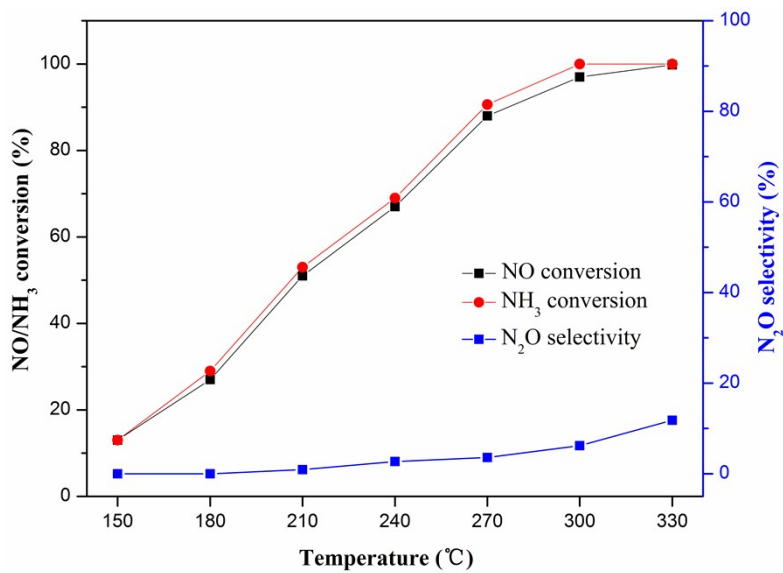


Figure S1. SCR performance and N<sub>2</sub>O selectivity of 240 °C-sulfated Ce/TiO<sub>2</sub>. Reaction conditions:

[NH<sub>3</sub>]=[NO]=600 ppm, [O<sub>2</sub>]=3%, N<sub>2</sub> balance, GHSV=40000 h<sup>-1</sup>

1.2 XRD analysis

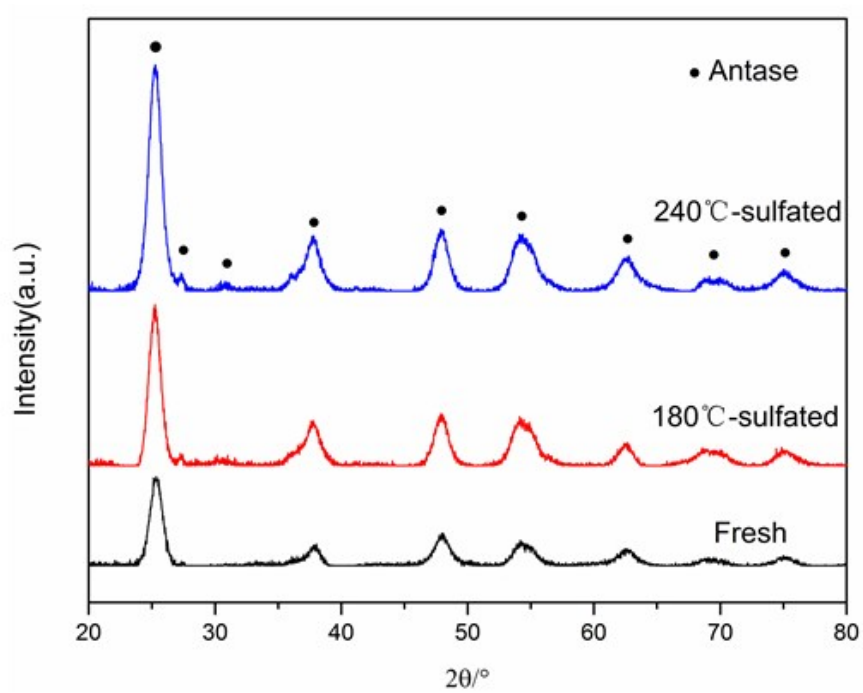


Figure S2. The XRD patterns of fresh Ce/TiO<sub>2</sub> and sulfated Ce/TiO<sub>2</sub> catalysts.

### 1.3 BET analysis

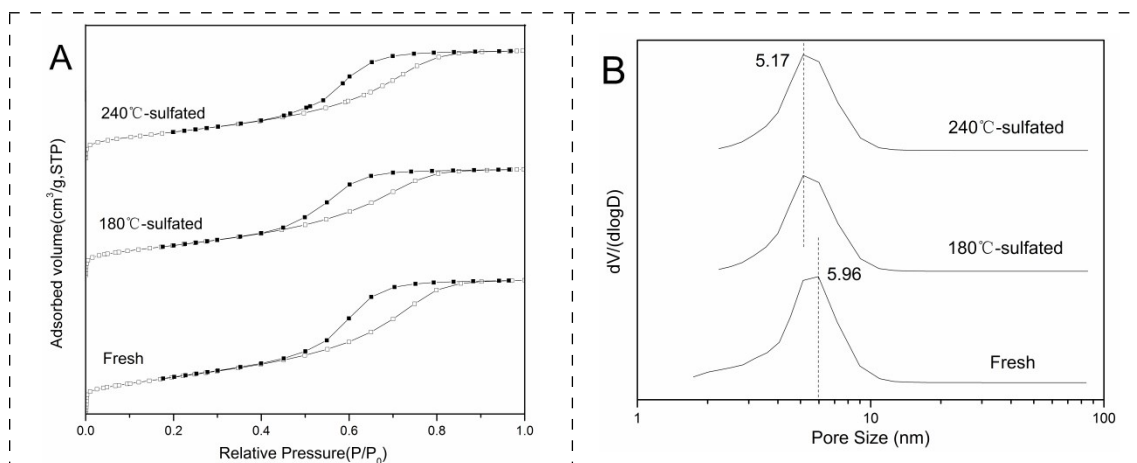


Figure S3. N<sub>2</sub> adsorption-desorption isotherm (A) and pore size distribution curves (B) of fresh catalysts and catalysts after sulfation treatment at 180 °C and 240 °C.

## 1.4 Surface acidity

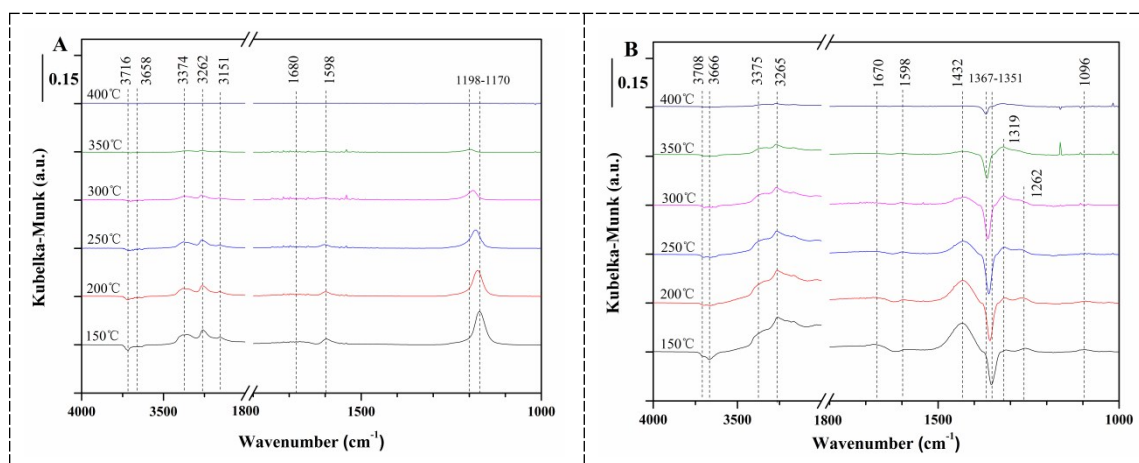


Figure S4. In-situ DRIFTS of  $\text{NH}_3$  adsorption/desorption over fresh catalyst and pre-sulfated catalysts (A) Fresh Ce/TiO<sub>2</sub>, (B) 180°C-sulfated catalyst.

Table S1. Normalized integration area from in-situ DRIFTS at 150 °C

Samples	Total surface acidities	Lewis acidities <sup>a</sup>	Bronsted acidities <sup>b</sup>	SO <sub>4</sub> <sup>2-</sup> <sup>c</sup>
Fresh Ce/TiO <sub>2</sub>	5.09	4.47	0.62	0
180 °C-sulfated	6.02	0.48	5.54	2.78

a. Integrated area from in-situ DRIFTS at 150 °C, peaks in the range of 1300-1150 cm<sup>-1</sup>

b. Integrated area from in-situ DRIFTS at 150 °C, peak centered at 1670 cm<sup>-1</sup> for original catalyst and 1430 cm<sup>-1</sup> for sulfated catalyst

c. Integrated area from in-situ DRIFTS at 150 °C, peak in the range of 1367-1351 cm<sup>-1</sup>

### 1.5 Reaction between $\text{NH}_3 + \text{O}_2$ and the adsorbed NO species

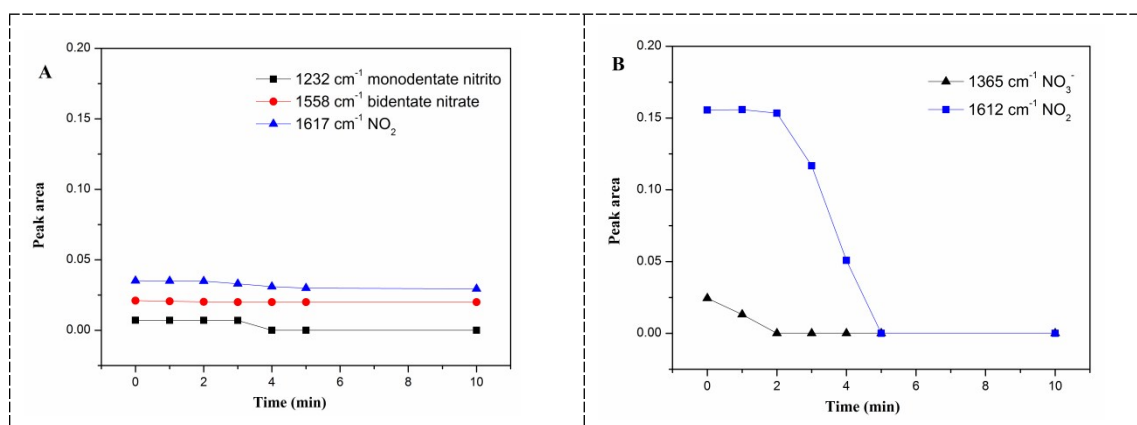


Figure S5. Integration area from in-situ DRIFTS of reaction between  $\text{NH}_3 + \text{O}_2$  and pre-adsorbed

NO over (A) fresh  $\text{Ce/TiO}_2$ , (B) 180 °C-sulfated catalyst

## 1.6 Kinetic study over fresh Ce/TiO<sub>2</sub> catalyst

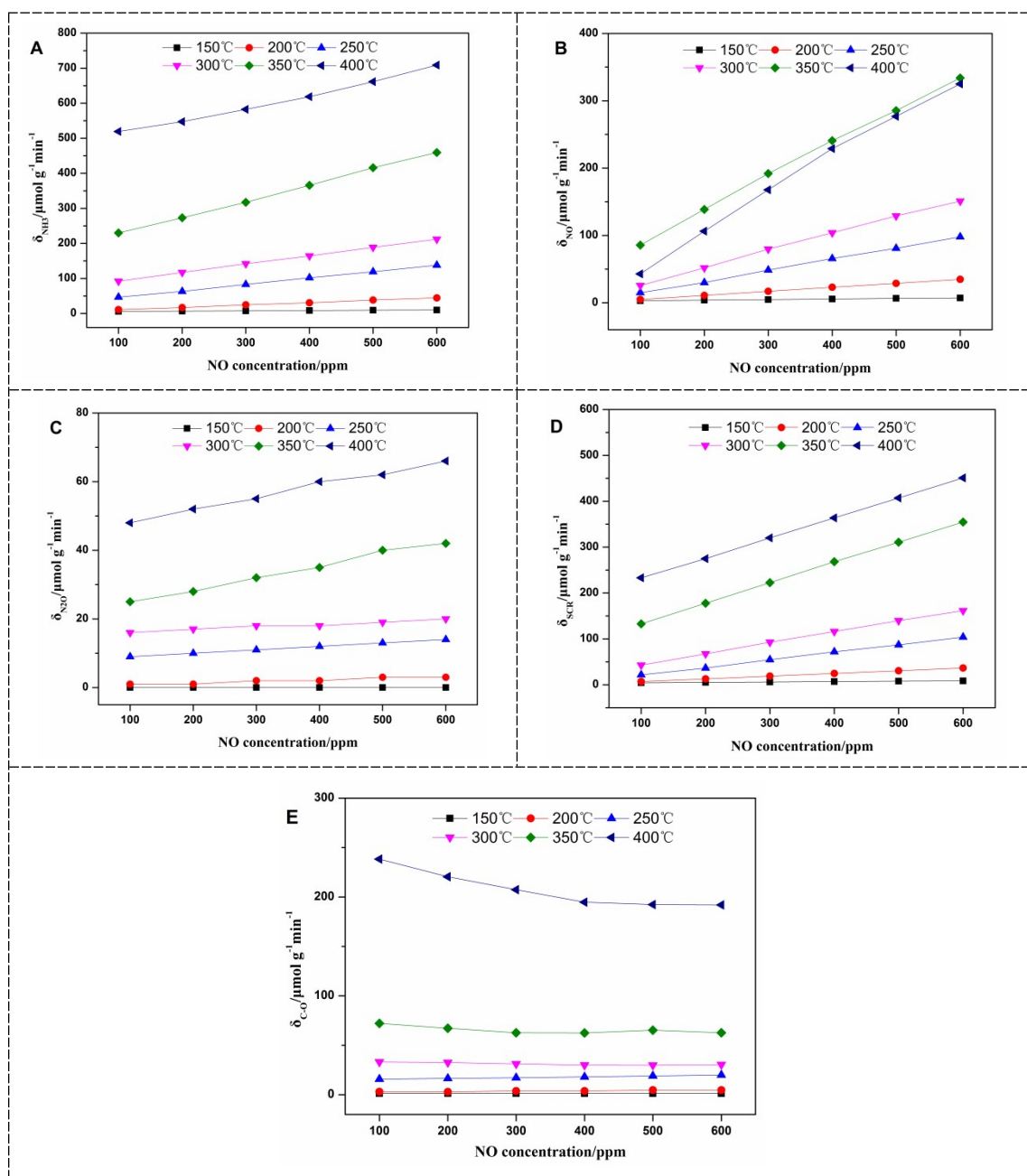


Figure S6. Dependences of (A) NH<sub>3</sub> conversion rate  $\delta_{\text{NH}_3}$ , (B) NO conversion rate  $\delta_{\text{NO}}$ , (C) N<sub>2</sub>O conversion rate  $\delta_{\text{N}_2\text{O}}$ , (D) the rate of SCR reaction  $\delta_{\text{SCR}}$ , (E) the rate of C-O reaction  $\delta_{\text{C-O}}$  on gaseous NO concentration over original Ce/TiO<sub>2</sub> catalyst. Reaction conditions: [NH<sub>3</sub>]=600ppm, [NO]=0-600ppm, [O<sub>2</sub>]=3%, catalyst mass=33.7-135mg, total flow rate=1350ml/min, the GHSV=600000-2400000cm<sup>-1</sup>g<sup>-1</sup>h<sup>-1</sup>.

### 1.7 Kinetic study over sulfated Ce/TiO<sub>2</sub> catalyst

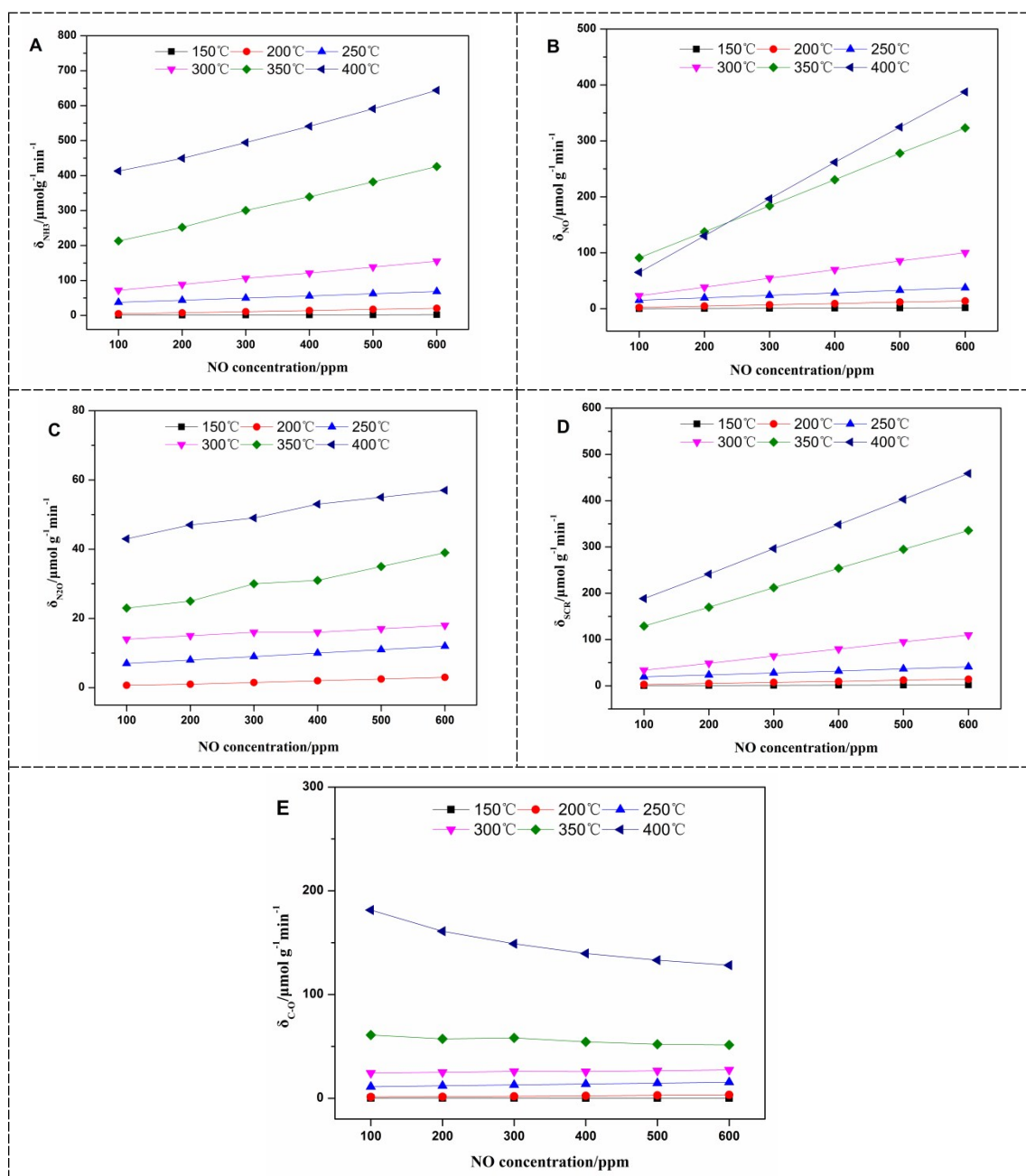


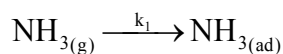
Figure S7. Dependences of (A) NH<sub>3</sub> conversion rate  $\delta_{\text{NH}_3}$ , (B) NO conversion rate  $\delta_{\text{NO}}$ , (C) N<sub>2</sub>O conversion rate  $\delta_{\text{N}_2\text{O}}$ , (D) the rate of SCR reaction  $\delta_{\text{SCR}}$ , (E) the rate of C-O reaction  $\delta_{\text{C-O}}$  on gaseous NO concentration over pre-sulfated Ce/TiO<sub>2</sub> catalysts. Reaction conditions: [NH<sub>3</sub>]=600ppm, [NO]=0-600ppm, [O<sub>2</sub>]=3%, catalyst mass=33.7-135mg, total flow rate=1350ml/min, the GHSV=600000-2400000cm<sup>-1</sup>g<sup>-1</sup>h<sup>-1</sup>.



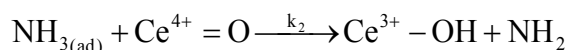
## Derivation of the NH<sub>3</sub>-SCR reaction kinetic model

### 1. Reaction mechanism

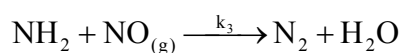
The SCR reaction and the NSCR reaction followed E-R reaction mechanism and C-O reaction can be described as follows<sup>1, 2</sup>:



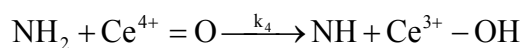
(1S)



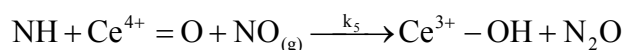
(2S)



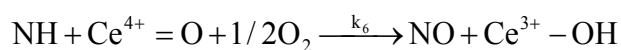
(3S)



(4S)



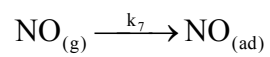
(5S)



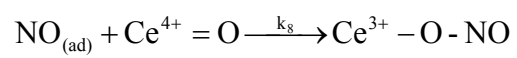
(6S)

Under the SCR condition, the gaseous NH<sub>3</sub> firstly intensely adsorbed on the surface of Ce/TiO<sub>2</sub> catalysts, especially on the pre-sulfated Ce/TiO<sub>2</sub> to form adsorbed NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> (i.e., **Reaction 1S**), which is demonstrated by many reporters<sup>3, 4</sup>. Then, the adsorbed NH<sub>3</sub> or NH<sub>4</sub><sup>+</sup> will be activated by the Ce<sup>4+</sup> on Ce/TiO<sub>2</sub> to form NH<sub>2</sub> (i.e., **Reaction 2S**), which then reacts with gaseous NO to form N<sub>2</sub> (i.e., **Reaction 3S**). Meanwhile, the NH<sub>2</sub> species on the surface can be further oxidized to NH due to the excessive H-abstraction (i.e., **Reaction 4S**), which will further react with NO to form N<sub>2</sub>O (i.e., **Reaction 5S**), which is also called NSCR. Furthermore, the NH can be deeply oxidized to NO by the **Reaction 6S**, which is also called C-O reaction. It could not be observed by DRIFT spectra due to the low concentration of intermediates (i.e., NH<sub>2</sub> and NH species).

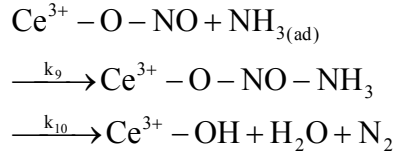
Besides, the NO reduction over original and pre-sulfated Ce/TiO<sub>2</sub> catalyst through L-H reaction mechanism can be described as follows<sup>5</sup>:



(7S)



(8S)



(9S)

Gaseous NO firstly adsorbed on the surface of Ce/TiO<sub>2</sub> and pre-sulfated Ce/TiO<sub>2</sub> catalysts to form physically adsorbed NO (i.e., **Reaction 7S**). Then, the physically adsorbed NO was oxidized by Ce<sup>4+</sup> to form NO<sub>2</sub><sup>-</sup> (i.e., **Reaction 8S**). Finally, the adsorbed NO<sub>2</sub><sup>-</sup> will react with adsorbed NH<sub>3</sub> to form NH<sub>4</sub>NO<sub>2</sub> or NH<sub>4</sub>NO<sub>3</sub>, which will further decompose to N<sub>2</sub> and H<sub>2</sub>O (i.e., **Reaction 9S**).

## 2. Reaction kinetic study

According to the **Reaction 3S** and **Reaction 9S**, the kinetic equation of SCR reaction following E-R reaction pathway and L-H reaction pathway can be described as:

$$\left. \frac{d[\text{N}_2]}{dt} \right|_{\text{E-R}} = k_3[\text{NO}_{(\text{g})}][\text{NH}_2] \quad (10\text{S})$$

$$\left. \frac{d[\text{N}_2]}{dt} \right|_{\text{L-H}} = k_{10}[\text{Ce}^{3+} - \text{O} - \text{NO} - \text{NH}_3] \quad (11\text{S})$$

Where,  $k_3$ ,  $k_{10}$ ,  $[\text{NH}_2]$  and  $[\text{Ce}^{3+}\text{-O-NO-NH}_3]$  were the kinetic constant of **Reaction 3S** and **Reaction 9S**, the concentration of adsorbed NH<sub>2</sub> and the NH<sub>4</sub>NO<sub>2</sub> or NH<sub>4</sub>NO<sub>3</sub> formed on the surface of Ce/TiO<sub>2</sub>, respectively.

Meanwhile, the kinetic equation of the formation of NH<sub>2</sub> can be described as:

$$\frac{d[\text{NH}_2]}{dt} = k_2[\text{Ce}^{4+} = \text{O}][\text{NH}_{3(\text{ad})}] \quad (12\text{S})$$

Where  $k_2$ ,  $[\text{Ce}^{4+}=\text{O}]$  and  $[\text{NH}_{3(\text{ad})}]$  were the rate constant of **Reaction 2S**, the concentration of  $[\text{Ce}^{4+}=\text{O}]$  and the adsorbed NH<sub>3</sub>.

The kinetic equation of the formation of NH<sub>4</sub>NO<sub>2</sub> can be described as:

$$\frac{d[\text{Ce}^{3+} - \text{O} - \text{NO} - \text{NH}_3]}{dt} = k_9[\text{Ce}^{3+} - \text{O} - \text{NO}][\text{NH}_{3(\text{ad})}] \quad (13\text{S})$$

Where  $k_9$ ,  $[\text{Ce}^{3+}\text{-O-NO}]$  and  $[\text{NH}_{3(\text{ad})}]$  were the rate constant of **Reaction 9S**, the concentration of NO<sub>2</sub><sup>-</sup> and the adsorbed NH<sub>3</sub>.

$$\frac{d[\text{Ce}^{3+} - \text{O} - \text{NO}]}{dt} = k_8[\text{Ce}^{4+} = \text{O}][\text{NO}_{(\text{ad})}] \quad (14\text{S})$$

Where  $k_8$  and  $[\text{NO}_{(\text{ad})}]$  were the rate constant of **Reaction 8S** and the adsorbed NO.

Due to the very high GHSV of the reaction system, it can be approximately considered that the adsorbed NO and  $\text{NH}_3$  on the surface of Ce/TiO<sub>2</sub> were saturated with the increase of NO concentration and reaction temperature. Thus, the  $[\text{NO}_{(\text{ad})}]$  and  $[\text{NH}_{3(\text{ad})}]$  can be seen as the constants during the kinetic experiments<sup>5</sup>. Therefore, the SCR reaction following L-H reaction pathway was nearly independent on the gaseous NO and  $\text{NH}_3$  concentration. Moreover, the saturated adsorbed  $\text{NH}_3$  contributed to the constant  $\text{NH}_2$  concentration on the surface as shown in **Reaction 2S**.

Therefore, the total SCR reaction rate can be described as follows:

$$\begin{aligned}\delta_{\text{SCR}} &= \frac{d[\text{N}_2]}{dt} \Big|_{\text{E-R}} + \frac{d[\text{N}_2]}{dt} \Big|_{\text{L-H}} \\ &= k_3[\text{NO}_{(\text{g})}][\text{NH}_2] + k_{10}[\text{Ce}^{3+} - \text{O} - \text{NO} - \text{NH}_3] \\ &= k_{\text{E-R}}[\text{NO}_{(\text{g})}] + k_{\text{L-H}}\end{aligned}\quad (15\text{S})$$

$$k_{\text{E-R}} = k_3[\text{NH}_2] \quad (16\text{S})$$

$$k_{\text{L-H}} = k_{10}[\text{Ce}^{3+} - \text{O} - \text{NO} - \text{NH}_3] \quad (17\text{S})$$

Where,  $k_{\text{E-R}}$ ,  $k_{\text{L-H}}$  were the kinetic constant of the SCR reaction following E-R reaction pathway and L-H reaction pathway.

According to **Reaction 3S**, **5S** and **6S**, the kinetic equation of the H-abstraction of  $\text{NH}_2$ , the oxidation of NH to  $\text{N}_2\text{O}$ , and the oxidation of NH to NO can be described as follows:

$$\frac{d[\text{NH}]}{dt} = -\frac{d[\text{NH}_2]}{dt} = k_4[\text{NH}_2][\text{Ce}^{4+} = \text{O}] \quad (18\text{S})$$

$$\frac{d[\text{NH}]}{dt} = -k_5[\text{NH}][\text{NO}_{(\text{g})}][\text{Ce}^{4+} = \text{O}] \quad (19\text{S})$$

$$\frac{d[\text{NH}]}{dt} = -k_6[\text{NH}][\text{Ce}^{4+} = \text{O}] \quad (20\text{S})$$

Where, the  $k_4$ ,  $k_5$ ,  $k_6$  and  $[\text{Ce}^{4+}=\text{O}]$  were the kinetic constant of the **Reaction 4S**, **5S**, **6S** and the concentration of surface  $\text{Ce}^{4+}$ .

As the reaction reached the steady state, the NH concentration on surface would not

vary. Therefore:

$$\frac{d[\text{NH}]}{dt} = k_4[\text{NH}_2][\text{Ce}^{4+} = \text{O}] - k_5[\text{NH}][\text{NO}_{(\text{g})}][\text{Ce}^{4+} = \text{O}] - k_6[\text{NH}][\text{Ce}^{4+} = \text{O}] \quad (21\text{S})$$

$$= 0$$

Thus, the NH concentration on the surface can be described as:

$$[\text{NH}] = \frac{k_4[\text{NH}_2]}{k_5[\text{NO}_{(\text{g})}] + k_6} \quad (22\text{S})$$

According to the **Reaction 5S**, the N<sub>2</sub>O formation through the E-R reaction pathway can be described as:

$$\frac{d[\text{N}_2\text{O}]}{dt} = -\frac{d[\text{NH}]}{dt} = k_5[\text{NH}][\text{NO}_{(\text{g})}][\text{Ce}^{4+} = \text{O}] \quad (23\text{S})$$

Therefore, according to **Eq.22S**, the N<sub>2</sub>O formation can be transformed as follows:

$$\delta_{\text{NSCR}} = \frac{d[\text{N}_2\text{O}]}{dt} = \frac{k_4 k_5 [\text{NH}_2]}{k_5 [\text{NO}] + k_6} [\text{NO}_{(\text{g})}] [\text{Ce}^{4+} = \text{O}]$$

$$= \frac{k_4 [\text{NH}_2] [\text{Ce}^{4+} = \text{O}]}{1 + \frac{k_6}{k_5 [\text{NO}_{(\text{g})}]}} \quad (24\text{S})$$

According to **Eq.20S**, the rate of C-O reaction can be described as:

$$\delta_{\text{C-O}} = \frac{d[\text{NO}]}{dt} = \frac{k_6 k_4 [\text{NH}_2]}{k_5 [\text{NO}_{(\text{g})}] + k_6} [\text{Ce}^{4+} = \text{O}]$$

$$= \frac{k_4 [\text{NH}_2] [\text{Ce}^{4+} = \text{O}]}{\frac{k_5 [\text{NO}_{(\text{g})}]}{k_6} + 1} \quad (25\text{S})$$

## References

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