

Supporting information for

Catalytic reduction of SO₂ by Gd@CeO_x catalysts: Stability enhancement and structural modulation

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1. Chemicals and Materials

All chemicals were purchased from commercial sources and used without further treatment. $\text{Ce}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Gd}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were purchased from Shanghai Macklin Biochemical Technology Co., LTD. The water used is deionized from laboratory preparation.

2. Catalytic activity and selectivity measurement

To determine the activity of the catalyst used for the reduction of SO_2 by CO, 1 mL of catalyst was fixed in a quartz tube (inner diameter 15 mm, outer diameter 20 mm), and then the catalyst was pre-sulfurized by passing a mixture of gases into the reactor at a total gas flow rate of 400 mL/min (1% SO_2 , 2% CO, and 97% N_2), and the catalyst had to be pre-sulfurized at 500 °C for 2 h. Then the system was cooled down and cooled to 400 °C, and the mixture conditions were changed to test the catalyst activity, with the total gas flow rate still 400 mL/min (2500 ppm SO_2 , 5000 ppm CO, and 99% N_2). Then the system was cooled down to 400°C and the mixture conditions were changed to test the catalyst activity at a total gas flow rate of 400 mL/min (2500 ppm SO_2 , 5000 ppm CO, 99.25 % N_2). The exhaust gas was analyzed after cooling down to the target temperature and stabilizing for 30 min. The SO_2 concentration at the inlet and outlet of the reactor was detected by a sulfur dioxide analyzer (HYP600, Shanghai Yidian Analytical Instrument Co., LTD) and the concentration of the main by-product COS in the exhaust gas was detected by gas chromatography (FPD detector, Trace1300, ThermoFisher Scientific).

The SO_2 conversion (X), the selectivity (Y_S) and the yield (Y) of monomeric sulfur are defined as follows.

$$X(\%) = \frac{[\text{SO}_2]_{in} - [\text{SO}_2]_{out}}{[\text{SO}_2]_{in}} * 100 \% \quad (2-1)$$

$$Y_S = \frac{[\text{SO}_2]_{in} - [\text{SO}_2]_{out} - [\text{COS}]_{out}}{[\text{SO}_2]_{in} - [\text{SO}_2]_{out}} \quad (2-2)$$

$$Y = XY_S \quad (2-3)$$

Among them, $[\text{SO}_2]_{in}$ represented the SO_2 concentration at inlet of the reactor, $[\text{SO}_2]_{out}$ represented the SO_2 concentration at outlet of the reactor, and $[\text{COS}]_{out}$

represented the COS concentration at the outlet of the reactor.

3. Catalyst characterization and analysis methods

X-ray diffraction (XRD) patterns were obtained from an X-ray diffractometer (Smartlab TM 3 kW, Rigaku, Japan). The scan speed was $10\text{ }^{\circ}\cdot\text{min}^{-1}$ and the 2θ scans covered $10\sim 85\text{ }^{\circ}$. The specific surface area and average pore diameter (BET method) of the samples were measured by N_2 adsorption/desorption isotherms at $-196\text{ }^{\circ}\text{C}$ using a surface-area analyzer (Micromeritics, 2020M V3.00H). All of the samples were degassed at $350\text{ }^{\circ}\text{C}$ under vacuum for 3 h prior to the adsorption experiments. The microstructural natures of the catalysts have been investigated using a transmission electron microscopy (JEOL, JEM-2010UHR).

The temperature programmed desorption of ammonia (NH_3 -TPD) was conducted on the CHEMBET-3000 (Quantachrome) to obtain the surface acid properties. All the catalysts were preheated at $400\text{ }^{\circ}\text{C}$ under a helium stream for 1 h, and then cooled to $50\text{ }^{\circ}\text{C}$ for the ammonia adsorption. Afterwards, ammonia was desorbed from $50\text{ }^{\circ}\text{C}$ to $800\text{ }^{\circ}\text{C}$ at a heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$. The temperature programmed desorption of carbon dioxide (CO_2 -TPD) was conducted on the CHEMBET-3000 (Quantachrome) to obtain the surface alkaline properties. All the catalysts were preheated at $400\text{ }^{\circ}\text{C}$ under a helium stream for 1 h, and then cooled to $50\text{ }^{\circ}\text{C}$ for the carbon dioxide adsorption. Afterwards, carbon dioxide was desorbed from $50\text{ }^{\circ}\text{C}$ to $800\text{ }^{\circ}\text{C}$ at a heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$. The Semiautomatic Micromeritics TPD/TPR 2900 instrument was used for the temperature programmed reduction of hydrogen (H_2 -TPR). All the catalyst carriers were preheated to $400\text{ }^{\circ}\text{C}$ under an argon stream for 1 h, and cooled to $50\text{ }^{\circ}\text{C}$. Then 5% H_2/Ar flow was switched, and the temperature increased from $50\text{ }^{\circ}\text{C}$ to $800\text{ }^{\circ}\text{C}$ at a $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ heating rate. The data were collected throughout the whole temperature range.

In-situ Diffuse Reflectance Infrared Fourier Transform Spectra (*in situ* DRIFTS) were also collected by a Nicolet IS50 spectrometer. 1% SO_2 was pumped into the system for 10 min when the temperature was $350\text{ }^{\circ}\text{C}$. Then stop entering SO_2 was stopped and 2% CO was pumped into the system for 10 min. Finally, 1% SO_2 and 2%

CO were pumped together into the system for 10 min.