

Ceria-tungsten-tin oxide catalysts with superior regeneration capacity after sulfur poisoning for NH₃-SCR process

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Includes 7 pages, 2 figures, 2 tables.

Catalytic activity tests and kinetic studies

NH₃-SCR activity tests of catalysts at steady-state were conducted in a quartz tube plug flow reactor. The feed gas consisted of 500 ppm NO, 530 ppm NH₃, 5 vol. % O₂, 5 vol. % H₂O and balance N₂. The gas flow rate was kept at 500 mL/min, which corresponded to a gas hourly space velocity (GHSV) of 120, 000 h⁻¹. The concentrations of NO, NH₃, NO₂, SO₂ and N₂O were continually monitored by an FTIR spectrometer (G470 Nicolet), which was equipped with a multiple path gas cell (2 m). The steady-state tests of NO/NH₃ oxidation activity were carried out on the same device as the NH₃-SCR activity test. The gas mixture used was comprised of 500 ppm NO_x/NH₃, 5 vol.% O₂ and N₂ balance with a flow rate of 500 mL/min.

The kinetic experiments for standard SCR were also performed in the same fixed-bed reactor as the activity test. The NO_x conversion was kept at less than 20% in the temperature range of 175-225 °C. The reaction rates of NO_x conversion normalized by the specific area were determined as follows:

$$-R_{\text{NO}_x} = (F_{\text{NO}_x} \times x) / (W \times S) \quad (S1) \quad \text{where } F_{\text{NO}_x} \text{ is the}$$

molar flow rate of NO (in mol s⁻¹), x is the conversion percentage of NO, W is the weight of catalyst (in g), and S is the specific surface area of catalyst (in m² g⁻¹). The apparent activation energies (E_a , in kJ mol⁻¹) were calculated from Arrhenius plots of the reaction rates.

Catalyst characterization

N₂ adsorption-desorption isotherms were measured at -196 °C on a Micromeritics TriStar II 3020 analyzer to investigate the specific surface area and pore structure of catalysts. The catalysts were outgassed at 150 °C for 8 h before being analyzed.

A Bruker D8 Advance diffractometer equipped with a Cu K_α X-ray tube was used for the collection of X-ray diffraction (XRD) patterns at 40 kV and 40 mA with a step size of 0.02° and a time per step of 0.2 s.

H₂ temperature programmed reduction (H₂-TPR) experiments were carried out on a Micromeritics AutoChem 2920 chemisorption analyzer. In a typical measurement, 120 mg of catalyst was firstly preprocessed at 400 °C for 0.5 h in Ar with a total flow rate of 50

mL/min, and then the temperature was decreased to 50 °C and held for another 0.5 h under the 10 vol. % H₂/Ar (50 mL/min) atmosphere. After that, the temperature was linearly increased from 50 to 1000 °C at a heating rate of 10 °C/min under the same atmosphere, and the H₂ consumption amount was detected by a thermal conductivity detector (TCD).

X-ray photoelectron spectroscopy (XPS) measurements were carried out on an X-ray photoelectron spectrometer (AXIS Supra/Ultra) with Al K α radiation (1486.7 eV). The binding energies were referenced to the C 1s line at 284.8 eV. Quantification of the Ce, W, Sn, S, N and O atomic fractions on the surface was obtained from the integration of Ce 3d, W 4f, Sn 3d, S 2p, N 1s and O 1s core level spectra with appropriate corrections for sensitivity factors.

The *in situ* DRIFTS experiments were performed using an FTIR spectrometer (Nicolet IS 50) equipped with an MCT/A detector. An Omega Programmable Temperature Controller was used to regulate the temperature for different experiments. Prior to each experiment, the catalyst was pretreated at 500 °C for 30 min in an air flow and then cooled down to 200 °C while purging with N₂. For the NH₃ adsorption experiments, the background spectrum was collected in flowing N₂, and then 500 ppm NH₃ was introduced to the catalyst surface. All spectra were recorded by accumulating 100 scans with a resolution of 4 cm⁻¹, and the background spectra were automatically subtracted from the sample spectra.

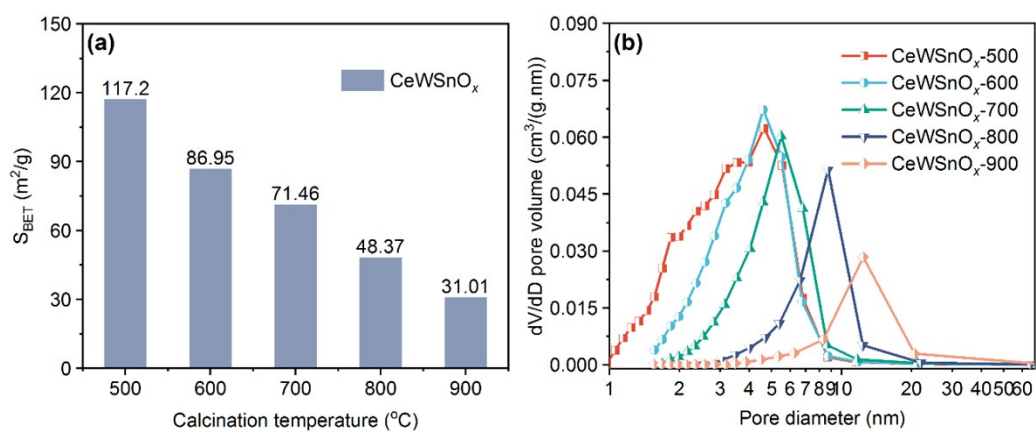


Figure S1. Effects of calcination temperature on the specific surface area (a) and BJH pore size distribution curves (b) of the CeWSnO_x catalysts.

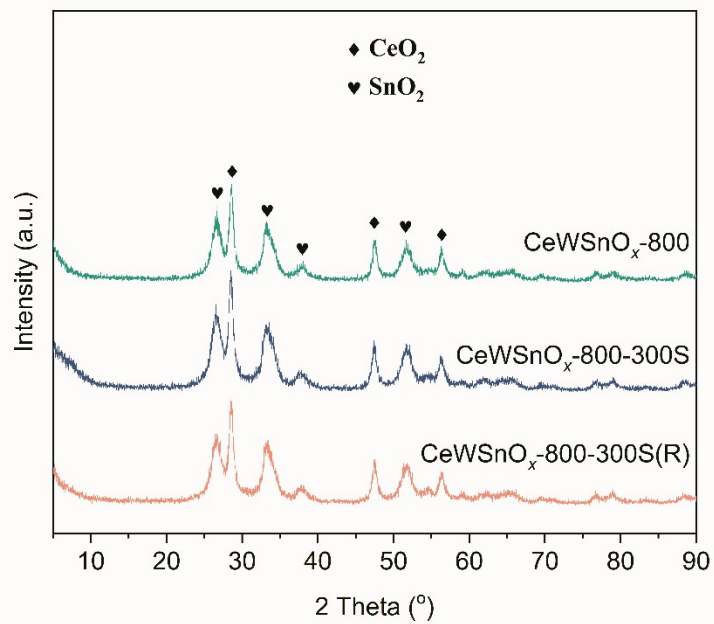


Figure S2. XRD patterns of CeWSnO_x-800, CeWSnO_x-800-300S and CeWSnO_x-800-300S(R) catalysts.

Table S1. The textural parameters of catalysts calculated from the N₂ adsorption-desorption results.

Catalysts	S _{BET}	D _{average}	V _{total}
CeWSnO _x -800	49.77	7.39	0.18
CeWSnO _x -800-300S	47.07	7.56	0.18
CeWSnO _x -800-300S(R)	51.78	7.18	0.19

Table S2. Surface chemical compositions of catalysts according to the XPS results.

Catalysts	Ce	O	Sn	W	N	S	S/N
CeWSnO _x -800	7.64	64.81	24.14	3.41	0.00	0.00	0.00
CeWSnO _x -800- 300S	6.96	66.46	21.86	3.17	0.05	1.50	3.00
CeWSnO _x -800- 300S(R)	7.23	65.30	24.01	3.46	0.00	0.00	0.00