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Supplementary information

Synthesis of Ce2Sn2O7 pyrochlore and Ce2Sn2O8+x solid solution to support FeOx for simultaneous NH3-SCR and CO oxidation: Study on the paramorphism effect

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1. Supplementary Experimental Information

1.1 Catalyst characterization

Powder X-ray diffraction (XRD) measurements of the prepared catalysts were recorded on Bruker AXSD8 Focus diffractometer instrument operating at 40 kV and 30 mA, with a Cu target and Kα-ray irradiation (λ= 1.54056 Å). Scans were set from 10 to 90 ° and with a step of 4 ° min^{-1}. To maintain good comparability of the data, all the samples were tested continuously.

X-ray Photoelectron Spectroscopy (XPS) tests were carried out on a Thermo Scientific K-Alpha system using a single Al-Kα-X-ray source (hv=1486.6 eV) operating at 12 kV of voltage. The data were obtained at ambient temperature with an ultrahigh vacuum ($< 5\times10^{-7}$ mbar). The binding energies were calibrated using the C 1s peak of graphite at 284.8 eV as a reference.

Element compositions of catalysts were ascertained *via* inductively coupled plasma optical emission spectrometry (ICP-OES) on the Agilent Technologies 5100 ICP-OES.

The morphology and microstructure of the catalysts were characterized by transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HR-TEM), and the elemental analysis was obtained by energy dispersive spectrometer (EDS), which were tested on FEI Talos F200x instrument.

Hydrogen temperature programed reduction (H_2-TPR) tests were carried out on the FINESORB-3010C-243 automatic temperature programmed chemical adsorption instrument. The catalyst amount used in the tests was 50 mg. First, the catalyst was pretreated in a 99.99% Ar flow of 30 mL min^{-1} at 120 ℃ for 60 min to remove any possible surface impurities and then cooled down to ambient temperature. Afterwards, the Ar gas was switched to a 10% H_2/Ar mixture with a flow rate of 30 mL min^{-1} until the baseline was stabilized. The temperature was then increased from ambient temperature to 800 ℃ with a heating rate of 10 ℃ min^{-1}. A thermal conductivity detector (TCD) was employed to monitor the H_2 consumption, which was quantified by using a CuO (99.99%) calibration standard.

O_2-TPD was measured on Micromeritics Auto Chem 2920 chemical adsorption instrument with a TCD. Generally, 50 mg catalyst was placed in a U-shape quartz reactor, and pretreated at 550 ℃ for 1 hour in an ultra-high purity He flow of 30 mL min^{-1}. Afterwards, the catalyst was cooled down to 50 ℃ and saturated with a 3% O_2/He flow of 30 mL min^{-1} for 1 hour. Following this step, the catalyst was purged again in a 99.99% He gas stream of 30 mL min^{-1} for 30 min to remove any physically adsorbed O_2. Then, a test was performed from 50 to 800 ℃ with a heating rate of 10 °C min^{-1}.

EPR tests was used to measure the oxygen vacancies of the Fe/$Ce_2Sn_2O_{8+x}$ and Fe/$Ce_2Sn_2O_7$ catalysts. 10 mg catalyst powder was dispersed in 5 mL of DDI water, and after ultrasonic vibration, 200 μL of mixed solution was taken out and 100 μL of DMPO solution with a concentration of 100 mM were added. Afterwards, the samples were put into a capillary tube, and transferred into liquid N_2 at 243 K and the EPR spectra were recorded at 243 K with Bruker A300 EPR Spectrometer, operating with a field modulation of 100 kHz and microwave frequencies of 9067.558 MHz.

NH_3-TPD and $NO+O_2$-TPD were carried out to determine the amount of surface acid sites and NO_x adsorption sites on the catalysts, which were measured on DAS-7000 chemical adsorption instrument with a TCD. Typically, 50 mg sample was placed in a quartz reactor and saturated with NH_3 or $NO+O_2$ at 50 °C. Afterwards, the sample was purged with a 30 mL min^{-1} 99.99% He flow for 60 min to remove any physically adsorbed molecules. TPD was then carried out from 50 to 550 °C with a heating rate of 10 ℃ min^{-1} in a 30 mL min^{-1} He flow. Especially, the NO and NO_2 concentration of gas mixture were collected by a flue gas analyzer of FGA10.

In situ diffuse reflectance infrared flourier transform spectra (In-situ DRIFTS) were conducted on a Bruker Vertex instrument (TENSOR II) equipped with an MCT detector chilled in liquid nitrogen. A micro-size in-situ FTIR furnace equipped with ZnSe windows was used. Prior to the experiments, the catalyst was pretreated at 400 °C for 1 h with an Ar flow, then cooled to 50 °C. In-situ DRIFTS spectra were recorded from 4000 to 1000 cm^{-1} with a resolution of 4 cm^{-1}. OPUS 7.5 software was used to process data. For each experiment, the background spectra were collected before the catalyst was exposed to the adsorbates. Subsequently, the reaction gas was introduced into the in-situ reactor, with the experiments carried out at desired temperatures.

1.2 Activity evaluation

The reaction performance of NO_x-SCR by NH_3 over the catalysts was tested in a fixed-bed horizontal straight quartz reactor containing 50 mg catalyst. The reaction feed consists of 5% O_2, 500 ppm NO, 500 ppm NH_3 with an Ar balance gas. The total flow rate is 50 mL min^{-1}, which is equivalent to a WHSV of 60,000 mL h^{-1} g_{cat}^{-1}. A thermocouple with its head point contacting the catalyst bed was used to control the reaction temperature. The kinetic data were obtained by raising the reaction temperature with a 50 °C gap. A FGA10 flue gas analyzer was used to analyze the products. In order to obtain steady-state kinetic data, the reaction was stabilized at a certain temperature for 30 min before the measurement. The conversion rate of NO_x was calculated by the following equation:

$$NO\ \text{Conversion} = \frac{[NO_x]_{in} - [NO_x]_{out}}{[NO_x]_{in}} \times 100\%$$

$$N_2\ \text{selectivity} = \left[1 - \frac{2[N_2O]_{out} + [NO_2]_{in}}{[NO_x]_{in} - [NO_x]_{out} + [NH_3]_{in} - [NH_3]_{out}}\right] \times 100\%$$

Where $[NO_x]_{in}$ and $[NO_x]_{out}$ represent the NO_x concentration (including NO and NO_2) in the inlet or outlet gas feed. The concentration of N_2 and N_2O in the outlet stream were determined by a mass spectrometry.

1.3 DFT calculation

In this investigation, Density Functional Theory (DFT) calculations were conducted using the Materials Studio software. The exchange-correlation energy was evaluated employing the Generalized Gradient Approximation (GGA) coupled with the Perdew-Burke-Ernzerhof (PBE) functional. The electron-ion interactions were modeled using the Projector Augmented Wave (PAW) method. A plane wave basis set with an energy cutoff of 400 eV was utilized. Convergence criteria were set at 10^{-5} eV for energy and 0.02 eV Å^{-1} for force. Additionally, dipole correction was implemented with symmetry operations disabled. The Fe/$Ce_2Sn_2O_7$ and Fe/$Ce_2Sn_2O_{8+x}$ catalysts modeled with Fe_2O_3/$Ce_2Sn_2O_7$ (222) and Fe_2O_3/$Ce_2Sn_2O_8$ (111), respectively. The k-point sampling grid for Fe_2O_3/$Ce_2Sn_2O_7$ (222) and Fe_2O_3/$Ce_2Sn_2O_8$ (111) were both 1x1x1. Furthermore, the self-consistent field, energy, force, atomic displacement, and stress components had convergence criteria of 1.0×10^{-6} eV/atom, 1.0×10^{-5} eV/atom, 0.03 eV/Å, 1.0×10^{-3} Å and 0.05 GPa, respectively. The vacuum space along the z direction was set to be 15 Å. The optimized lattice parameters of the bulk tetragonal $Ce_2Sn_2O_8$ (a=b=c=10.822 Å) and bulk tetragonal $Ce_2Sn_2O_7$ (a=b=c=10.826 Å)， which were in good agreement with the previous report.

$$E_{ov} = E_{def} - E_{bulk} + 1/2E_{O_2}$$

Where: E_{def} is the total energy of the defective structure containing oxygen vacancy; E_{bulk} is the total energy of the ideal crystal. E_{O_2} is the energy of oxygen molecules in the gaseous state.

2.Supplementary Results

2.1 Supplementary Figures

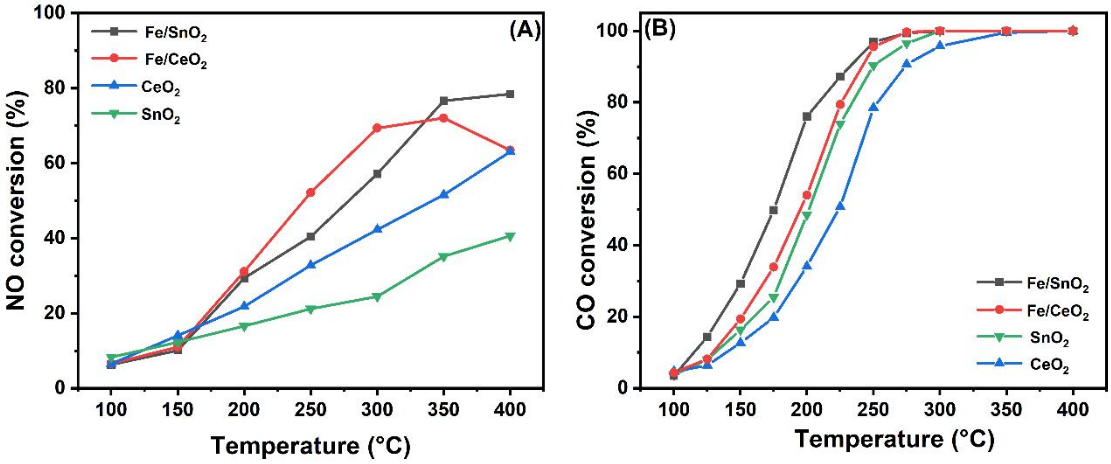

Figure S1. (A) NO conversion and (B) CO conversion over CeO_2, SnO_2, Fe/CeO_2 and Fe/SnO_2.

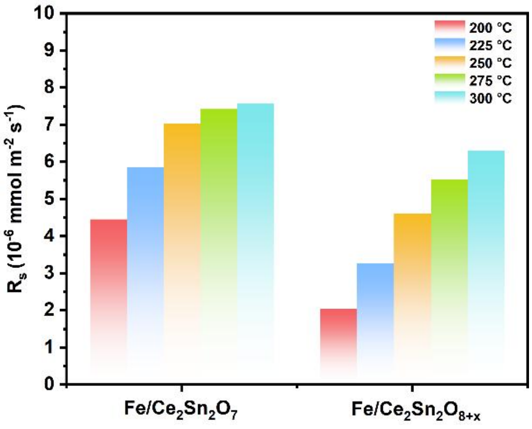

Figure S2. NO conversion rates (R_S) of Fe/$Ce_2Sn_2O_7$ and Fe/$Ce_2Sn_2O_{8+x}$.

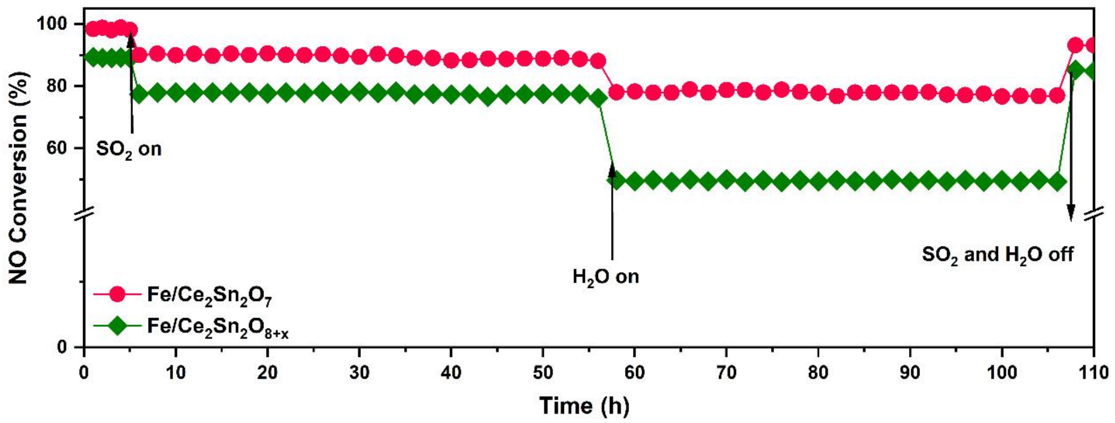

Figure S3. stability tests of Fe/$Ce_2Sn_2O_7$ and Fe/$Ce_2Sn_2O_{8+x}$ catalysts with H_2O and/or SO_2 at 300 °C.

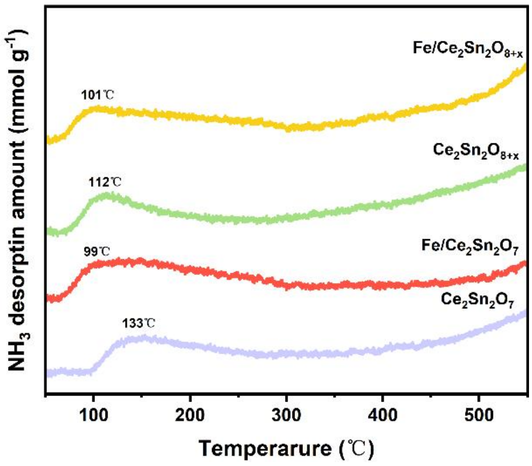

Figure S4. NH_3-TPD profiles of the catalysts and corresponding supports.

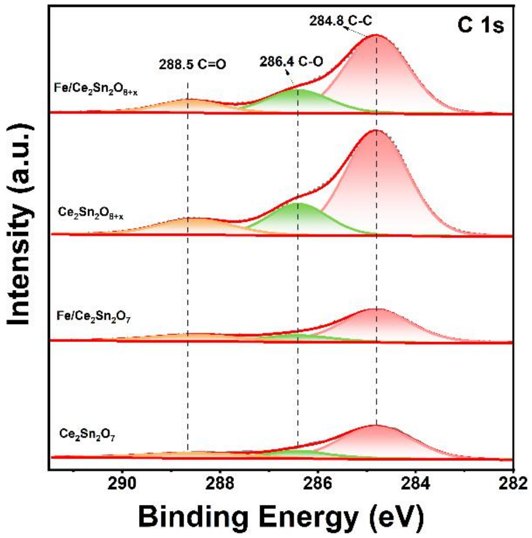

Figure S5. C 1s curves of the catalysts and corresponding supports.

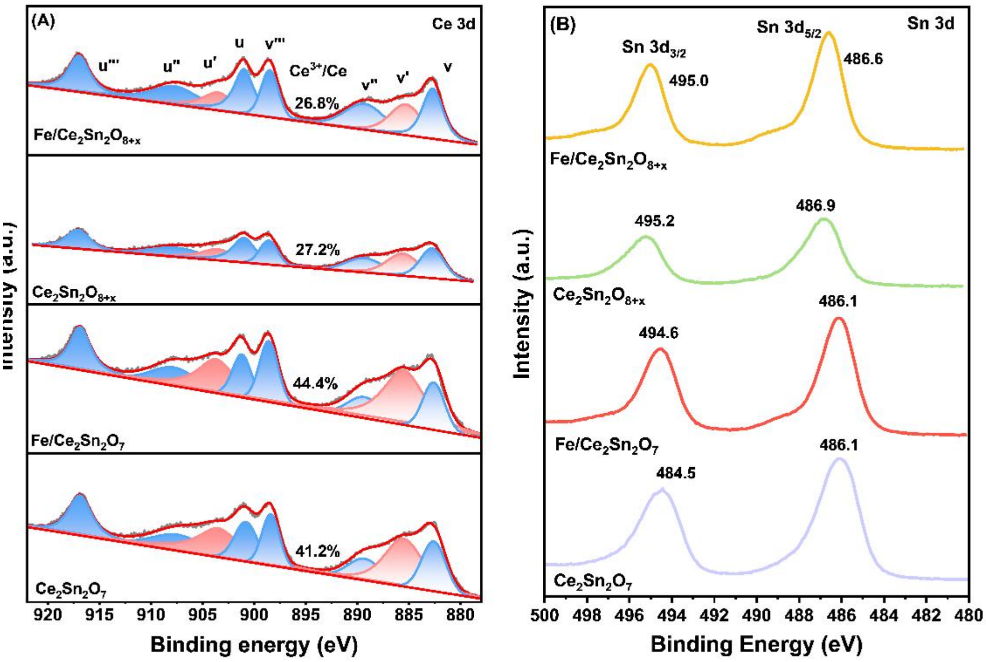

Figure S6. XPS of Ce 3d (A) and Sn 3d (B) on the catalysts and corresponding supports.

2.2 Supplementary Tables

Table S1. NH_3-SCR performance over the catalysts and corresponding supports.

Catalysts	R_W [a]	R_S [b]	Ea
	(10^{-5} mmol g^{-1} s^{-1})	(10^{-7} mmol m^{-2} s^{-1})	kJ mol^{-1}
$Ce_2Sn_2O_7$	5.72	8.54	49
$Fe/Ce_2Sn_2O_7$	9.06	19.04	33
$Ce_2Sn_2O_{8+x}$	5.06	8.00	52
$Fe/Ce_2Sn_2O_{8+x}$	6.34	12.08	46

a R_W: the NO_x conversion rates normalized by catalyst mass at 115 ℃; b R_S: the NO_x conversion rates normalized by catalyst surface area at 115 ℃.

Table S2. Quantified H_2-TPR results of the catalysts and corresponding supports.

Catalysis	H_2 consumption		
	Peak below 350 ℃ （mmol/g_{cat}）	Peak above 350 ℃ （mmol/g_{cat}）	Total H_2 consumption （mmol/g_{cat}）
$Ce_2Sn_2O_7$	0.74	0.36	1.10
$Fe/Ce_2Sn_2O_7$	0.87	0.40	1.27
$Ce_2Sn_2O_{8+x}$	0.34	2.17	2.51
$Fe/Ce_2Sn_2O_{8+x}$	0.29	2.44	2.73

Table S3. Quantified O_2-TPD results of the catalysts and corresponding supports.

Catalysts	O_2 Desorption (a.u.)				
	α peak	β peak	γ peak	α+β	Total amount
$Ce_2Sn_2O_7$	29	26	36	55	91
Fe/$Ce_2Sn_2O_7$	32	28	40	60	100
$Ce_2Sn_2O_{8+x}$	14	37	0	51	51
Fe/$Ce_2Sn_2O_{8+x}$	17	32	0	49	43

Table S4. Quantified NO+O_2-TPD result over the catalysts and corresponding supports.

Catalysts	NO Desorption			NO_2 Desorption			Total
	T_1 (°C)	T_2 (°C)	Amount (a.u.)	T_1 (°C)	T_2 (°C)	Amount (a.u.)	Amount (a.u.)
$Ce_2Sn_2O_7$	119	300	32	117	315	4	36
Fe/$Ce_2Sn_2O_7$	110	209	50	117	221	8	58
$Ce_2Sn_2O_{8+x}$	123	293	45	125	280	11	56
Fe/$Ce_2Sn_2O_{8+x}$	131	360	71	136	340	29	100