

Supplementary Material

Study on monolayer dispersion behavior of SnO₂ on ZSM-5 for NO_x-SCR by C₃H₆: the remarkable promotional effects of air plasma treatment

*Lihong Zhang^{a, ‡}, Qiang Lai^{a, ‡}, Yaqian Liu^a, Xian Li^a, Wenqi Zhang^a, Xianglan Xu^a, Xiuzhong Fang^a, Junwei Xu^a, Xiang Wang^{a, *}*

^a Key Laboratory of Jiangxi Province for Environment and Energy Catalysis, College of Chemistry, Nanchang University, Nanchang, 330031, PR China

* Corresponding author. E-mail: xwang23@ncu.edu.cn (X. Wang)

[‡] These authors contributed equally.

1. Supplementary Experimental Information

1.1 Catalyst characterization

XRD patterns of the catalysts were recorded on Bruker AXSD8 Focus diffractometer instrument operating at 40 kV and 30 mA, with a Cu target and $K\alpha$ -ray irradiation ($\lambda = 1.5405 \text{ \AA}$). Scans were taken from 10 to 80 ° and with a step of 0.02° s⁻¹. In order to maintain good comparability of the data, all the samples were tested continuously.

XPS tests were carried out on a PerkinElmer PHI1600 system using a single Mg-K-X-ray source operating at 300 W and 15 kV of voltage. The spectra were obtained at ambient temperature with an ultrahigh vacuum. The binding energies were calibrated using the C 1s peak of graphite at 284.8 eV as a reference.

N₂ sorption was used to examine the pore structure of the prepared samples. The measurements were carried out at 77 K on Micromeritics ASAP 2020 instrument. Before testing, all samples were pre-treated in vacuum at 200 °C for 6 hours. The Specific surface areas was calculated using the Brunauer-Emmett-Teller (BET) method. The micropore volume was obtained from the t-graph method.

TEM and HRTEM images of the catalysts were taken to discern the catalyst morphologies and SnO₂ distribution over ZSM-5 zeolite support with a FEI Talos F200s transmission electron microscope. EDX-mapping experiments were conducted to identify the element distribution of the catalysts by on the same apparatus equipped with a Super-X EDS Detector, which is operated at 300 KeV.

H₂-TPR experiments were carried out on the FINESORB 3010C automatic temperature programmed chemical adsorption instrument. The catalyst amount used in the tests was 100 mg. First, the catalyst was pretreated in an Ar flow of 30 mL min⁻¹ at 120 °C for 60 min and then cooled down to room temperature. Afterwards, the feed gas was switched to a 10% H₂/Ar mixture with a flow rate of 30 mL min⁻¹. After the baseline is stabilized, the temperature was then increased from ambient temperature to 750 °C with a heating rate of 10 °C min⁻¹. A thermal conductivity detector (TCD) was employed to monitor the H₂ consuming amount, which was quantified by using a CuO

(99.99%) calibration standard.

EPR technique was used to measure the surface oxygen property of SnO₂/Beta catalysts. The catalysts were pretreated with 100 Torr oxygen at 300 °C for 30 min and then cooled down to room temperature, which was followed by evacuation at the same temperature. Afterwards, the samples were transferred into liquid N₂ at 77 K and the EPR spectra were recorded at 77 K with a JEOL FA-200 EPR Spectrometer, operating with a field modulation of 100 kHz and microwave frequencies of 9067.558 MHz.

NH₃-TPD and C₃H₆-TPD were carried out to determine the amount of surface acid sites and C₃H₆ adsorption sites on SnO₂/Beta catalysts. Typically, 100 mg of sample was placed in a quartz reactor and saturated with NH₃ or C₃H₆ at room temperature. Afterwards, the sample was purged with a 30 mL min⁻¹ 99.99% He flow for 30 min to remove any physically adsorbed molecules. TPD was then carried out from 100 °C to 600 °C with a heating rate of 10 °C min⁻¹ in a 30 mL min⁻¹ He flow.

In situ DRIFTS was used to monitor the reaction intermediates and elucidate the reaction mechanism. The equipment used in this article is TENSOR II03040404 (Bulake technology co., ltd) and is equipped with an MCT detector. Before the experiment, the sample was pretreated in Ar atmosphere at 400 °C for 1 h, then cooled to 50 °C, and the background spectrum of the sample was recorded. Subsequently, the desired reaction gas was introduced and the reaction was carried out at 400 °C.

Density functional theory (DFT) calculations were performed using the Vienna Ab-initio Simulation Package (VASP) code. A plane wave cutoff energy of 500 eV was used for total energy calculations. The electron-ion interactions were described by using projector augmented wave (PAW) method. The generalized gradient approximation (GGA) was employed with the exchange-correlation functional of Perdew-Burke-Ernzerhof (PBE). The Monkhorst-Pack grid was chosen based on the cell size. The structures were relaxed until total energy change between two steps was smaller than 0.01 meV. The force tolerance of 0.01 eV/Å was used. A vacuum region of 15 Å was adopted to avoid interactions between slabs in the z-direction. Bader's analysis method was used to obtain the electron population. VESTA software was used to visualize the results from VASP.

1.2. Activity evaluation

The reaction activity test was carried out in a fixed bed horizontal straight quartz reactor, usually using 50 mg of catalyst to test the reaction performance of NO_x-SCR by C₃H₆ over the catalysts. In order to accurately control the reaction temperature, a thermocouple was placed close to the catalyst bed. The reaction feed consists of 5% O₂, 500 ppm NO, 500 ppm C₃H₆ 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. An online SHP8400 PMS process mass spectrometer was used to analyze the gas composition after the reaction. The mass-to-charge ratios of NO, O₂, N₂ and N₂O are 30, 32, 28 and 44, respectively. The temperature was raised to 100 °C at a rate of 5 °C min⁻¹, and the data was collected for the first time after 30 minutes of constant temperature; and then the kinetic data was measured every 50 °C. Meanwhile, in order to obtain stable kinetic data, the reaction was stabilized at a certain temperature for 30 minutes before measurement. In order to obtain steady-state kinetic data, The NO_x conversion rate was calculated by the following equation:

$$\begin{aligned} NO_x \text{ Conversion} &= \frac{[NO_x]_{in} - [NO_x]_{out}}{[NO_x]_{in}} \times 100\% \\ N_2 \text{ Selectivity} &= \frac{[NO_x]_{in} - [NO_x]_{out} - 2[N_2O]_{out}}{[NO_x]_{in}} \times 100\% \\ C_3H_6 \text{ Conversion} &= \frac{[C_3H_6]_{in} - [C_3H_6]_{out}}{[C_3H_6]_{in}} \times 100\% \end{aligned}$$

Where [NO_x]_{in} and [NO_x]_{out} represent the NO_x concentration (including NO and NO₂) in the inlet or outlet gas feed. The [C₃H₆]_{in} and [C₃H₆]_{out} represent the C₃H₆ concentration in the inlet or outlet gas feed. The N₂ and N₂O concentration in the outlet flow was directly measured by the mass spectrometry.

2. Supplementary Results

2.1. Supplementary Figures

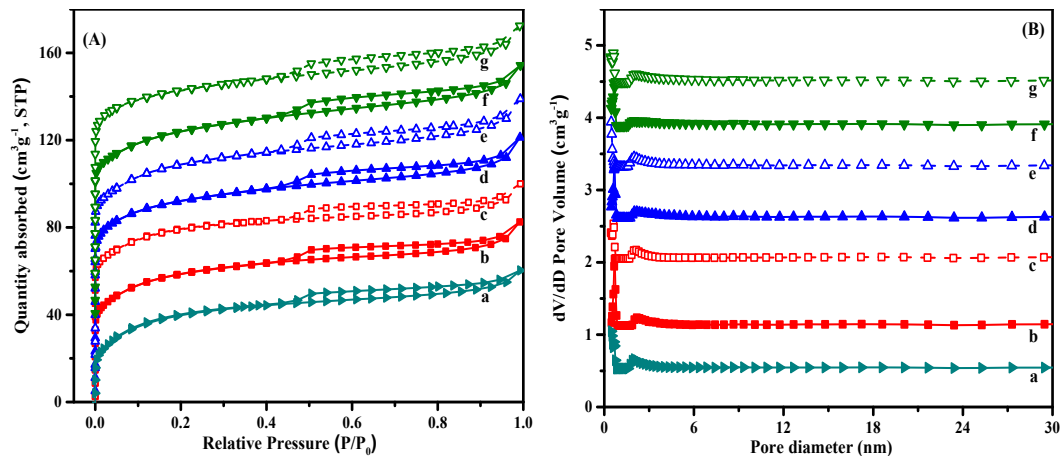


Fig. S1. N₂ adsorption-desorption profiles of the catalysts. (A) Isotherms; (B) Pore size distribution profiles. a. ZSM-5, b. 10% SnO₂/ZSM-5, c. 10% SnO₂/ZSM-5-P, d. 15% SnO₂/ZSM-5, e. 15% SnO₂/ZSM-5-P, f. 20% SnO₂/ZSM-5, g. 20% SnO₂/ZSM-5-P.

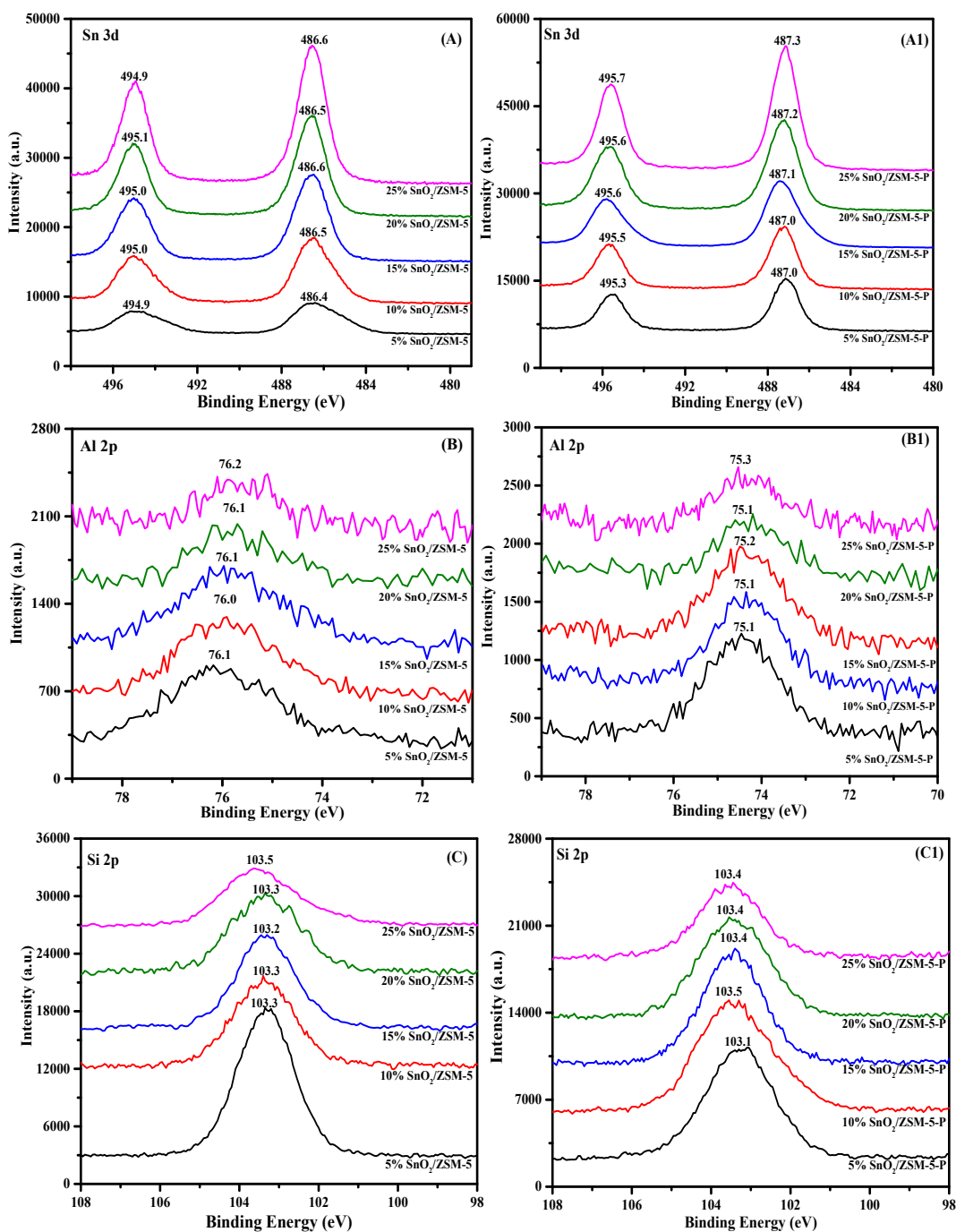


Fig. S2. XPS spectra of the catalysts. (A) Sn 3d, (A1) Sn 3d spectra with plasma treating; (B) Al 2p, (B1) Al 2p spectra with plasma treating. (C) Si 2p, (C1) Si 2p spectra without plasma treating.

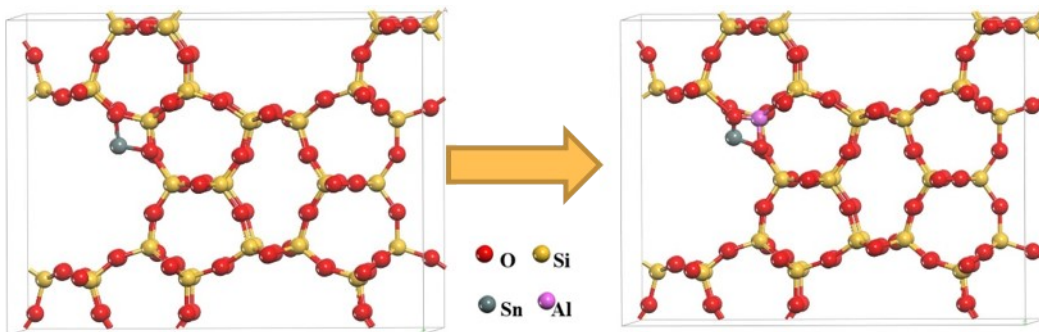


Fig. S3. Electron transfer configuration of the SnO₂/ZSM-5(Si) and SnO₂/ZSM-5(Si, Al).

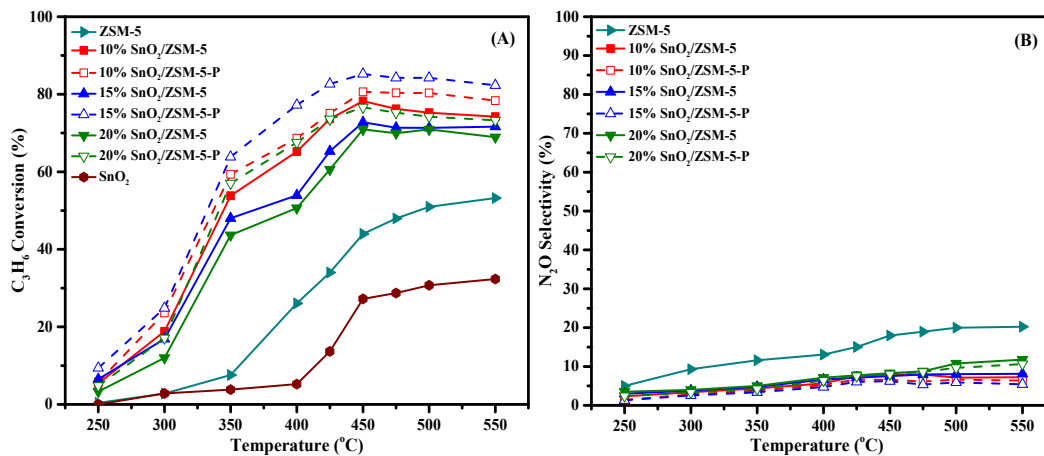


Fig. S4. NO_x-SCR by C₃H₆ over the catalysts. (A) C₃H₆ conversion, (B) N₂O selectivity.

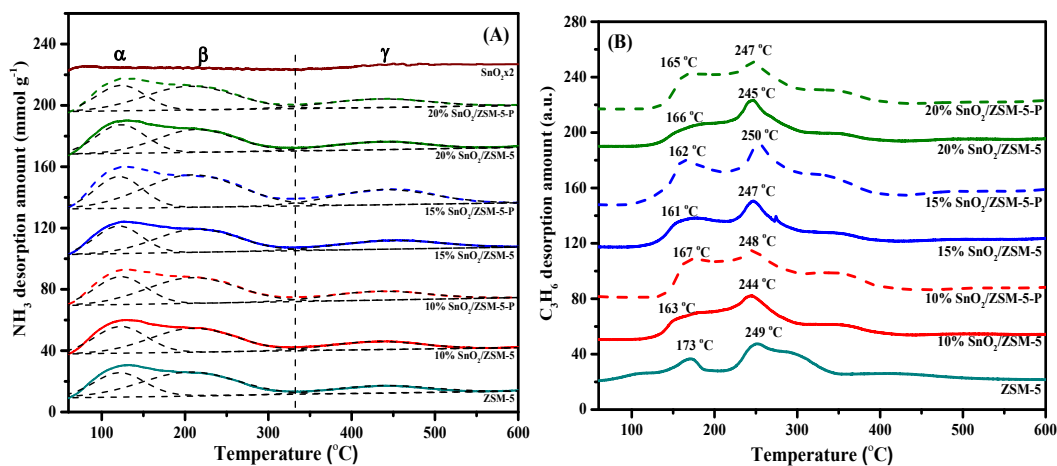


Fig. S5. (A) NH₃-TPD profiles of the catalysts; (B) C₃H₆-TPD profiles of the catalysts.

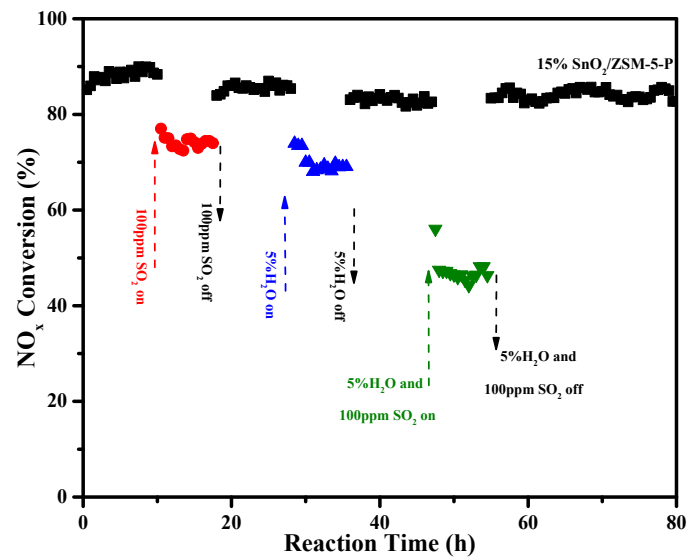


Fig. S6. Stability test of SnO₂/ZSM-5 in the presence of SO₂ or/and H₂O for NO_x-SCR by C₃H₆ at 450 °C.

2.2. Supplementary Tables

Table S1

Electron transfer configuration of the SnO₂/ZSM-5(Si) and SnO₂/ZSM-5(Si, Al).

Catalysts	The total electrons gained or lost			
	Sn	Si	Al	O
SnO ₂ /ZSM-5(Si)	+0.20	+0.02	--	-0.22
SnO ₂ /ZSM-5(Si, Al)	-0.18	+0.02	+0.34	-0.19

Table S2

Reaction performance of SnO₂/ZSM-5 samples

Sample	R _w (10 ⁻⁶ mmol g ⁻¹ s ⁻¹) ^a			R _s (10 ⁻⁸ mmol m ⁻² s ⁻¹) ^b		
	425 °C	450 °C	475 °C	425 °C	450 °C	475 °C
5% SnO ₂ /ZSM-5	5.2	9.1	7.3	1.6	2.8	2.3
5% SnO ₂ /ZSM-5-P	7.6	13.8	11.1	2.4	4.3	3.6
10% SnO ₂ /ZSM-5	14.6	19.6	16.8	4.5	6.1	5.2
10% SnO ₂ /ZSM-5-P	17.1	27.8	25.3	5.3	8.6	7.9
15% SnO ₂ /ZSM-5	12.6	15.1	14.0	3.9	4.7	4.4
15% SnO ₂ /ZSM-5-P	23.3	30.4	28.6	7.2	9.5	8.8
20% SnO ₂ /ZSM-5	9.8	12.1	10.7	3.1	3.7	3.5
20% SnO ₂ /ZSM-5-P	15.3	23.8	22.7	4.7	7.4	7.0
25% SnO ₂ /ZSM-5	7.0	11.1	9.8	2.2	3.5	3.1
25% SnO ₂ /ZSM-5-P	14.0	21.6	19.0	4.3	6.7	5.0

^a NO_x conversion rate normalized by catalyst weight.

^b NO_x conversion rate normalized by catalyst surface area.

Table S3H₂-TPR quantification results of the catalysts.

Catalysts	Consumed H ₂ amount		O/Sn atomic ratio
	mmol g _{cat} ⁻¹	mmol g _{SnO₂} ⁻¹	
ZSM-5	--	--	--
5% SnO ₂ /ZSM-5	0.56	13.2	2.0
5% SnO ₂ /ZSM-5-P	0.59	13.4	1.8
10% SnO ₂ /ZSM-5	1.23	13.4	2.0
10% SnO ₂ /ZSM-5-P	1.21	13.3	1.9
15% SnO ₂ /ZSM-5	1.93	13.4	2.0
15% SnO ₂ /ZSM-5-P	1.91	13.3	1.9
20% SnO ₂ /ZSM-5	2.51	13.4	2.0
20% SnO ₂ /ZSM-5-P	2.49	13.2	1.8
SnO ₂	13.4	13.4	2.0