

Supporting Information

Birnessite as a Highly Efficient Catalyst for Low-Temperature NH₃- SCR: The Vital Role of Surface Oxygen Vacancies

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Characterization of Catalysts

X-ray diffraction (XRD) patterns of the samples were carried out on an X-ray diffractometer (DX-2700, HaoYuan, China) with Cu K ($\lambda = 0.15418$ nm) radiation in the 2θ range $5\sim 80^\circ$. The measurement was taken at a tube voltage of 40 kV and a current of 30 mA.

Scanning electron microscopy (SEM) was performed on a scanning electron microscope (JSM-7500F, JEOL, Japan) at 5 kV. Transmission electron microscope (Tecnai G2 F20, Thermo Fisher, USA) with an accelerating voltage of 150 kV was applied to transmission electron microscope (TEM) observations. The catalyst powders were treated ultrasonically in ethanol for 30 min, then deposited on carbon-coated Cu grids.

The thermogravimetry (TG) and derivative thermogravimetry (DTG) curves were obtained using a TG/DTG apparatus (SDT Q600, TA, USA) under highly pure nitrogen atmosphere, and the test temperature range from 50 to 800 °C.

Nitrogen adsorption-desorption was performed on a fully automatic specific surface area and pore size distribution analyzer (ASAP 2460, Micromeritics, USA). The specific surface areas, pore size distributions and pore volumes were calculated using Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively. Catalyst samples were out-gassed under vacuum prior to the measurements at 110 °C, 150 °C and 200 °C for 5 h, respectively.

X-ray photo-electron spectroscopy (XPS) was performed on a spectrometer (XSAM-800, KRATOS, UK) with a pass energy of 20 eV and Al K α ($h\nu = 1486.6$ eV) as an X-ray excitation source. The binding energies were calibrated by referring to the C1s line at 284.8 eV.

The reduction behavior was studied by hydrogen temperature-programmed reduction (H₂-TPR) in a TPD/TPR analyzer (TP-5076, XianQuan, China). About 50 mg of the calcined sample was initially flushed in He (200 ml/min) stream at 110 °C, 150 °C and 200 °C for 1 h (heating rate 10 °C/min), respectively.

Afterward, when the sample cooled to 50 °C, passed a 5% H₂/He flow (100 ml/min) through the bed containing the sample while temperature was increased up to 600 °C (heating rate 5 °C/min). The surface acidity of catalysts were determined by temperature-programmed desorption of ammonia (NH₃-TPD) by a TPD/TPR analyzer (TP-5076, XianQuan, China). About 100 mg of sample was pretreated as well as that in the H₂-TPR. Subsequently, the sample was treated with 1 vol% NH₃ (100 ml/min) for 1 h. After that, the sample was purged in He to remove weakly adsorbed NH₃. Finally, the TPD operation was conducted by heating the sample up to 700 °C with a heating rate of 10 °C/min. A thermal conductive detector (TCD) was used to detect the amount of NH₃ desorbed. A similar procedure was used for NO-TPD with 1 vol% NO and O₂-TPD with 5 vol% O₂. Because of the low pretreatment temperature, the samples still contained some interfering substances (such as strongly adsorbed water, OH groups, and oxygen released by decomposition of manganese oxide). In order to eliminate these interferences, we did a background experiment without adsorption process.

In situ FTIR was performed on a FTIR spectrometer (NICOLET iS50, Thermo Fisher, USA). The samples were pretreated at 150 °C under N₂ flow for 1 h. According to the conditions of the activity test, the samples were treated with NH₃ (500 ppm) at 150 °C for 30 min and purged by N₂ for 20 min. After that, the samples were treated at the flow of NO (500 ppm) and NO (500 ppm) + O₂ (5 vol%), respectively. The in situ FTIR experiment of NO (500 ppm) + O₂ (5 vol%) pre-adsorption and then purged by NH₃ (500 ppm) + O₂ (5 vol%) was operated as described above. The in situ FTIR experiment of SCR was operated at the flow of NH₃ (500 ppm) + NO (500 ppm) + O₂ (5 vol%). All spectra were recorded with a resolution of 4 cm⁻¹ and an accumulation of 32 scans. The total flow rate was controlled at 100 ml/min and used N₂ as the balance gas.

Table S1. Low temperature NH₃-SCR catalytic activity of MnO₂ in previous literature.

Catalyst	Test conditions	T _{90%}	T _{100%}	Reference
Birnessite (MnO ₂ nanosheets)	500 ppm NO, 500 ppm NH ₃ , 5 vol% O ₂ , N ₂ balance, GHSV ~ 30000 h ⁻¹	90	99	This work
K-MnO ₂	1000 ppm NO, 1000 ppm NH ₃ , 6% O ₂ , N ₂ balance, GHSV ~ 30000 h ⁻¹	95	110	[1]
δ-MnO ₂	1000 ppm NO, 1000 ppm NH ₃ , 2 vol% O ₂ , N ₂ balance, GHSV~ 38000 h ⁻¹	/	/	[2]
		(T _{40%} > 150)		
δ-MnO ₂	720 ppm NO, 800 ppm NH ₃ , 3 vol% O ₂ , N ₂ balance, GHSV ~ 30000 h ⁻¹	180	/	[3]
MnO ₂ nanospheres	500 ppm NO, 500 ppm NH ₃ , 3 vol% O ₂ , N ₂ balance, GHSV ~ 28000 h ⁻¹	150	200	[4]
MnO ₂ nanorods	550 ppm NO, 550 ppm NH ₃ , 6 vol% O ₂ , N ₂ balance, GHSV ~ 36000 h ⁻¹	250	300	[5]

Table S2. Physical properties, content of different source of water of as-synthesized samples.

Sample	BET surface area (m ² / g)	Pore volume (×10 ⁻² cm ³ / g)	Average pore diameter (nm)	Content (%)		
				Weakly adsorbed water	Strongly adsorbed water	Hydroxyl group
NB-110	42.5	12.7	12.3	3.06	10.17	2.78
NB-150	50.0	29.5	24.2	4.37	4.79	3.20
NB-200	42.0	27.0	26.3	2.84	1.75	3.25

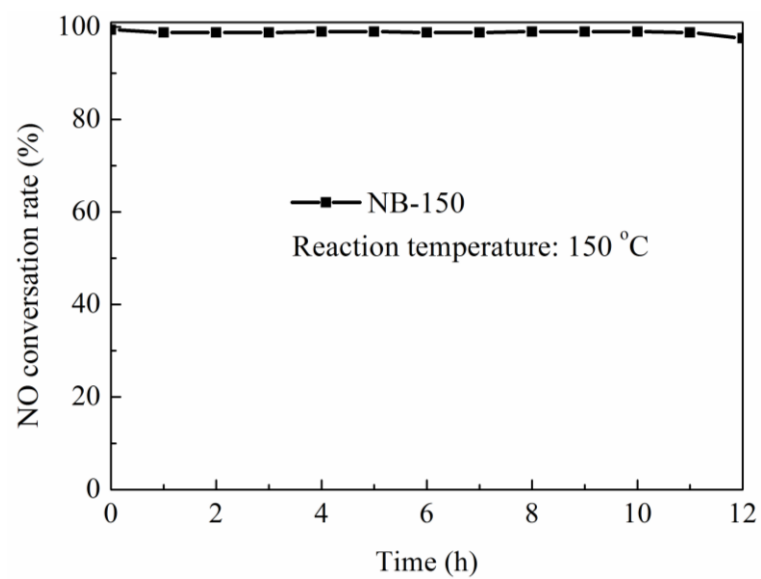


Fig. S1. Long time stability of NB-150 at 150 °C.

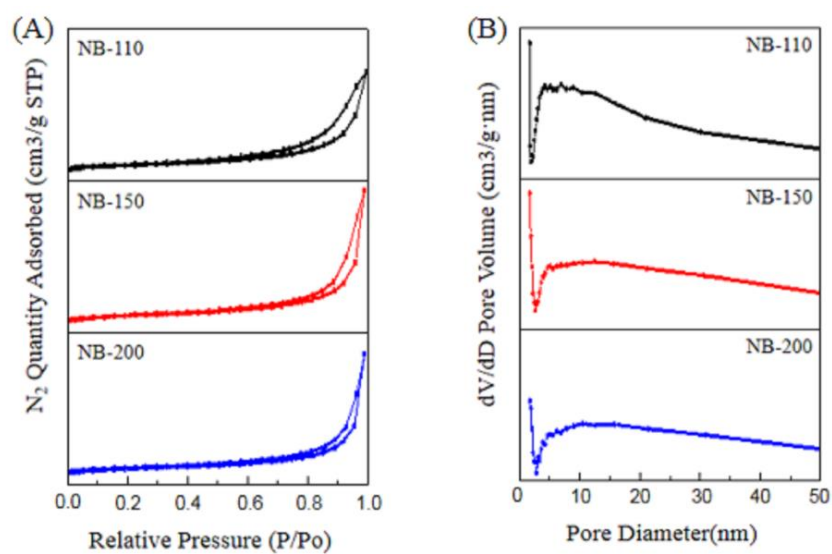


Fig. S2. (A) N_2 adsorption-desorption isotherms and (B) Pore size distribution of different samples.

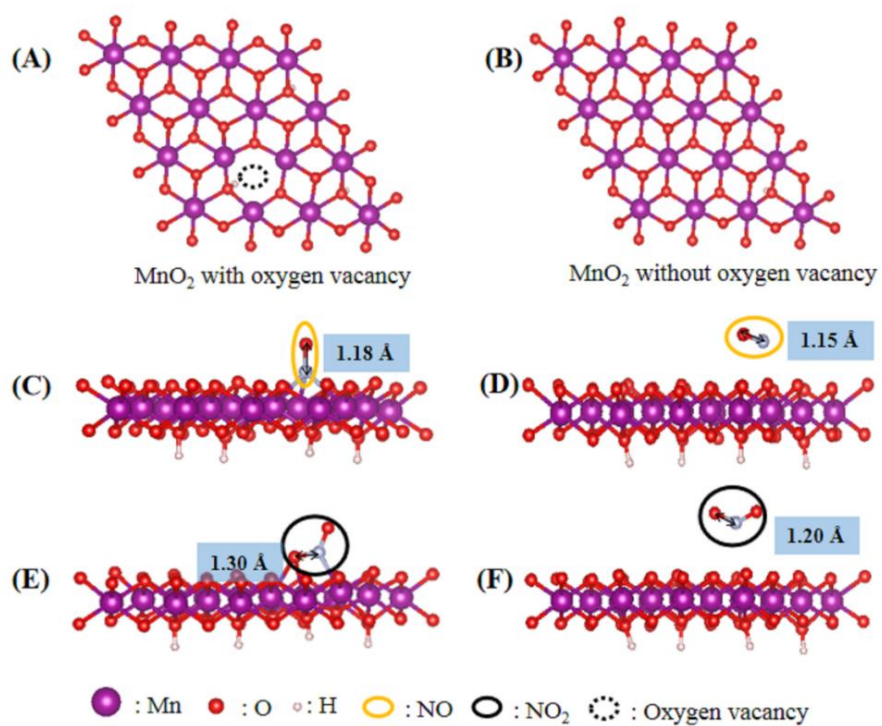


Fig. S3. The structure of NO and NO_2 adsorbed on MnO_2 : (A) MnO_2 with oxygen vacancy; (B) MnO_2 without oxygen vacancy; (C) NO and (E) NO_2 adsorbed on MnO_2 with oxygen vacancy; (D) NO and (F) NO_2 stood on the top of MnO_2 without oxygen vacancy.

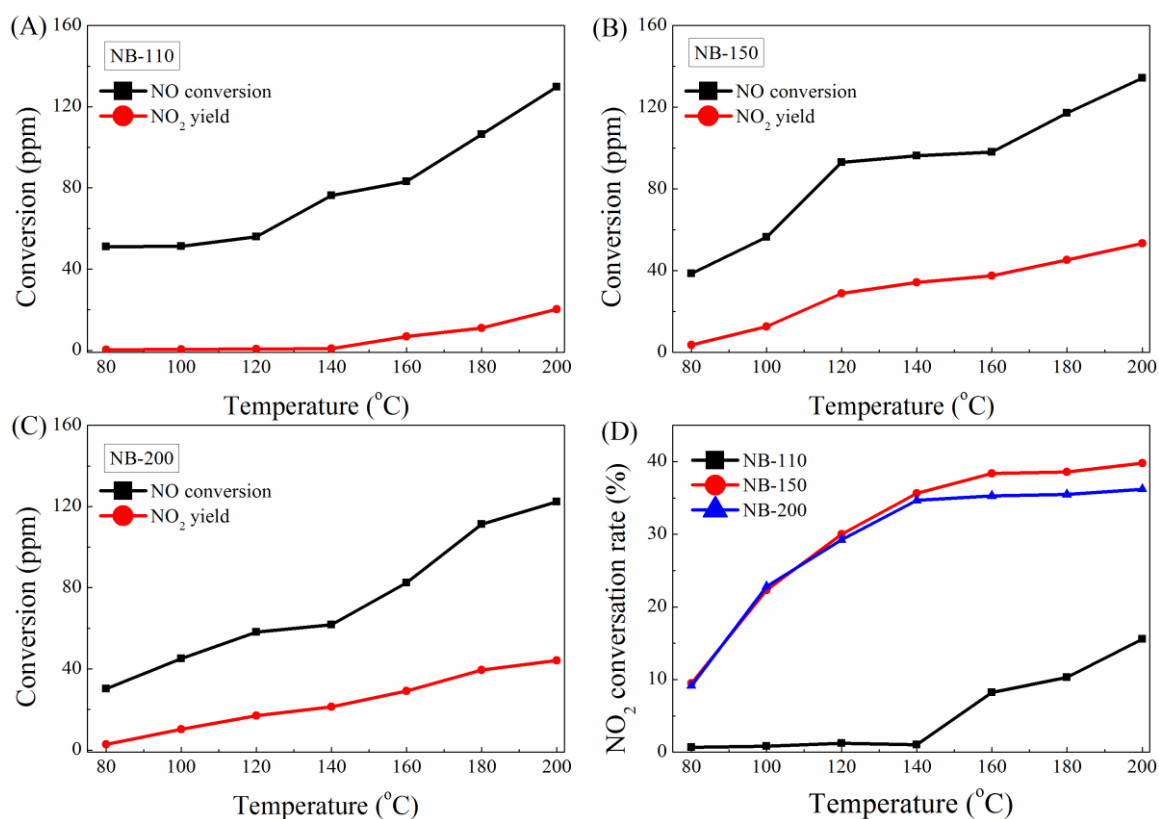


Fig. S4. NO oxidation over (A) NB-110, (B) NB-150 and (C) NB-200 and comparison of NO₂ conversion rate over different samples. Reaction condition: [NO] = 500 ppm, [O₂] = 5%, GHSV = 30000 h⁻¹. NO₂ conversion

rate was obtained by:
$$\text{NO}_2 \text{ conversion rate (\%)} = \frac{[\text{NO}_2]_{\text{out}}}{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}} \times 100\%$$

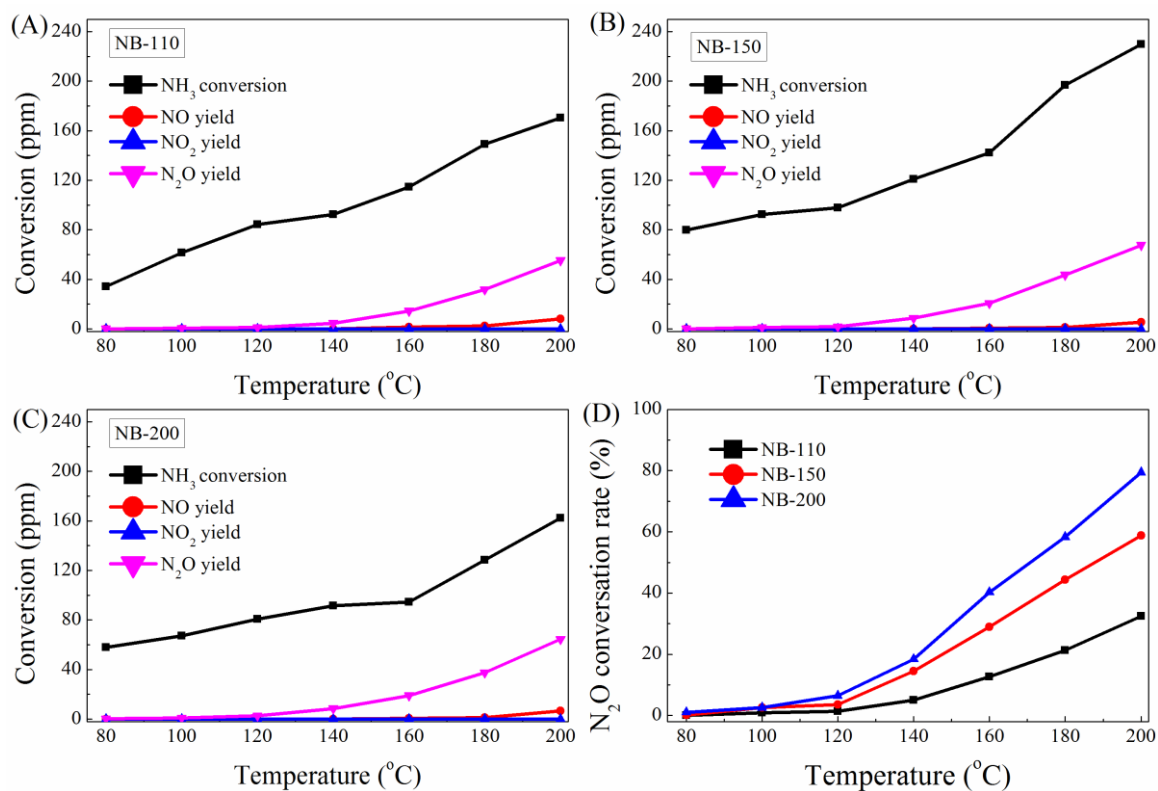


Fig. S5. NH₃ oxidization over (A) NB-110, (B) NB-150 and (C) NB-200 and comparison of NO₂ conversion rate over different samples. Reaction condition: [NH₃] = 500 ppm, [O₂] = 5%, GHSV = 30000 h⁻¹. N₂O

conversion rate was obtained by:
$$\text{N}_2\text{O conversion rate (\%)} = \frac{2 \times [\text{N}_2\text{O}]_{\text{out}}}{[\text{NH}_3]_{\text{in}} - [\text{NH}_3]_{\text{out}}} \times 100\%$$

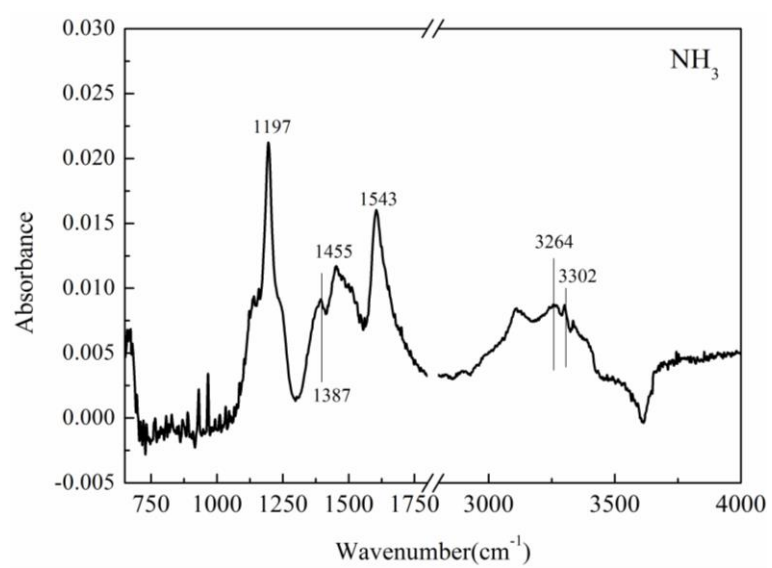


Fig. S6. The full spectra of in situ FTIR of NH_3 over NB-150.

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