

Electronic Supplementary Information

Fabrication of Mn-CeO_x/CNTs catalysts by redox method and their performance in low-temperature NO reduction with NH₃

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Experimental section

1. Catalyst preparation

The multiwall CNTs of 60-100 nm in diameter (Shenzhen Nanotech Port Co., Ltd) were refluxed in concentrated HNO₃ under stirring for 8 h at 140 °C. Then, certain amount of cerium chloride and acid-treated CNTs were dispersed in 120 ml deionized water with continuous stirring for 10 h. After that, 120 ml of potassium permanganate solution was introduced into the above mixture and stirred at room temperature for 10 h. Finally, the solid was filtered, and rinsed with deionized water, and dried at 105 °C in air overnight. The as-obtained catalyst is denoted as z Mn-CeO_x/CNTs, where z stands for the molar ratio of (Mn+Ce)/C. For comparison, the Mn-CeO_x/CNTs-MI catalyst with the optimum Mn/(Mn+Ce) molar ratio was fabricated by a modified impregnation method.¹

2. Catalyst characterization

The textural properties of the catalysts were determined by N₂-adsorption on an

ASAP 2020 M (Micromeritics, USA), and the tests were carried out in liquid N₂ temperature (-196 °C). The surface area was calculated by Brunauer-Emmett-Teller (BET) method, and the pore volume was evaluated from the adsorbed amounts at a relative pressure (P/P⁰) of 0.99. The powder X-ray diffraction (XRD) was recorded on an X'Pert Pro MPD X-ray diffractometer using Cu-K α radiation ($\lambda=0.15406$ nm). The data were collected with a scattering angle (2 θ) ranging between 5 to 80° with a 0.02° step size. The morphologies of the catalysts were observed by transmission electron microscopy (TEM, JEM 2010 EX). X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific ESCALAB 250 spectrometer equipped with a dual Al/Mg anode with about 0.6 eV resolution at the C1s peak. Temperature-programmed reduction by hydrogen (H₂-TPR) was measured on a custom-made TCD apparatus: 50 mg of catalyst was pretreated in N₂ at 160 °C for 1 h before the H₂-TPR experiment, and then, carried out in pure N₂ containing 6 % H₂ at a flow rate of 30 ml/min and a heating rate of 10 °C/min.

3. Catalytic activity tests

The SCR activity tests were performed in a fixed-bed quartz reactor. 0.2 g of catalyst was used in each test. The typical reactant gas composition was as follows: 500 ppm NO, 500 ppm NH₃, 5% O₂ and balance N₂. The total flow rate was 700 ml/min corresponding to a weight hourly space velocity (WHSV) of 210 000 ml/g_{cat} h. The gas concentration was measured by a flue gas analyzer (Kane International Limited, KM950). All data were collected after 30 min when the SCR reaction reached steady state.

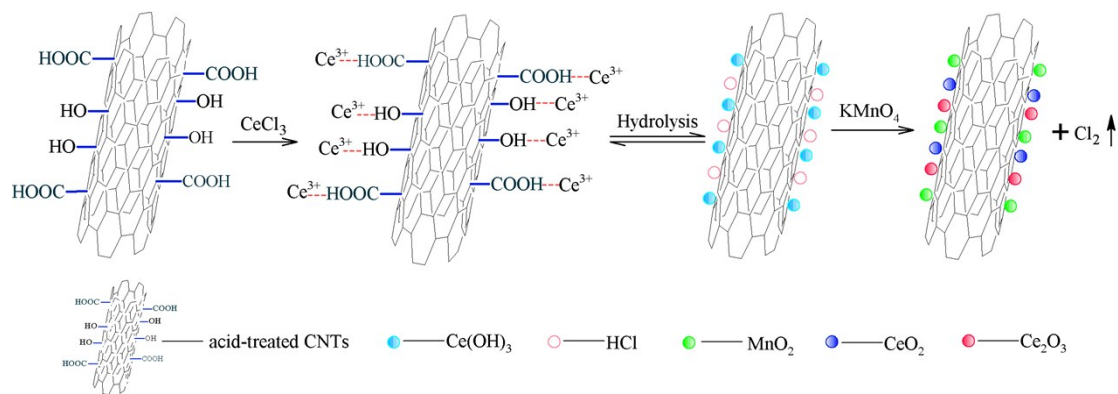


Fig. S1 Schematic illustration of the preparation procedure of Mn-CeO_x/CNTs catalyst.

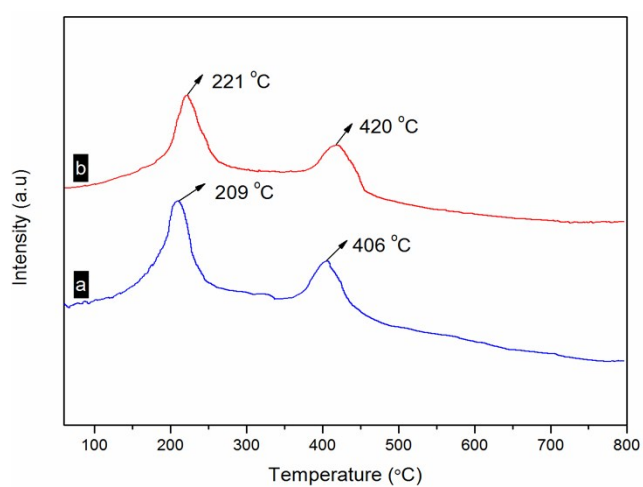


Fig. S2 H₂-TPR profiles of (a) 6% Mn-CeO_x/CNTs and (b) Mn-CeO_x/CNTs-MI.

Table S1 The BET surface area, pore volume and average pore diameter of acid-treated CNTs and Mn-CeO_x/CNTs catalysts

Sample	S _{BET} (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Average pore diameter (nm)
Acid-treated CNTs	54.5	0.1075	8.34
2% Mn-CeO _x /CNTs	61.7	0.1785	11.58
4% Mn-CeO _x /CNTs	45.5	0.1623	14.28
6% Mn-CeO _x /CNTs	37.8	0.1024	10.85
8% Mn-CeO _x /CNTs	83.5	0.2026	9.71
Mn-CeO _x /CNTs-MI	104.4	0.2109	8.08

Table S2 The relative concentration ratios of Ce and O for CNTs-based catalysts

Samples	Ce (%)		Ce ³⁺ /(Ce ³⁺ + Ce ⁴⁺)	O (%)	
	Ce ³⁺	Ce ⁴⁺		O _α	O _β
6% Mn-CeO _x /CNTs	16.1	83.9	0.161	55.5	44.5
Mn-CeO _x /CNTs-MI	11.9	88.1	0.119	51.8	48.2

References

- 1 L. Zhang, D. Zhang, J. Zhang, S. Cai, C. Fang, L. Huang, H. Li, R. Gao and L. Shi, *Nanoscale.*, 2013, **5**, 9821.