

Electronic supplementary materials

Fabrication and formation mechanism of $\text{Ce}_2\text{O}_3\text{-CeO}_2\text{-CuO-MnO}_2/\text{CNTs}$ catalysts and application in low-temperature NO reduction with NH_3

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Part 1 Experimental section

1. Catalyst preparation

Carbon nanotubes (CNTs, O.D=60-100 nm; Shenzhen Nanoport Company, China) were firstly treated with HNO_3 . Subsequently, the $\text{Ce}(\text{Cl}_3)_3 \cdot 7\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, and acid-treated CNTs were mixed with 80 mL deionized for 8 h. Afterwards, 80 mL KMnO_4 solution (certain concentration) was introduced into the above mixture stirring for another 8 h at ambient temperature. Finally, the product was filtered, and washed with distilled water and ethanol, followed by drying at 120 °C under vacuum for 12 h. The as-fabricated catalyst was denoted as $z \text{Ce}_2\text{O}_3\text{-CeO}_2\text{-CuO-MnO}_2/\text{CNTs}$, where Z was defined as the molar ratio of $(\text{Ce}+\text{Cu}+\text{Mn})/\text{CNTs}$. As comparison, the $\text{Ce-Cu-MnO}_x/\text{CNTs-IM}$ catalyst with the optimal loading was synthesized through an impregnation method.

2. Catalyst characterization

A ZEISS SUPRA 55 equipped with an X-ray probe using 10 keV primary electron energy and about 127 eV energy resolution was applied to observed the Field emission scanning electron microscopy (FESEM) images of the catalysts. An X'Pert Pro MPD X-ray diffractometer (XRD) using $\text{Cu-K}\alpha$ radiation ($\lambda=0.15406 \text{ nm}$) with a 2θ of $5\text{-}80^\circ$ was used to obtained the XRD patterns of the catalysts. A JEOL model JEM 2010 EX instrument was applied to analyse the Transmission electron microscopy (TEM) images. A custom-made TCD apparatus was utilized to detect the

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Temperature-programmed reduction by H₂ (H₂-TPR) curves of the catalysts. Prior to the H₂-TPR test, 50 mg catalyst was firstly purged with N₂ at 200 °C for 1.5 h, and then tested in N₂ (containing 1 % H₂) with a heating rate of 10 °C/min. A Thermo Scientific ESCALAB 250 spectrometer equipped with a dual Al/Mg anode (0.6 eV resolution) was adopted to evaluate the X-ray photoelectron spectroscopy (XPS) spectra.

3. Catalytic activity tests

The activity tests were performed in a fixed-bed quartz reactor using 150 mg catalyst in each test. The mixture gas included [NO]=[NH₃]= 420 ppm, [O₂]= 5%, and N₂ as balance gas. The total flow rate was 700 mL/min, which was corresponded to a weight hourly space velocity (WHSV) of 280000 mL·g_{cat}⁻¹·h⁻¹. Flue gas analyzer (Kane International Limited, KM950) installed with the sensors of NO₂, SO₂, NO, and O₂ was applied to analyse the gas content. All data were collected after 30 min when the catalytic reaction reached a balanced-state.

Part 2 Supplementary data

Table S1 BET surface area and pore volume over based-CNTs samples

Sample	S _{BET} (m ² ·g ⁻¹)	Pore volume (cm ³ ·g ⁻¹)
Acid-treated CNTs	96.5	0.284
2% Ce ₂ O ₃ -CeO ₂ -CuO-MnO ₂ /CNTs	102.2	0.183
4% Ce ₂ O ₃ -CeO ₂ -CuO-MnO ₂ /CNTs	87.3	0.166
6% Ce ₂ O ₃ -CeO ₂ -CuO-MnO ₂ /CNTs	45.2	0.148
8% Ce ₂ O ₃ -CeO ₂ -CuO-MnO ₂ /CNTs	97.1	0.179
Ce-Cu -MnO _x /CNTs-IM	70.7	0.198

Table S2 Relative contents of Ce³⁺, Ce⁴⁺, O_x, and O_y over CNTs-based samples

Samples	Ce ³⁺ %	Ce ⁴⁺ %	Ce ³⁺ / (Ce ³⁺ + Ce ⁴⁺)	O _x %	O _y %	O _y / (O _x + O _y)
6% Ce ₂ O ₃ -CeO ₂ -CuO-MnO ₂ /CNTs	16.2	83.8	0.162	20.1	79.9	0.799
Ce-Cu -MnO _x /CNTs-IM	13.8	86.2	0.138	22.	77.3	0.773

Table S3 XPS and ICP-MS data for pristine CNTs, acid-treated CNTs, Ce–Cu–MnO_x/CNTs-IM, and 6% Ce₂O₃–CeO₂–CuO–MnO₂/CNTs

Samples	O/C	Mn/C	Ce/C	Cu/C	ICP-MS (%)		
					Mn	Ce	Cu
pristine-CNTs	0.016	0	0	0	0	0	0
acid-treated CNTs	0.041	0	0	0	0	0	0
Ce–Cu–MnO _x /CNTs-IM	0.087	0.024	0.018	0.0089	9.37	5.17	2.63
6% Ce ₂ O ₃ –CeO ₂ –CuO–MnO ₂ /CNT	0.25	0.055	0.043	0.0061	10.9	12.3	0.77

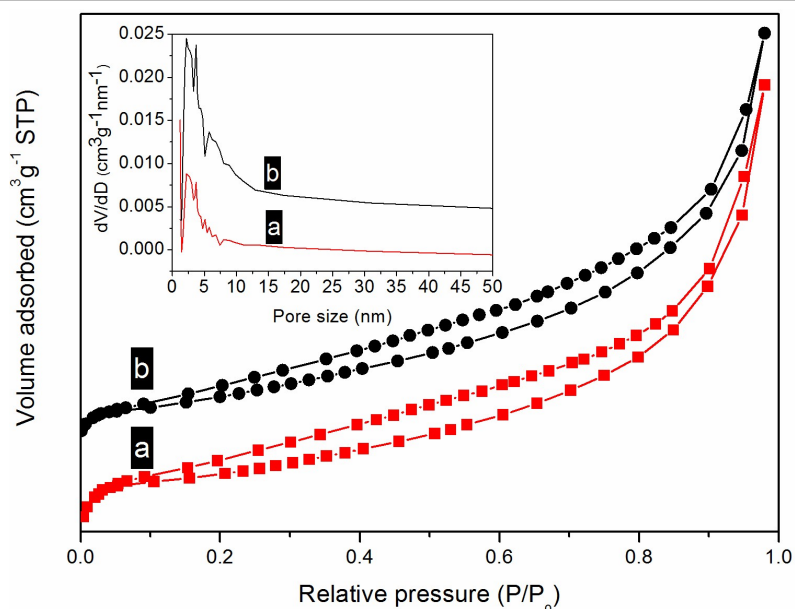


Fig. S1 N₂ adsorption-desorption and pore size distribution (inset) curves of (a) 6% Ce₂O₃–CeO₂–CuO–MnO₂/CNTs and (b) Ce–Cu–MnO_x/CNTs-IM.

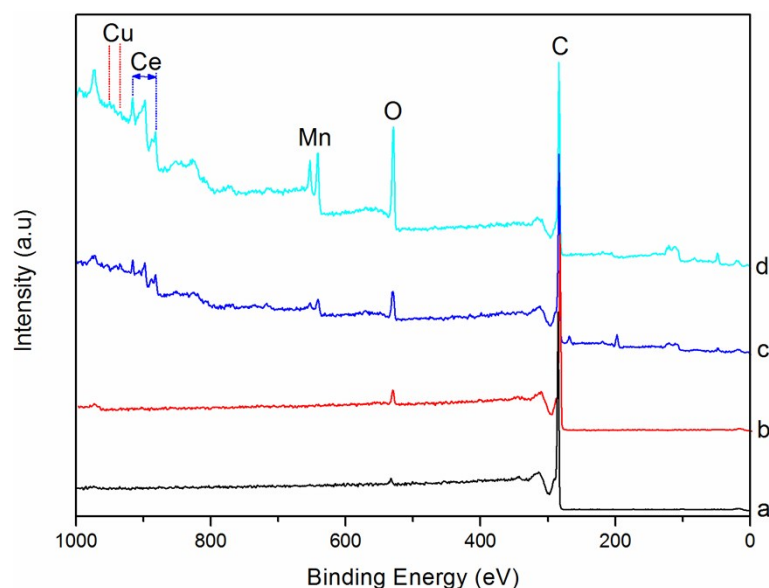


Fig. S2 XPS spectra of (a) pristine CNTs, (b) acid-treated CNTs, (c) Ce–Cu–MnO_x/CNTs-IM, and (d) 6% Ce₂O₃–CeO₂–CuO–MnO₂/CNTs.

Part III Discussions of XPS and ICP-MS data for pristine CNTs, acid-treated CNTs, and the as-obtained catalysts

1. XPS and ICP-MS for pristine CNTs, acid-treated CNTs, and the as-obtained catalysts

As shown in Fig. S2 and Table S3, it is clear that the O/C ratio (0.016) over pristine CNTs was the lowest owing to only the presence of adsorption H₂O. After being treated by HNO₃, the O/C ratio was increased and reached 0.041. The above phenomenon was attributed to the existence of –OH and –COOH from the oxidation of HNO₃, which was conducive to the loading of active components.

For Ce–Cu–MnO_x/CNTs-IM, the O/C ratio (0.087) further increased with being supported by mixed metal oxide catalysts, which profited from the increase of surface and lattice oxygen from the catalysts. As for 6% Ce₂O₃–CeO₂–CuO–MnO₂/CNTs, the O/C (0.25), Mn/C (0.055), and Ce/C (0.043) ratios further increased than that of O/C (0.087), Mn/C (0.024), and Ce/C (0.018) for Ce–Cu–MnO_x/CNTs-IM, indicating a better loading of catalysts, which was related with the results of NO conversion. It is worthy to mention that the two catalysts have the same loading, while the SCR activity for 6% Ce₂O₃–CeO₂–CuO–MnO₂/CNTs catalyst prepared by redox method is better than that of Ce–Cu–MnO_x/CNTs-IM fabricated by impregnation method, proving that high efficiency SCR catalyst could be prepared via the redox route in our paper.

As for ICP-MS data, it is clear that the content of Mn (10.9%) and Ce (12.3%) for 6% Ce₂O₃–CeO₂–CuO–MnO₂/CNTs is higher than that of Mn (9.37%) and Ce (5.17%) for Ce–Cu–MnO_x/CNTs-IM. Normally, high content of active components is helpful for the catalytic activity, which is line with the results of NO conversion.