Electronic supplementary materials

Selective catalytic reduction of NO with NH₃ over MnO₂/PDOPA@CNTs

catalysts prepared by poly(dopamine) functionalization

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Part I Experimental section

1. Catalyst preparation

1.1 Preparation of POPDA@CNTs

Firstly, 3g multi-wall carbon nanotubes (CNTs; OD: 60-100 nm) were dispersed in 500 mL deionized water under ultrasound 2h. Subsequently, certain quantities of Tris (0.005 mol/L) and dopamine (2 g/L) were introduced into the above mixture by stirring for 24 h at ambient-temperature. At last, the product was filtered, and rinsed with deionized water and ethanol, and then dried in vacuum at 50 °C overnight. The as-obtained sample was designated as PDOPA@CNTs.

1.2 Fabrication of MnO₂/PDOPA@CNTs catalysts

0.3g POPDA@CNTs and certain amount of Mn(CH₃COO)₂ were added in 60 ml

deionized water with stirring for 12 h. Afterward, certain concentration of KMnO₄ solution was introduced into the above mixture under stirring for another 12 h at 5-10 °C. Finally, the solid was filtered, and washed with deionized water and ethanol, and then dried at 105 °C for 12 h. The as-fabricated catalysts were denoted as y $MnO_2/PDOPA@CNTs$, where y standed for the molar ratio of [KMnO₄+ $Mn(CH_3COO)_2$]/CNTs. For comparison, $MnO_x/PDOPA@CNTs$ catalyst with the optimal loading was prepared by an impregnation method (IM).¹

2. Catalyst characterization

Micromeritics ASAP 2020 system was used to investigate the textural properties of the samples. The specific surface area was calculated by Brunauer-Emmett-Teller (BET) method from the desorption branches of the isotherm. X-ray diffraction (XRD) patterns were appraised with an X'Pert Pro MPD X-ray diffractometer using Cu-K α radiation (λ =0.15406 nm) with a 2 θ range between 5 and 80°. X-ray photoelectron spectroscopy (XPS) was analysed by a Thermo Scientific ESCALAB 250 spectrometer installed with a dual Al/Mg anode (0.6 eV resolution). Field emission scanning electron microscopy (FESEM) images were recorded with ZEISS SUPRA 55 equipped with an X-ray probe using 10 keV primary electron energy (about 127 eV energy resolution). Transmission electron microscopy (TEM) images were performed on a JEOL model JEM 2010 EX instrument. Thermogravimetric (TG) was carried out on NETZSCH 449F5 from 60 to 800 °C at a rate of 10 °C/min with N₂ flow rate of 40 mL/min.

Temperature-programmed reduction by H2 (H2-TPR) was conducted on a custom-

made TCD apparatus. Before the H₂-TPR experiments, 50 mg catalyst was firstly purged in N₂ at 200 °C for 1.5 h, and then performed in N₂ (containing 6 % H₂) with a heating rate of 10 °C/min. Temperature programmed desorption of ammonia (NH₃-TPD) was carried out on a custom-made TCD apparatus. Before the NH₃-TPD test, the samples (100 mg) were preheated under a N₂ atmosphere at 400 °C for 1 h, and then saturated with 4% NH₃ in N₂ at room temperature for 1h. Finally, the samples were heated to 800 °C at a heating rate of 10 °C/min, and the NH₃-TPD data were detected by TCD.

3. Catalytic activity tests

The SCR activity tests were performed in a fixed-bed quartz reactor, and 200 mg catalyst was used in each test. The reaction gas is compose of $[NO] = [NH_3] = 500$ ppm, $[O_2] = 5\%$, and N_2 as balance gas. The total flow rate is 700 mL/min corresponding to a weight hourly space velocity (WHSV) of 210 000 mL·g_{cat}⁻¹·h⁻¹. The concentration of NO, NO₂, SO₂, and O₂ were monitored by Flue gas analyzer (Kane International Limited, KM950). All data were recorded after 30 min until the SCR reaction achieved a steady-state.

Part II Supplementary data

Sample	$S_{BET}(m^2 g^{-1})$	Pore volume (cm ³ g ⁻¹)
Pristine-CNTs	43.4	0.127
PDA@ CNTs	35.7	0.108
6% MnO ₂ /PDOPA@CNTs	83.8	0.150
8% MnO ₂ /PDOPA@CNTs	91.7	0.162
10% MnO ₂ /PDOPA@CNTs	98.4	0.159
12% MnO ₂ /PDOPA@CNTs	106.4	0.183
MnO _x /PDOPA@CNTs	51.0	0.0769

Table S1 BET surface area and pore volume for pristine CNTs, POPDA@CNTs and

as-obtained catalysts



Fig. S1 Adsorption-desorption and pore size distribution (inset) profiles of (A) 10%

MnO₂/PDOPA@CNTs and (B) MnO_x/PDOPA@CNTs.



Fig. S2 FESEM images for (a) pristine CNTs, (b) 10% MnO₂/PDOPA@CNTs, (c) MnO_x/PDOPA@CNTs, and (d) EDS spectrum of 10% MnO₂/PDOPA@CNTs (red region of Fig. 2B).



Fig. S3 XRD patterns of (1) pristine CNTs, (2) PDOPA@CNTs, (3) 6%MnO2/PDOPA@CNTs,(4)8%MnO2/PDOPA@CNTs,(5)10%MnO2/PDOPA@CNTs,(6)12%MnO2/PDOPA@CNTs,and(7)MnOx/PDOPA@CNTs.



Fig. S4 H_2 -TPR profiles of (A) 10% MnO₂/PDOPA@CNTs and (B)

MnO_x/PDOPA@CNTs catalysts.



Fig. S5 NH₃-TPD profiles of (A) 10% MnO₂/PDOPA@CNTs and (B)

MnO_x/PDOPA@CNTs catalysts.



Fig. S6 TGA curves of PDOPA@CNTs and 10% MnO₂/PDOPA@CNTs.



Fig. S7 Cyclic and long-period stabilities of the 10% MnO₂/PDOPA@CNTs catalyst.



Fig. S8 FESEM (A) and TEM (B) of 10% MnO₂/PDOPA@CNTs catalyst after three

cycles.



Fig. S9 SO₂-tolerance study of 10% MnO₂/PDOPA@CNTs and MnO_x/PDOPA@CNTs catalysts at 180 °C. Reaction conditions: $[NO] = [NH_3] = 500$ ppm, $[O_2] = 5$ vol%, $[SO_2] = 50$ ppm (when used), and N₂ as balance gas.

Part III Results and discussion for BET surface area, adsorption-desorption curves, FESEM images, XRD, TPR/TPD and stabilities

1. BET surface area

The surface area of the as-obtained samples was listed in tables S1, it is apparent that the surface area of PDOPA@CNTs was smaller than that of pristine CNTs, which may result from the CNTs covered by PDOPA, and thus reduce the blockage of pores. After being supported with catalyst, the surface areas of MnO₂/PDOPA@CNTs became larger with the increase of loading. Besides, all MnO₂/PDOPA@CNTs catalysts presented larger BET surface area than that of MnO_x/PDOPA@CNTs catalyst. Generally, large BET surface area was in favor of the catalytic reaction,² which was associated with the results of NO conversion.

2. Adsorption-desorption profiles

N₂ adsorption-desorption and pore size distribution profiles of 10% MnO₂/PDOPA@CNTs and MnO_x/PDOPA@CNTs were shown in Fig. S1. For adsorption-desorption curves, typical type IV isotherm together with a type-H4 loop could be observed from the two catalysts, demonstrating the existence of mesopore structure.^{3, 4} As for pore distribution profiles, the pore size distributions of the samples were from 2.8 and 10 nm, further proving the presence of mesopore structure. Again, the pore distribution of 10% MnO₂/PDOPA@CNTs mainly was at around 2.8 nm, which was smaller than that of MnO_x/PDOPA@CNTs. It is worth noting that small pore was favorable for the improvement of BET surface area,¹ which was correlated to the results of Table. S1.

3. FESEM images

Fig. S2 shows the images of as-obtained samples. As displayed in Fig. S-2A and S-2B, the pristine CNTs presents smooth external surface, while they became coarse after being supported by active component, indicating that the catalyst has successfully been decorated on CNTs. For 10% MnO₂/PDOPA@CNTs (Fig. S-2B), it is obvious that the catalyst was evenly coated on CNTs. As for MnO_x/PDOPA@CNTs (Fig. S-2C), it was observed that agglomerate catalyst mainly scattered among the CNTs but not on CNTs. Compared with the aggregate catalyst, highly-dispersed active component on catalyst support was conducive to the catalytic activity,⁵ which was in line with the results of Fig. 1.

4. XRD patterns

XRD patterns of the as-prepared samples were displayed in Fig. S3. Obviously, typical feature peaks due to the graphite could be found at around 26.3 °, 42.7 °, 53.7 °, and 77.7 ° in all samples.⁶ For MnO₂/PDOPA@CNTs, weak MnO₂ diffraction peak (centered at 37. 2 °, PDF#53-0633) could be observed after supported by the catalyst, demonstrating the formation of MnO₂, which was related to the results of FESEM, TEM, and STEM. It is worthy to mention that high valence state and weak crystallinity of MnO₂ were conducive to the SCR activity,^{7, 8} which was in good accordance with the results of Fig. 1. As for MnO₂/PDOPA@CNTs, clear characteristic peaks assigning to the Mn₃O₄ could be seen in Fig.S3-(7), revealing the generation of high crystalline Mn₃O₄, which was consistent with the conclusion of Fig. 3E. Previous studies reported that the low-temperature SCR activity of manganese

oxide catalysts complied with the following sequence: $MnO_2 > Mn_2O_3 > Mn_3O_4 > MnO_9$, which was correlated to the NO conversion results.

5. H₂-TPR analysis

The essence of catalysis is redox procedure, and thus the redox property plays an important role in the catalytic cycle.¹⁰ The H₂-TPR profiles of 10% MnO₂/PDOPA@CNTs and MnO_x/PDOPA@CNTs catalysts were listed in Fig. S4. For 10% MnO₂/PDOPA@CNTs (Fig. S4-A), two reduction peaks were observed at around 216 °C and 389 °C. It should be noted that the former peak was due to the reduction of MnO₂ and Mn₂O₃ to Mn₃O₄, while the later peak was attributed to the reduction of Mn₃O₄ to MnO.¹¹ As for the MnO_x/PDOPA@CNTs (Fig. S4-B), only one reduction peak corresponding to the reduction of Mn₃O₄ to MnO could be detected at around 412 °C, which was higher than that of 10% MnO₂/PDOPA@CNTs catalyst. On view of the above results, the redox performance of 10% MnO₂/PDOPA@CNTs catalyst was better than MnO_x/PDOPA@CNTs catalyst, which was correlated with the results of NO conversion.

6. NH₃-TPD analysis

In NH₃-SCR reaction, the activation and adsorption of NH₃ on catalyst surface are crucial, which are influenced by the strength of acid sites on catalyst surface.¹² Therefore, the NH₃-TPD technology was applied to detect the acid sites of catalysts. As displayed in Fig. S5, the 10% MnO₂/PDOPA@CNTs and MnO_x/PDOPA@CNTs catalysts all have two NH₃-TPD peaks. The former peaks were ascribed to the ionic NH₄⁺ bounded to the Brønsted acid sites, and the later peaks were attributed to the

coordinated NH₃ bounded to Lewis acid sites.¹³ Note that the NH₃-TPD peaks over 10% MnO₂/PDOPA@CNTs catalyst were centered at 177 °C and 378 °C, whereas the relevant peaks center of MnO_x/PDOPA@CNTs catalyst were at around 169 °C and 360 °C, respectively, revealing that the strength of Brønsted and Lewis acid sites of 10% MnO₂/PDOPA@CNTs catalyst over the poly(dopamine) functionalization method were stronger than that of MnO_x/PDOPA@CNTs catalyst over the impregnation method. Usually, the stronger acid sites were in favor the NH₃-SCR activity, which was related to the results of NO conversion.

7. TG analysis

The TG analysis were applied to investigate the thermal stabilities of PDOPA@CNTs and 10% MnO₂/PDOPA@CNTs. It could be seen from Fig. S6 that the initial weight loss temperature of PDOPA@CNTs was 254.6 °C, whereas its test temperature was 80-180 °C. Therefore, the sample of PDOPA@CNTs was thermally stable below 254.6 °C, which was conducive to the application of PDOPA@CNTs at 80-180 °C. After the loading of MnO₂ active component, the initial weight loss temperature over 10% MnO₂/PDOPA@CNTs catalyst reached to 365.2 °C, further demonstrated that it had better thermal stability and could be used as SCR catalyst between 80 °C to 180 °C. Based on the above results, the samples of PDOPA@CNTs and 10% MnO₂/PDOPA@CNTs all possessed excellent thermal stabilities below 200 °C, validating that PDOPA functionalization is kind of a mild and non-pollution method for obtaining functional CNTs with catechol groups, which provides a versatile secondary reaction platform for the preparation of functional CNTs-based

materials.

8. Cyclic and long-term stabilities

Cyclic and long-period stabilities are important properties to catalysts in the practice application, and the relevant results were listed in Fig. S7. For cyclic stability (Fig. S7-A), the 10% MnO₂/PDOPA@CNTs catalyst exhibited similar catalytic activities after three cycles, suggesting its excellent cyclic stability. Besides, the longperiod stability result (Fig. S7-B) displayed that the catalytic activity of optimum catalyst remained at around 93%, which was similar to the initial catalytic activity at 180 °C (93.4%), further meaning its outstanding long-period stability. Based on the 10% MnO₂/PDOPA@CNTs favorable performances, catalyst prepared by poly(dopamine) functionalization possessed of excellent cyclic and long-period stabilities, which would provide potential application for 10% а MnO₂/PDOPA@CNTs.

9. FESEM and TEM for 10% MnO₂/PDOPA@CNTs catalyst after three cycles

To investigate the reason of 10% MnO₂/PDOPA@CNTs with favorable cyclic and long-period stabilities, the FESEM and TEM of 10% MnO₂/PDOPA@CNTs after three cycles were displayed in Fig. S8. In view of Fig, S8-A (FESEM), the active component corresponding to MnO₂ was uniformly covered on CNTs after three cycles, evidencing that the 10% MnO₂/PDOPA@CNTs catalyst possessed excellent structural stability. Note that the catalyst with outstanding structural stability was favorable for the catalytic activity, which was correlated to the results of NO conversion. Regarding TEM image (Fig. S8-B), it was clear that the active component was evenly decorated on CNTs, and the obvious changes could not be detected between the new 10% MnO₂/PDOPA@CNTs catalyst (Fig. 2-B) and 10% MnO₂/PDOPA@CNTs catalyst after three cycles. In light of the above results, the structural stability of 10% MnO₂/PDOPA@CNTs catalyst was first-class, which was in line with the result of Fig. S7-A, and thus was conducive to the catalytic activity.

10. SO₂-resistance study

In practice applications, the presence of SO₂ can induce the poisoning and deactivation. Hence, the influence of SO₂ on catalyst was investigated and displayed in Fig. S9. For 10% MnO₂/PDOPA@CNTs catalyst, its catalytic activity remained at 93.4% in the absence of SO₂, and reduced to 65.0% after the addition of SO₂, and then remained at around 65.0% after the disconnection of SO₂. By comparison, the catalytic activity of MnO_x/PDOPA@CNTs catalyst decreased to 25.2%, and exhibited slow downward trend after the interruption of SO₂. These results revealed that 10% MnO₂/PDOPA@CNTs catalyst possessed better SO₂-tolerence than that of MnO_x/PDOPA@CNTs catalyst, which may be originated from the formation of high state MnO₂.

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