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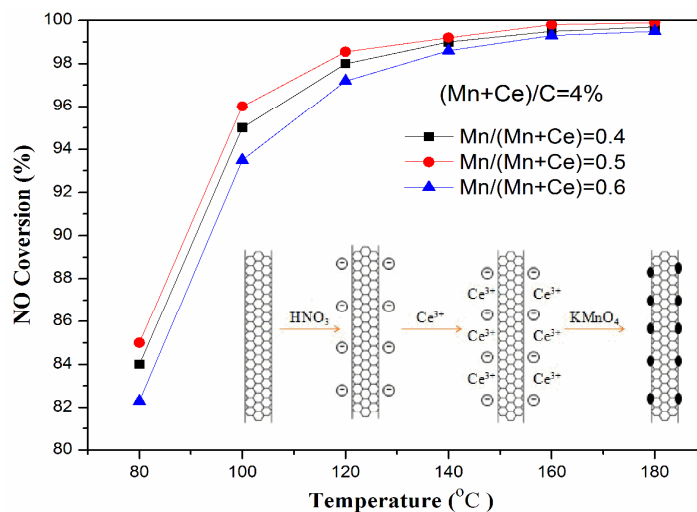


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Mn-CeO_x/CNTs prepared by liquid-phase method showed excellent low-temperature activity for NO reduction with NH₃.

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ARTICLE TYPE

Low-temperature NO reduction with NH₃ over Mn-CeO_x/CNTs catalysts prepared by a liquid-phase method

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Herein, we report a simple and effective way to prepare Mn-Ce mixed-oxide catalysts supported on carbon nanotubes for low-temperature selective catalytic reduction of NO with NH₃. The catalysts with amorphous structure all showed nearly 100 % NO conversion at 120-180 °C with a space velocity of 30,000 h⁻¹.

Introduction

Nitrogen oxide (NO_x) remains a major source of air pollution, and it is very harmful for the ecosystem and humanity.^{1, 2} The major technology for abatement of nitrogen oxide emissions from stationary sources is selective catalytic reduction (SCR) of NO_x with NH₃.^{3, 4} However, the commercial catalyst is active in a narrow temperature range of 300-400 °C, which can also be affected by the high concentration of ash and SO₂.^{5, 6} It would be favorable to place the SCR unit at the tail-end of the system configuration for economic or spatial reasons, and the catalyst will not be influenced by the ash and SO₂.⁷ Therefore, development of low-temperature SCR catalysts has become a hot topic in the past decade.^{4-6, 8, 9}

Recently, many attempts have been devoted to investigate the de-NO_x activity of carbon nanotubes (CNTs) based catalysts due to their unique structure and thermal stability. Examples of these catalysts are VO_x/CNTs,¹⁰ CeO₂/CNTs,^{11, 12} and MnO_x/CNTs.^{13, 14} But, these catalysts only showed high activity in the medium temperature range of 200-300 °C. So, there remains a potential improvement space for the CNTs based catalysts to obtain excellent low-temperature (< 200 °C) de-NO_x activity.

As we know, the activity in the SCR reaction is greatly associated with the surface property and morphology of active components on the support, and thus the synthetic method is crucial to the SCR catalysts.^{9, 15, 16} Mn-Ce mixed oxides catalysts possessed high SCR activity and robust SO₂ resistance at low temperatures, and ceria was found to increase the dispersion and oxygen storage capability of MnO_x.¹⁷⁻¹⁹ Zhang *et al.*^{20, 21} reported two kinds of novel methods to synthesize Mn-CeO_x/CNTs catalysts, but the low-temperature SCR activity for the catalysts was still unsatisfactory due to the low valence state of manganese oxides. In our previous report, Mn-Ce/CNTs catalysts prepared by calcined in air showed high activity in the low temperature range, but the catalysts had to bear a mass loss during the calcination process.²² In this communication, a liquid-phase method operated at room temperature was introduced to prepare

Mn-CeO_x/CNTs catalysts. As illustrated in Fig. 1, Ce³⁺ ions were firstly attached on acid-treated CNTs, and then they were oxidized to CeO_x by potassium permanganate solution. At the same time, the potassium permanganate was *in situ* reduced to manganese oxides on CNTs. The as-prepared Mn-CeO_x/CNTs catalysts were used for selective catalytic reduction of NO with NH₃, which displayed high NO conversion at low temperatures.

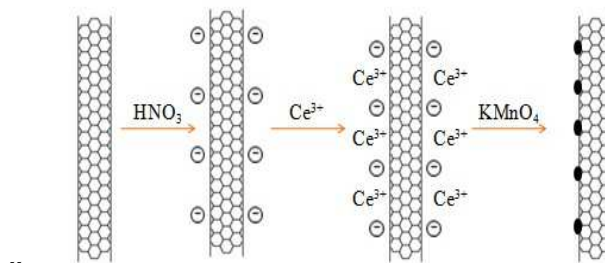


Fig. 1 Schematic illustration of the synthesis process of Mn-CeO_x/CNTs.

Results and discussion

Fig. 2 shows the NO conversion as a function of temperature for Mn-CeO_x/CNTs catalysts prepared by the liquid-phase method with constant Ce/C molar ratio (2 %) but different Mn/(Mn+Ce) molar ratios (ratio of KMnO₄ to the total of KMnO₄ and Ce(NO₃)₃ used in the preparation process). The catalysts

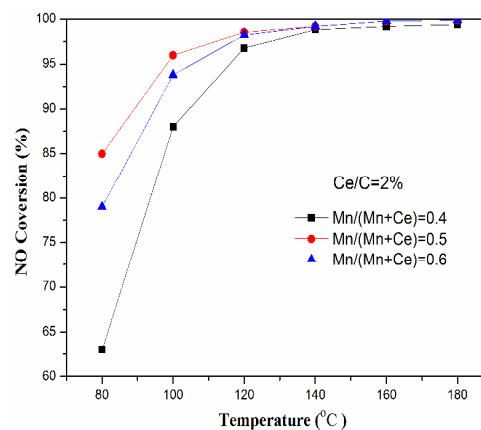


Fig. 2 NO conversions as a function of temperature for Mn-CeO_x/CNTs catalysts prepared by the liquid-phase method with constant Ce/C molar ratio (2 %) but different Mn/(Mn+Ce) molar ratios. Reaction conditions: [NO] = [NH₃] = 500 ppm, [O₂] = 5 %, N₂ as balance gas, GHSV = 30,000 h⁻¹, 180 mg sample.

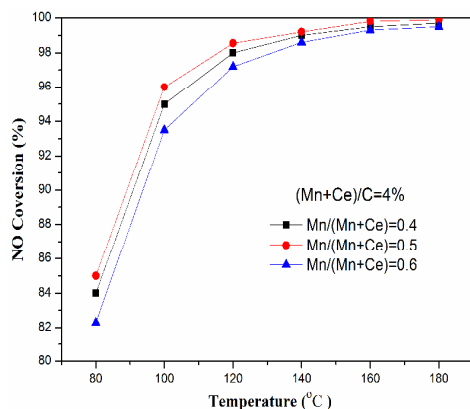


Fig. 3 NO conversions as a function of temperature for Mn-CeO_x/CNTs catalysts prepared by the liquid-phase method with constant (Mn+Ce)/C molar ratio (4 %) but different Mn/(Mn+Ce) molar ratios. Reaction conditions: [NO] = [NH₃] = 500 ppm, [O₂] = 5 %, N₂ as balance gas, GHSV = 30,000 h⁻¹, 180 mg sample.

showed excellent activities at low temperatures. 63-85 % NO conversions were obtained even at 80 °C with a space velocity of 30,000 h⁻¹. As the temperature increased, NO conversion moved up significantly and reached nearly 100 % at 120-180 °C. The SCR activity at low temperatures decreased in the following sequence: Mn(0.5)-CeO_x/CNTs > Mn(0.6)-CeO_x/CNTs > Mn(0.4)-CeO_x/CNTs. However, it was worth noting that the loadings of the Mn-CeO_x/CNTs catalysts increased in the following sequence: Mn(0.4)-CeO_x/CNTs < Mn(0.5)-CeO_x/CNTs < Mn(0.6)-CeO_x/CNTs, which was in accordance with the usage of potassium permanganate.

In another experiment, Mn-CeO_x/CNTs catalysts with constant (Mn+Ce)/C molar ratio (4 %) but different Mn/(Mn+Ce) molar ratios were also prepared by the liquid-phase method. The effect of the ratio of Mn/(Mn+Ce) on the activity are given in Fig. 3. The SCR activities of Mn(0.4)-CeO_x/CNTs, Mn(0.5)-CeO_x/CNTs and Mn(0.6)-CeO_x/CNTs catalysts in the whole temperature range were very close to each other. The similar redox properties of these catalysts based on the H₂-TPR experiment (Fig. S1, ESI[†]) may support this result. Additionally, obvious changes on the reducibility of CNTs in Mn-CeO_x/CNTs catalysts in Fig. S1 implied an interaction between the metal oxides and CNTs.¹³ More interestingly, the loadings of the three Mn-CeO_x/CNTs catalysts were almost the same. Therefore, we inferred that the catalytic active of Mn-CeO_x/CNTs catalysts prepared the liquid-phase method may be mainly determined by the loading of Mn-Ce mixed oxides. Even so, a Mn/(Mn+Ce) molar ratio of 0.5 would be optimum for preparing the Mn-CeO_x/CNTs catalyst by

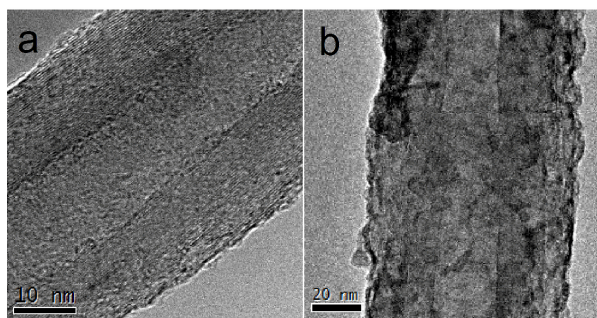


Fig. 4 TEM images of (a) acid-treated CNTs and (b) Mn(0.5)-CeO_x/CNTs.

this method based on the result of Fig. 3.

The TEM images of CNTs before and after supported catalysts are shown in Fig. 4. The external surface of acid-treated CNTs was clean (Fig. 4a), whereas it became splotchy after supported Mn-Ce mixed-oxide catalysts (Fig. 4b). The surface of CNTs were coated by something like metal nanoflakes for the Mn(0.5)-CeO_x/CNTs catalyst. The HRTEM images (Fig. S2, ESI[†]) showed that the metal nanoflakes displayed irregular shape and fuzzy crystal lattice, which suggested the metal oxides supported on CNTs prepared by the liquid-phase method should be amorphous phase. This conclusion was also supported by the XRD results (Fig. S3, ESI[†]), which only showed the typical peaks of CNTs. For the SCR reaction, amorphous oxides showed higher activity than its crystalline counterpart at low temperatures.^{9, 23}

The XPS was applied to provide the information of the content and the metal oxidation states in the near-surface region. The surface atomic percentages of C, O, Mn, Ce for Mn(0.5)-CeO_x/CNTs catalyst were 76.18 %, 16.97 %, 3.08 % and 3.76 %, respectively. The Mn 2p core level spectrum of Mn(0.5)-CeO_x/CNTs catalyst is shown in Fig. 5a. The binding energies of Mn 2p^{3/2} (642.30 eV) and Mn 2p^{1/2} (654.04 eV) and their spin energy difference (11.74 eV) are consistent with the values of Mn⁴⁺ of MnO₂ reported in literature.²⁴ Kapteijn *et al.*²⁵ had investigated the SCR activity of different pure manganese oxides, and found that MnO₂ exhibited the highest activity. Thus, a high valence state of manganese oxides with amorphous structure could be obtained from the potassium permanganate solution, which should be the main reason for the high activity of Mn-CeO_x/CNTs catalysts prepared by the liquid-phase method. The

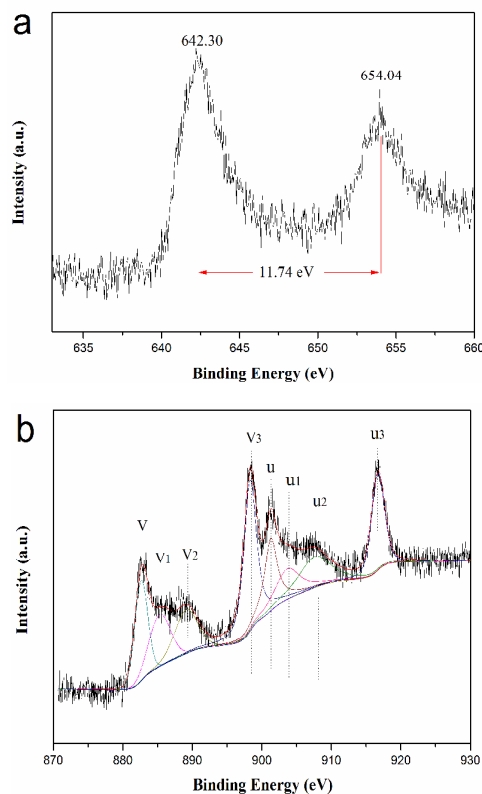


Fig. 5 XPS spectra and the peak deconvolution for (a) Mn 2p and (b) Ce 3d in the Mn(0.5)-CeO_x/CNTs catalyst.

Ce 3d spectrum in Fig. 5b was deconvoluted by the curve-fitting procedure. The peaks labelled v (882.63 eV), v_2 (889.11 eV), v_3 (898.31 eV), u (901.28 eV), u_2 (907.59 eV) and u_3 (916.69 eV) were assigned to the Ce^{4+} species, while the peaks denoted v_1 (885.3 eV) and u_1 (903.67 eV) implied that part of Ce^{3+} species still existed in this catalyst.²⁶ It was reported that the presence of partial Ce^{3+} species could create the oxygen vacancies and unsaturated chemical bands on the catalyst surface, which could facilitate the activation of the active oxygen species and hence increase the SCR activity and N_2 selectivity.^{19, 27} To investigate the stability of the catalyst, thermogravimetric analysis (TGA) and cyclic activity tests were performed on the Mn(0.5)- CeO_x /CNTs catalyst. The TGA graph showed the catalyst can be stable below 200 °C (Fig. S4, ESI†). On the other hand, cyclic activity tests (Fig. S5, ESI†) showed an increase of NO conversions in the second run, which may be ascribed to removal of the combined water formed in the preparation process after the first run. And only a slight decline of the conversions could be observed in the fourth run even though the catalyst was laid in lab for one month. Finally, the catalyst showed no change in the XRD profile even after three test runs (Fig. S3, ESI†). All of these results indicated that Mn- CeO_x /CNTs catalysts prepared by the liquid-phase method exhibited excellent stability.

Conclusions

In summary, a series of Mn-Ce mixed-oxide catalysts supported on CNTs were firstly prepared by a liquid-phase method and used for the selective catalytic reduction of NO with NH_3 . A Mn/(Mn+Ce) molar ratio of 0.5 was found to be optimum for the SCR reaction, and nearly 100 % NO conversion was obtained at 120-180 °C with a high space velocity. The amorphous structure, high valence state of manganese oxides and part of Ce^{3+} species were the essential characteristics of the Mn(0.5)- CeO_x /CNTs catalyst prepared by the liquid-phase method. Further work on the water and SO_2 resistance is needed. In addition, the interaction of Mn-Ce mixed oxides remains unclear.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [Experimental details, H_2 -TPR profiles, HRTEM images, XRD results, cyclic activities tests and TGA of the Mn(0.5)- CeO_x /CNTs catalyst]. See DOI: 10.1039/b000000x/

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