

Facile synthesis of flake-like MnO₂/CNFs catalysts and their activity in low-temperature NO reduction with NH₃

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Published in Micro & Nano Letters; Received on 30th June 2016; Revised on 9th September 2016; Accepted on 16th September 2016

A series of MnO₂/carbon nanofibres (CNFs) catalysts were prepared by a facile co-precipitation method for low-temperature selective catalytic reduction (SCR) of NO with NH₃. These catalysts were characterised by the techniques of specific surface area measurements (BET), X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and H₂ temperature-programmed reduction (H₂-TPR). The XRD, FESEM and TEM results showed that the CNFs were surrounded by MnO₂ nanoflakes. Compared with the MnO_x/CNFs catalyst prepared by the wet impregnation method, the MnO₂/CNFs catalysts exhibited better low-temperature SCR activity at low temperature. The XPS results indicated that a higher concentration of Mn⁴⁺ and more surface oxygen species existed on the surface for 8% MnO₂/CNFs catalyst. The H₂-TPR profiles displayed that the 8% MnO₂/CNFs catalyst presented stronger low-temperature reducibility than the MnO_x/CNFs catalyst. Based on the abovementioned favourable properties, the 8% MnO₂/CNFs catalyst has an excellent performance in the low-temperature SCR of NO with NH₃.

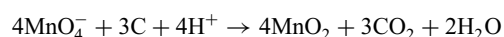
1. Introduction: Nitrogen oxide (NO_x) remains a major source of air pollution and is very harmful to both the ecosystem and the humanity [1]. Selective catalytic reduction (SCR) of NO with NH₃ is regarded as an efficient technology for abatement of nitrogen oxides from stationary sources [2, 3]. However, the commercial catalysts (V₂O₅-WO₃/TiO₂) for this process are active within the narrow temperature window of 300–400°C, and they will be deactivated by high concentrations of SO₂ or dust [4]. Since the temperature of the flue gas after the desulfuriser and electrostatic precipitator is generally below 200°C, it is very important to develop highly active catalysts at relatively low working temperature [5, 6].

Some researchers have used carbon materials to improve the low-temperature SCR performance of manganese oxides, such as activated carbon (AC) [7], AC fibre [8] and carbon nanotubes (CNTs) [9], but optimal catalytic activity still require high operating temperature window (200–300°C). In recent years, carbon nanofibres (CNFs) have become materials of renewed interest because of their high length-to-diameter ratio, strong mechanical strength and superb thermal stability [10]. It has been demonstrated that transition metals or their oxides (such as manganese, copper, cobalt and iron) embedded in CNFs displayed high oxidation activity of NO to NO₂ at low temperature [11, 12]. Additionally, they are found to be superior sorbents for nitrogen oxides [13]. Therefore, CNFs hold great potential as low-temperature SCR catalyst supports. However, to the best of our knowledge, the use of CNFs as the support material for the low-temperature (<200°C) SCR catalysts was scarcely reported and still needed further investigation.

As is well known, the good dispersion of active components on the carrier is associated with high activity and good stability in the NH₃-SCR reaction [14], and the synthetic method is crucial for controlling the dispersion of active constituent on the carrier [15]. Generally, almost all of the carbon-based catalysts were prepared by the impregnation method, which made it difficult to ensure that MnO_x was uniformly dispersed on the surface of the support and aggregates were prone to form during the catalytic process. Therefore, it is still a challenge to uniformly disperse the active components on the carbon materials. Previously, we reported the co-precipitation method to prepare highly dispersed MnO₂ on

CNTs and these catalysts both presented good low-temperature activity [16, 17]. Given this, a facile co-precipitation method was adopted to prepare the highly active MnO₂/CNFs catalysts. The schematic illustration of the MnO₂/CNFs catalysts is described in Fig. 1. At first, the big bundles of CNFs were separated into individual and/or small bundle fibres by forming supramolecular self-assembly of SDS half-cylinders on the surface of CNFs [18]. Second, H⁺ cations were absorbed on the surface of SDS supramolecular self-assembly due to the electrostatic interaction between H⁺ cations and the anionic groups of sulphate in SDS molecules. Finally, MnO₂ nanoflakes were synthesised on the CNFs by a redox reaction between carbon and KMnO₄ in acid solution.

2. Experimental: The preparation procedure of MnO₂/CNFs catalysts was described as follows: 300 mg pristine CNFs (Beijing DK Nano Technology Co. Ltd., China) were added in 50 ml of 0.002 M SDS aqueous solution followed with 1 h ultrasonication at room temperature. Then, a trace amount of concentrated HNO₃ (65–68%) solution (1:1, the molar ratio of HNO₃ to KMnO₄) was subsequently added to the mixture and stirred continuously for 12 h at room temperature. After that, 20 ml of KMnO₄ aqueous solution was added dropwise into the above suspension and further stirring another 90 min at 70°C. The MnO₂ catalysts were synthesised via the following reaction: [19, 20]



Finally, the precipitate was filtered and washed with deionised water several times and dried at 105°C in air for 12 h. The as-obtained catalyst was denominated as Y MnO₂/CNFs catalyst, where Y represents the percentage of Mn⁷⁺/C molar ratio. For comparison, an MnO_x/CNFs catalyst with an optimised loading (the molar ratio of Mn⁷⁺/C is 8%) was also prepared by the wet impregnation method and calcined at 300°C according to the literature [21].

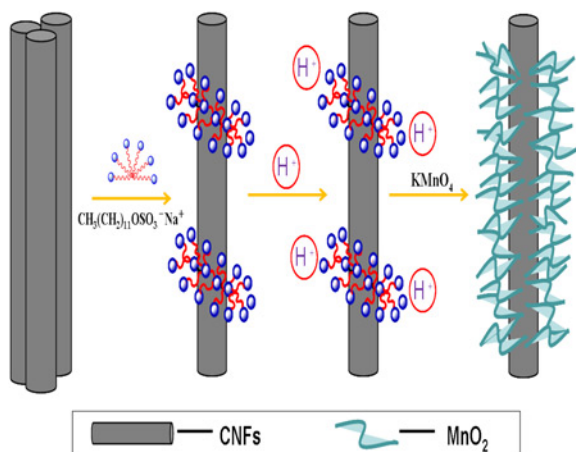


Fig. 1 Schematic representation for preparing MnO_2/CNFs catalysts

3. Characterisation: The surface features of the prepared catalysts were determined by N_2 adsorption–desorption on an ASAP 2020 M and porosity analyser at -196°C . Specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method, and pore size distribution was estimated from BJH method. The X-ray diffraction (XRD) patterns were recorded on an X'Pert Pro MPD X-ray diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$). The morphologies of the catalysts were observed by transmission electron microscopy (TEM) (JEOL model JEM 2010 EX instrument) and field emission scanning electron microscopy (FESEM) with ZEISS SUPRA. X-ray photoelectron spectroscopy (XPS) pattern was obtained with a Thermo Scientific ESCALAB 250 spectrometer using monochromated $\text{AlK}\alpha$ as a radiation source. H_2 temperature-programmed reduction (H_2 -TPR) was measured on a custom-made TCD setup. 50 mg of catalyst was firstly pretreated in N_2 at 200°C for 1 h, and then TPR test was carried out with the linear heating rate ($10^\circ\text{C}/\text{min}$) in pure N_2 containing 6% H_2 at a flow rate of 30 ml/min and a heating rate of $10^\circ\text{C}/\text{min}$.

4. Activity tests: The SCR activity measurements were carried out in a fixed-bed quartz reactor at the temperature range of 80 – 180°C (200 mg catalyst of each test). The simulated gas for all catalytic activity measurements contained 400 ppm NO, 400 ppm NH_3 , 5%

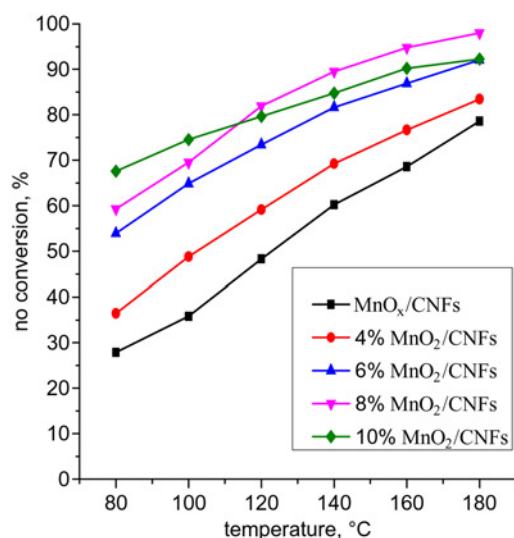


Fig. 2 SCR activity of MnO_2/CNFs catalysts and MnO_x/CNFs catalyst. Reaction conditions: $[\text{NO}] = [\text{NH}_3] = 400 \text{ ppm}$, $[\text{O}_2] = 5\%$, N_2 as balance gas, $\text{WHSV} = 210,000 \text{ ml/gcat h}$, 200 mg sample

Table 1 BET surface area, pore volumes and average pore size of pristine CNFs, acid-treated CNFs and different catalyst samples

Samples	BET surface area, m^2/g	Pore volume, cm^3/g	Average pore size, nm
pristine CNFs	40.24	0.0649	6.4513
acid-treated CNFs	44.76	0.0830	7.4180
MnO_x/CNFs	38.29	0.0627	6.5500
4% MnO_2/CNFs	77.25	0.1829	9.4724
6% MnO_2/CNFs	100.72	0.2380	9.4519
8% MnO_2/CNFs	125.67	0.2619	8.3370
10% MnO_2/CNFs	131.06	0.2859	8.7242

O_2 and N_2 as balanced gas. 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 (NO , NO_2 and O_2) was measured by a flue gas analyser (Kane International Limited, KM950). All data were collected after 30 min when the SCR reaction reached steady state (Fig. 2).

5. Results and discussion: Fig. 1 shows a plot of NO conversion versus temperature for the as-prepared catalysts. Compared with MnO_x/CNFs catalyst, the NO conversions over MnO_2/CNFs catalysts were higher, and achieved 38–98% during the test temperature range. It can be seen that the catalyst preparation method exerted significant influence on the catalytic performance. Additionally, it was worth noting that the 8% MnO_2/CNFs catalyst presented the first-rate SCR activity, which reached 89–98% at 140 – 180°C .

Table 1 lists the surface area, pore volume and average pore size of various samples. In Table 1, it was shown that the BET surface area and pore volume of MnO_2/CNFs catalysts were enlarged after being supported by the metal oxides. In the case of the MnO_x/CNFs catalyst, the BET surface area and pore volume were reduced after being doped with MnO_x , which may be due to the agglomeration of metal oxides (Fig. 5b). It should be noted that the 8% MnO_2/CNFs catalyst was possessed of optimal SCR activity but relatively small surface area, suggesting that the BET surface area was not a crucial factor for SCR activity [22]. Fig. 3 shows the N_2 adsorption–desorption isotherms of the 8% MnO_2/CNFs and

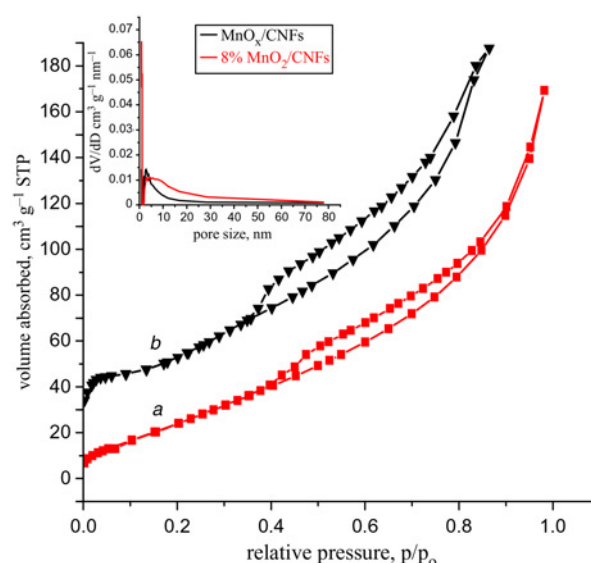


Fig. 3 N_2 adsorption–desorption isotherms of a 8% MnO_2/CNFs catalyst
b MnO_x/CNFs catalyst

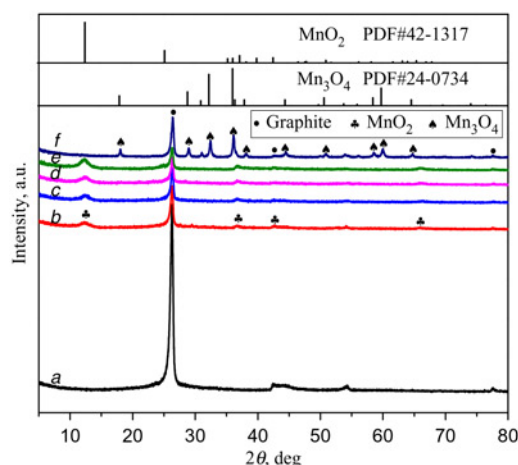


Fig. 4 XRD patterns of
a Pristine CNFs
b 4% MnO₂/CNFs
c 6% MnO₂/CNFs
d 8% MnO₂/CNFs
e 10% MnO₂/CNFs
f MnO_x/CNFs

MnO_x/CNFs catalysts as well as their pore size distribution curves (inset). Clearly, the sorption isotherms and hysteresis loops of the two catalysts were corresponded to the type IV and type H₃, which was the characteristic feature of mesoporous solids [23]. In addition, the two catalysts displayed a distribution centred at ~3 nm, further demonstrating the mesopore structure of the catalysts. Besides, part of the pore size for 8% MnO₂/CNFs was >3 nm (inset of Fig. 3), and these big pores might result from the staggered arrangement of the nanoflakey MnO₂ (Fig. 5d).

The XRD patterns of various catalysts were given in Fig. 4. It was observed that all patterns emerged the typical diffraction peaks at

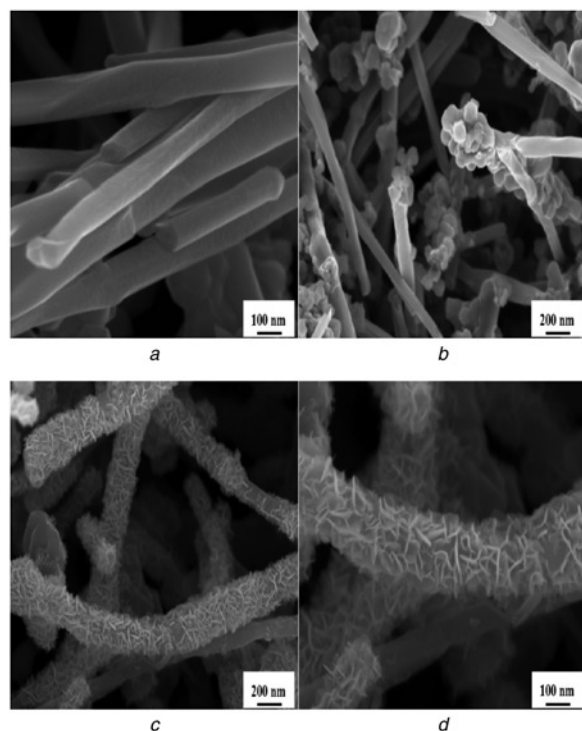


Fig. 5 FESEM images of
a Pristine CNFs
b MnO_x/CNFs catalyst
c, d 8% MnO₂/CNFs catalyst

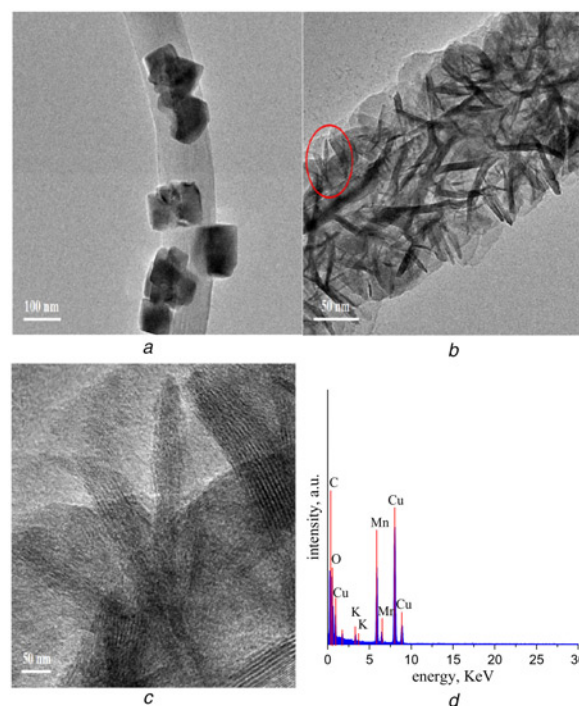


Fig. 6 TEM images of
a MnO_x/CNFs catalyst
b 8% MnO₂/CNFs catalyst
c HRTEM image of 8% MnO₂/CNFs catalyst
d EDX spectrum of 8% MnO₂/CNFs catalyst for the red region in (b)

~26°, 43°, 54° and 77°, which were well indexed to graphitic carbon [24]. After being loaded with the manganese oxides catalysts, the diffraction peaks intensity of MnO₂/CNFs catalysts were declined, which may be due to an interaction between CNFs and manganese oxides. Figs. 4b–e show the typical patterns of the MnO₂/CNFs catalysts. The three major diffraction peaks at ~12°, 37° and 66° were indexed to birnessite-type MnO₂ (PDF#-42-1317, δ-MnO₂), which consisted of 2D edge-shared MnO₆ octahedron layers with K⁺ cations and water molecules in the interlayer space [25]. The weak and broad XRD peaks of MnO₂ implied that most MnO₂ was in amorphous phase. For MnO_x/CNFs catalyst, strong diffraction peaks at ~18°, 29°, 36°, 39°, 44° and 60° corresponding to Mn₃O₄ could be observed (PDF#-24-0734) [26], indicating the existence of crystalline Mn₃O₄.

The FESEM images of pristine CNFs, MnO_x/CNFs and 8% MnO₂/CNFs catalysts were exhibited in Fig. 5. In Fig. 5a, it was clear that pristine CNFs exhibited regular morphology. After the addition of MnO_x, obvious aggregated nanoparticles could be observed on the surface of CNFs (Fig. 5b). Compared with MnO_x/CNFs catalyst, the 8% MnO₂/CNFs catalyst showed good dispersion of MnO₂ nanoflakes (Fig. 5c). In addition, the high-magnification FESEM images of 8% MnO₂/CNFs catalyst (Fig. 5d) present that nanoflakey MnO₂ were cross-linked and uniformly distributed on the surface of CNFs.

TEM and high resolution transmission electron microscopy (HRTEM) were further employed to investigate morphology of catalysts fabricated by the two different methods. Fig. 6a shows the TEM image of the MnO_x/CNFs catalyst prepared using the wet impregnation method. It can be seen that some aggregates were seen on the surface of CNFs, which maybe Mn₃O₄ crystals, based on the XRD analysis. However, the 8% MnO₂/CNFs catalyst prepared using the co-precipitation method showed well-dispersed MnO₂ nanoflakes on the CNFs in Fig. 6b. Additionally, the obvious lattice fringe was not found from HRTEM of 8% MnO₂/CNFs catalyst (Fig. 6c), implying amorphous manganese oxides supported on the surface of CNFs. This conclusion was related to the XRD results, and the

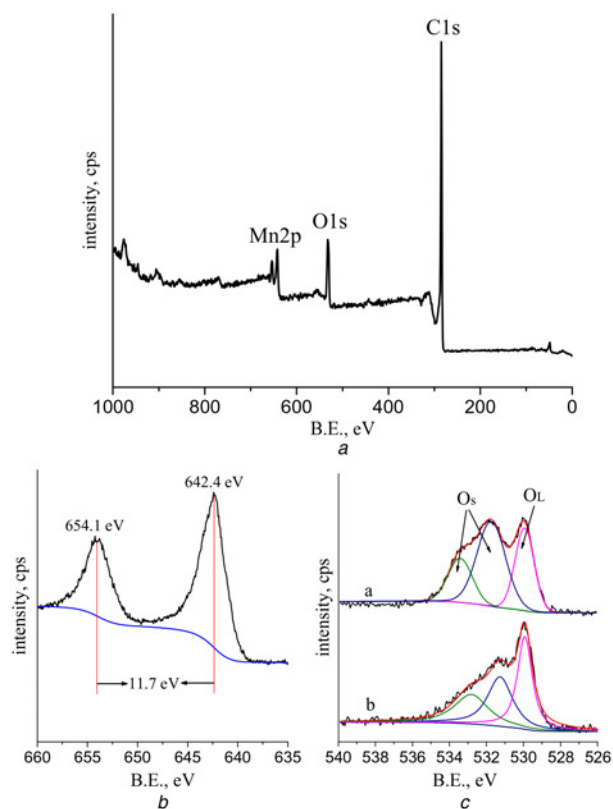


Fig. 7 XPS spectra of
a Full spectra
b Mn 2P for 8% MnO₂/CNFs catalyst
c O1s for (a) 8% MnO₂/CNFs catalyst and (b) MnO_x/CNFs catalyst

amorphous oxides presented higher SCR activity than their crystal oxides at low temperature [17, 27]. Moreover, the EDX spectrum of 8% MnO₂/CNFs catalyst (Fig. 6d) shows the presence of Mn, O, C as well as K on the CNFs, confirming the existence of manganese oxides catalysts. It was worthy to mention that a small amount of K⁺ cations was conductive to stabilise the layer structure in formation of δ -MnO₂ [25, 28].

The XPS spectra were shown in Fig. 7 to provide information on the content and the metal oxidation states in 8% MnO₂/CNFs and MnO_x/CNFs catalysts. The full spectrum of XPS (Fig. 7a) displays the signals of C, O and Mn, indicating the existence of C, O and Mn elements. The Mn 2p core-level spectra (Fig. 7b) of 8% MnO₂/CNFs catalyst exhibited that the binding energies for Mn 2p^{2/3} and Mn 2p^{1/2} were centred at 642.4 and 654.1 eV respectively. The peak values well agreed with those reported for MnO₂, indicating 4+ oxidation state for Mn [29]. The O1s spectra (Fig. 7c) of the two catalysts were deconvoluted by the peak-fitting process. The peaks centred at 529.9 eV could be ascribed to the lattice oxygen (O_L) species based on Mn, and the high binding energy at 531.4–534.0 eV was assigned to the surface oxygen (O_S) species bound to Mn [30]. Moreover, the calculation (Table 2) demonstrated that the relative content of O_S of 8% MnO₂/CNFs catalyst (68.9%) was higher than that of MnO_x/CNFs catalyst (61.5%). Usually, the O_S was more active in oxidation reaction than that of

Table 2 Relative content of O for 8% MnO₂/CNFs and MnO_x/CNFs catalyst from XPS results

Samples	O _S , %	O _L , %
8% MnO ₂ /CNFs	68.9	31.1
MnO _x /CNFs	61.5	38.5

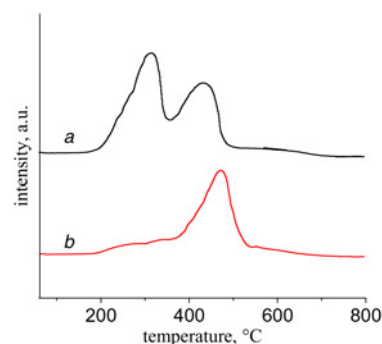


Fig. 8 H₂-TPR profiles of
a 8% MnO₂/CNFs catalyst
b MnO_x/CNFs catalyst

O_L owing to its high mobility, which was favourable for NO oxidation to NO₂, and thus, facilitated the ‘fast SCR’ reaction [31].

The H₂-TPR technique was employed to investigate the reducibility of various catalysts. As shown in Fig. 8a, the 8% MnO₂/CNFs catalyst presented two reduction peaks at 175–358 and 363–517°C, which were ascribed to the reduction of MnO₂ and Mn₂O₃ to Mn₃O₄, Mn₃O₄ to MnO respectively [32]. For MnO_x/CNFs catalyst, there was only a reduction peak at 355–549°C. The peak was assigned to the reduction of Mn₃O₄ to MnO, which was consistent with the result of XRD (Fig. 4f). Comparing the peak position of the as-synthesised catalysts, the lower onset temperatures of 8% MnO₂/CNFs catalyst were indicative of stronger reducibility.

6. Conclusion: In summary, highly dispersed MnO₂/CNFs catalysts were successfully synthesised by a facile co-precipitation method, and exhibited excellent low-temperature SCR activity at 80–180°C. The 8% MnO₂/CNFs catalyst showed first-rate SCR activity, which could be ascribed to the amorphous MnO₂, higher O_S content, as well as the stronger low-temperature reducibility. The BET surface area has some effect on the catalyst’s activity, but is not the main factor.

7. Acknowledgments: This work was supported by Scientific and Technological Program-Funded Project of Fuzhou City (grant no. 2015H0016).

8 References

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