

Journal of Materials Chemistry A

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Facile preparation of MnO₂ doped Fe₂O₃ hollow nanofibers for low temperature SCR of NO with NH₃

Sihui Zhan,^{*a} Mingying Qiu, ^{*a} Shanshan Yang^a, Dandan Zhu,^a Hongbing Yu^a and Yi Li^{*b}*Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX*

DOI: 10.1039/b000000x

Abstract: A series of MnO₂ doped Fe₂O₃ hollow nanofibers with different Mn/Fe molar ratios were successfully synthesized by the electrospinning method for the low temperature selective catalytic reduction (SCR) of NO with NH₃ in the presence of excess O₂. The SEM and TEM showed obvious hollow tubular structure of electrospun nanofibers. The hollow nanofibers with Mn/Fe molar ratio of 0.15 exhibited highest catalytic activity, nearly 100% of NO conversion from 150 to 300 °C, among the catalysts investigated. The TPR, XPS and in situ FTIR results revealed that Mn⁴⁺ was the main active species for SCR reaction and the addition of Mn species enhanced the surface concentration and acidity of Lewis acid sites.

1. Introduction

Nitrogen oxides (NO_x) from industrial flue gas have been leading to more and more environmental problems including photochemical smog, acid rain and ozone depletion.¹⁻⁴ So far, selective catalytic reduction (SCR) of NO_x with NH₃ is the most effective technology for removing of NO_x,⁵⁻⁶ and commercial V₂O₅-WO₃/TiO₂ catalysts has been widely used for the removal of NO_x from stationary sources.⁷⁻¹¹ However, there are some drawbacks of V₂O₅-WO₃/TiO₂ catalysts, such as high cost, the toxicity of vanadium species and narrow temperature window of 300-400 °C.¹² Thereby, it is necessary to develop novel low-temperature SCR catalysts, which can be set down at downstream of desulfurization scrubber or particulate control device, in order to avoid deactivation and save energy.^{13,14}

Previous studies have showed that mixed transition metal oxides including Cu, Fe, Co, Mn, Ce, Cr, and Ni have the advantages of good low-temperature SCR activity and low cost. Among them, manganese and iron oxides are attracting much attention because of their high SCR activity at low temperature, low cost, and non-toxicity.¹⁵⁻²⁰ However, these Fe-base catalysts were prepared usually with the impregnation approach and were prone to be easily deactivated by SO₂ present in the treated flue gas. Therefore, the stability of catalytic activity, sulfur tolerance, and water resistance should be enhanced through formulation modification and structure adjustment.

In the past years, various methods have been used to synthesize nanoparticles including hydrothermal methods,²⁰⁻²³ sol-gel,²⁴ and co-precipitation.²⁵ However, in catalytic processes, pore diffusion resistance is obvious for nanoparticles, which is hard to handle and usually causes many serious problems of high pressure drop in industrial application.²⁶ To overcome these disadvantages, electrospinning is applied for synthesizing hollow nanofibers or tubules, which have attracted much attention for their hierarchical

tubules-within-a-tubule structure, as well as fibrous mat structure, large surface area and sufficient mechanical integrity. Just because of these advantages, the long hollow fibers could act as a micro-reactor and could be packed or constructed in the best form to fit the particular application in many fields, such as energy storage, semiconductor, gas sensor, and so on.²⁷⁻²⁹ However, to the best of our knowledge, there is no report on using electrospun nanofibers as SCR catalyst to remove NO_x with NH₃.

In this paper, manganese doped iron-based hollow nanofiber were successfully synthesized by electrospinning the corresponding precursor and calcination. The activities for the low temperature SCR of NO with NH₃ in the presence of excess O₂ at the relatively high space velocity of 50000 h⁻¹ were investigated. The hollow nanofibers with Mn/Fe molar ratio of 0.15 exhibited an excellent NO_x SCR performance of complete NO reduction at as low as 150 °C, which can be attributed to its relatively high surface area, high surface Mn⁴⁺ concentration, and the high concentration of Lewis acid sites, as well as, as characterized by BET, XPS, TPR, and in situ FTIR.

2. Experimental Section

2.1 Catalyst Preparation

All used chemicals were analytical grade. Citric acid, ferric citrate and manganese acetate were purchased from Sinopharm chemical reagent company without further purification.

In a typical process, 0.03 mol of citric acid and 0.01 mol of ferric citrate were dissolved into 50 mL deionized water with magnetic stirring for 3h, which is then filtered to remove insoluble contaminants to obtain a transparent solution A. Meanwhile, 0.001 mol manganese acetate was dissolved in 5 mL deionized water in order to obtain solution B. After being dissolved completely, solution B was poured into solution A with magnetic

stirring for 30 min at room temperature, then the mixed solution was aged at 60 °C for 24 h to 4-5 Pa·s.

In a typical electrospinning process, the spinnable sol was transferred into a plastic injector, and the sol was pressurized with a syringe pump (Cole-Parmer 74900-05, USA). The metallic needle was connected to a high-voltage supply (DW-P503-4ACCD, Tianjin, China), and a piece of stainless steel board was used to collect the gel fibers. All the experiments were conducted at room temperature, the applied voltage was 15 kV, the distance between the spinneret and the collector was 10 cm. Finally, the xerogel fibers were calcined at 400 °C for 4 h in air at a heating rate of 0.5 °C·min⁻¹ to get the desired products. The hollow nanofibers were denoted as MnFe(x) ("x" represented the MnOx/Fe₂O₃ molar ratio; x = 0, 0.01, 0.05, 0.10, 0.15, 0.20). All the above catalysts were ground and sieved to 40-60 mesh for further measurements.

2.2. Catalyst Characterization

The morphology and structure of the fibers were observed by using a scanning electron microscope (SEM, Shimadzu SS-550) and a high-resolution transmission electron microscopy (HRTEM, Tecnai G2F20). The X-ray diffraction (XRD) patterns of samples were recorded via an X-ray diffractometer (Rigaku D/Max 2200PC) with a graphite monochromator and CuK α radiation ($\lambda=0.15418$ nm) in the range of 20-80°. The voltage and current were 40 kV and 40 mA, respectively. The Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a Nicolet 5DX-FTIR spectrometer using KBr pellet method in the range of 400-4000 cm⁻¹. N₂ adsorption-desorption data were obtained using a Quantachrom SI Micromeritics apparatus. X-ray photoelectron spectroscopy (XPS) spectra were collected on an ESCALAB 250 multi-technique X-ray photoelectron spectrometer (UK) using a monochromatic AlK α X-ray source (h ν =1486.6 eV). All XPS spectra were recorded using an aperture slot of 300*700 microns, and survey spectra were recorded with pass energy of 160 eV, and high resolution spectra with a pass energy of 40 eV. Temperature-programmed reduction (H₂-TPR) experiments were conducted on a Micromeritics ChemiSorb 2720 using approximately 20 mg of samples. Samples were pretreated at 300 °C for 1 h in N₂ flow. The temperature was increased linearly from 50 to 1000 °C at 10 °C/min while H₂ consumption was recorded continuously. The in situ DRIFTS spectra were recorded with on an AVATAR 370 Fourier transform infrared spectrometer. Prior to each experiment, the sample was heated to 350 °C in He for 1h and then cooled to 150 °C. The spectra were recorded by accumulating 32 scans at a resolution of 4 cm⁻¹.

2.3. SCR Activity Measurements

The catalytic activities were evaluated using a bench-scale experimental system. In each test, hollow fibrous catalyst was loaded in a temperature controlled fixed-bed quartz flow reactor (i.d. 20 mm) containing 0.5 g of catalyst to control the reaction temperature. All individual flue gas components were precisely controlled by mass flow controllers (MFC), with a total flow rate of 300 mL·min⁻¹ (refers to 1 atm and 298 K), which corresponded to a gas hourly space velocity (GHSV) of 50,000 h⁻¹. The typical composition of the initial reactant gas was: 500 ppm NO, 500 ppm NH₃, 5 vol % O₂, and balance N₂. The NO, NH₃, NO₂ and N₂O concentrations at both the inlet and outlet of the reactor were

measured online by a FTIR spectrometer (Gaset FTIR DX4000, Finland). The reaction system was kept for 1 h at each reaction temperature to reach a steady state before the analysis of the catalyst was performed. The NO_x conversion as follows:

$$\text{NO conversion (\%)} = 100\% \times (1 - [\text{NO}_x]_{\text{out}}/[\text{NO}_x]_{\text{in}})$$

$$\text{N}_2 \text{ selectivity (\%)} = 100\% \times [1 - ([\text{NO}_2]_{\text{out}} + 2 [\text{N}_2\text{O}]_{\text{out}})/([\text{NO}_x]_{\text{in}} + [\text{NH}_3]_{\text{in}} - [\text{NH}_3]_{\text{out}})]$$

Where [NO_x] = [NO] + [NO₂], and the subscripts "in" and "out" indicate the inlet concentration and outlet concentration at steady state, respectively.

3. Results and Discussion

3.1 Characteristics

To obtain structural information of the MnFe composite hollow nanofibers, XRD patterns were shown in Fig. 1. There were five diffraction peaks at 31.28, 35.08, 43.18, 56.58 and 62.88°, which belonged to magnetite Fe₂O₃ (PDF#19-0629). With increasing manganese content, the diffraction peak of Fe₂O₃ became lower and lower, indicating its composed nanoparticles became larger and larger.^{30,31} However, no visible phase of Mn species could be observed, it may be due to the fact that MnOx is well incorporated into the matrix of Fe₂O₃ or that the Mn oxides were in a highly dispersed state or the crystallites formed were less than 5 nm beyond detection limitation. Furthermore, the full width at half-maximum (fwhm) of the peaks for MnFe(x=0.01-0.2) were lower than those for Fe₂O₃, indicating that the grain size of Fe₂O₃ on MnFe(x=0.01-0.2) was smaller than that on Fe₂O₃. This meant that the existence of MnOx could lower the crystallinity of Fe₂O₃ and thus enhance the dispersion of Fe₂O₃ on the catalyst surface.

The N₂ adsorption-desorption isotherms were shown in Fig 2, and data of pore size distribution, pore volume, and surface area were listed in Table 1. From Fig 2, all MnFe(x) hollow nanofibers with different Mn/Fe mole ratio showed typical IV curves and H1 type hysteresis loop, indicating that mesoporous structure come into being.^{4,32} Upon increasing Mn doping content, the surface area improved from 96.5 to 137.1 m²/g (Table 1), meanwhile higher manganese loading would enhance NO conversion until the mole ratio of MnOx/Fe₂O₃ reached 0.15. Beyond this value, a further increase of manganese loading could lead to sintering or the collapsing of the structure, which was harmful to the BET surface and catalytic activity. It is implied that the low-temperature reduction activity of NO_x is related to the apparent surface properties to some extent. As shown in Table 1 and Fig. 6, both the BET surface (124.4 m²/g) and the low temperature activity of MnFe(0.20) catalyst were lower than that of MnFe(0.15). This phenomenon is also verified by the scanning electron microscopic (SEM) images of these catalysts (Figure 3a-c).

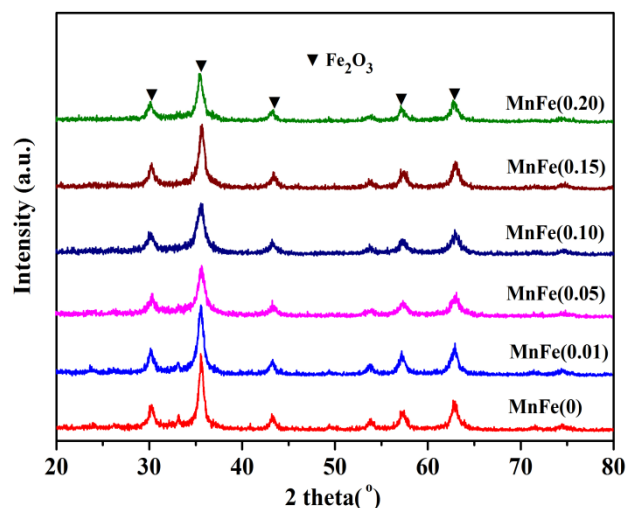


Fig. 1. XRD patterns of MnFe hollow nanofibers.

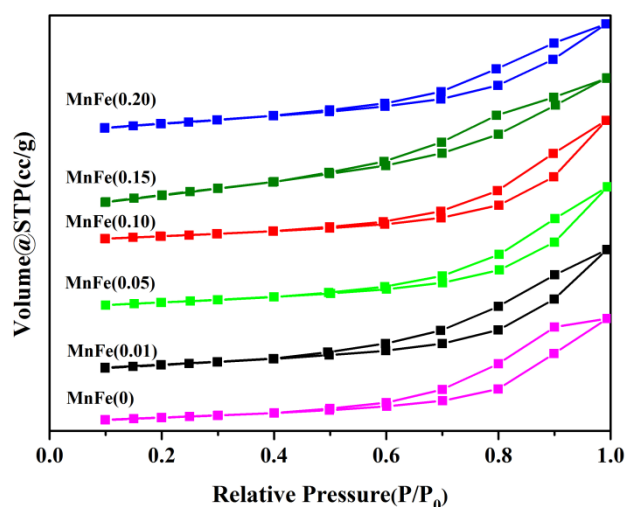


Fig. 2. Nitrogen adsorption isotherms of MnFe nanofibers

Table 1 The specific area, pore volume and pore diameter distribution of MnFe nanofibers

materials	specific area (m ² /g)	pore volume (cc/g)	pore diameter (nm)
Fe ₂ O ₃	96.5	0.29	8.8
MnFe(0.01)	102.2	0.29	8.8
MnFe(0.05)	108.2	0.26	8.8
MnFe(0.10)	112.8	0.30	6.1
MnFe(0.15)	137.1	0.35	6.6
MnFe(0.20)	124.4	0.27	6.8

3.2 SEM and TEM analysis

Fig. 3 showed a typical scanning electron microscopy (SEM)

and transmission electron microscopy (TEM) image of the as-prepared MnFe hollow nanofibers. From Fig. S1, it can be seen that the MnFe (0.05) nanofibers had hollow structure but non-uniform size. As to MnFe (0.20) (Fig. S2), the hollow structure is partially incomplete and collapsed, the result was consistent with the N₂ adsorption-desorption isotherms conclusion. As shown in Fig. 3c, all of MnFe (0.15) nanofibers were hollow structure and almost nanofibers were quite uniform in cross-section, and there were almost 60% of hollow nanofibers with outer diameter from 50 nm to 200 nm. The change of outer diameter should be attributed to the gradual loss of citrate agents from the nanofibers and the crystallisation of Fe₂O₃. After calcinations, the hollow MnFe(0.15) nanostructured fibers were smooth and composed of numerous nanoparticles with relatively uniform distribution of normally 5-20 μm long and have larger coarser surfaces, which provided a larger accessible surface area between the gas molecules and catalyst. Fig. 3b clearly indicated that the uniform tubular structure with an outer diameter 312 nm and 10 nm of wall thickness. TEM and HRTEM were also used to check the microstructure of catalyst MnFe (0.15). As shown in Fig. 3a, a typical hollow tubular structure with average outer diameter of about 140 nm and well-uniform wall thickness could be observed easily. Additionally, High-resolution transmission electron microscopy (HRTEM) was used to characterize the lattice structure. In addition, the two different lattice fringes can be clearly observed in Fig. 3d, one was around 0.361 nm, which matched with Fe₂O₃ (0.361 nm) in plane (011) and the other was 0.293 nm, corresponding to Fe₂O₃ (0.295 nm) in (110) or manganese oxides (0.291 nm) in (201).^{20,33} These results indicate that the synthesized hollow fibers have good crystallinity and provide a large accessible surface area.

The possible formation mechanism of electrospun hollow nanofibers is the following: After electrospinning the xerogel nanofibers, a rigid outer shell came into being. However, it was still fluid in center of fibers that time, and a large amount of solvent and citric acid anions remained in the gel fibers. When the gel fiber was calcined in a tubular furnace, the sol particles diffused to the inner surface of the outer shell with the evaporation of the organic compounds, and thus the novel tubular structure first formed. Even at this stage, there were still many organic parts remaining in the fibers. Upon increasing the heating temperature, citrate anions began to decompose to produce CO₂ and H₂O gases, which went out of the fibers through the tube, and a crystallized hollow fiber produced.³⁴

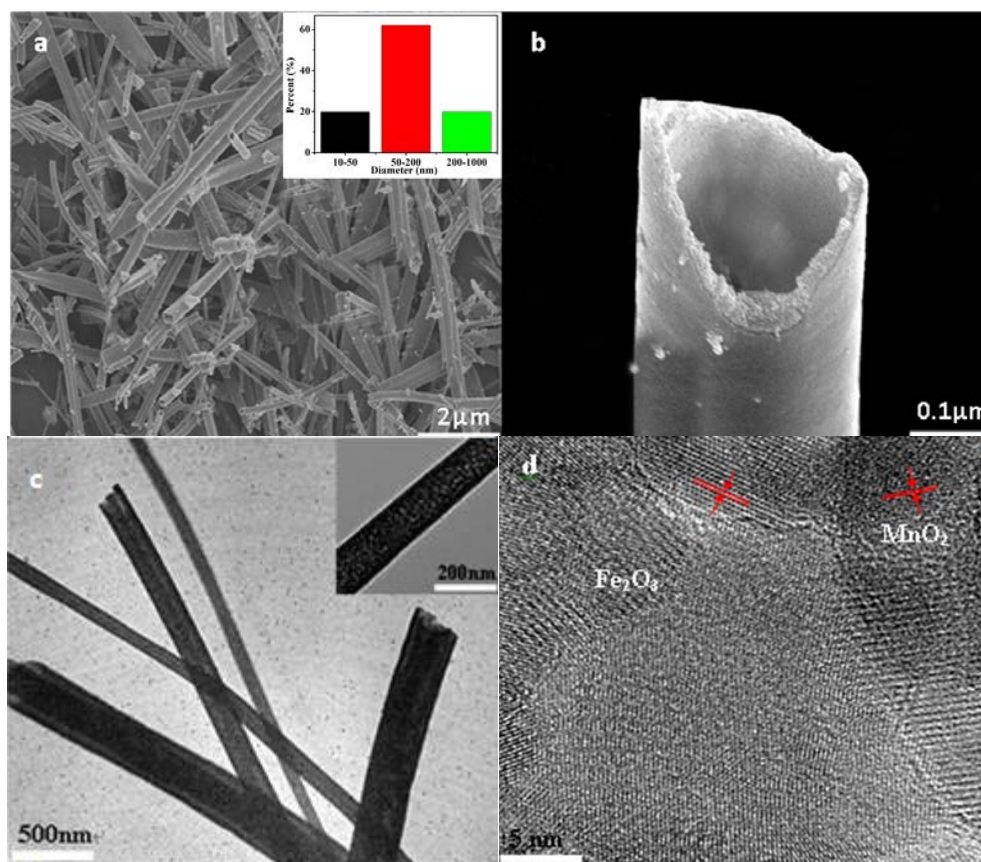


Fig. 3. (a) SEM image of electrospun MnFe (0.15) hollow nanofibers (inset: under high magnification); (b) SEM image of the cross-section; (c) TEM image of MnFe (0.15) hollow nanofibers; (d) HRTEM image of MnFe (0.15) hollow nanofibers.

4.1 H₂-TPR and XPS analysis

H₂-TPR is a widely used technique to investigate the redox properties of catalyst. The H₂-TPR profiles of Fe₂O₃, MnFe (0.05), and MnFe (0.15) catalyst were illustrated in Fig. 4. All H₂ consumption peaks could be attributed to the reduction of iron, manganese species, and their reduction behavior was very different. For the Fe₂O₃ sample, there were two peaks spanned over 250–550 °C and 600–800 °C, which was corresponding to the following reduction steps: Fe₂O₃–Fe₃O₄ (327 °C) and Fe₃O₄–FeO (619 °C), respectively.^{35,36} It can be seen from this figure that the peak positions shifted to higher temperatures after the introduction of manganese. The peak from 300 °C to 400 °C can be ascribed to the combined reduction of Fe³⁺ and Mn³⁺ (or Mn⁴⁺) with a structural transformation from Fe_{2–y}Mn_yO₃ to (Fe–Mn)₃O₄.^{24,37} For these catalysts, there is likely to be a stronger metal-support interaction, thereby making it more difficult to carry out the reduction. For the MnFe (0.15) sample, increasing Mn loading decreases the temperature required for reduction of Fe₃O₄–FeO (662 °C) compared to the MnFe (0.05) sample (705 °C), it is suggested that the mobility of surface oxygen was enhanced after the addition of Mn, and therefore there was more

chemisorbed oxygen formed on the catalyst surface.³⁸

In order to understand the nature of the interaction between the two metal oxide species, the oxidation states of Fe 2p_{3/2}, Mn 2p_{3/2}, and O 1s in on MnFe hollow nanofibers were detected by XPS in Fig. 5, which had been calibrated against the C 1s peak standardized at 284.6 eV. As shown in Fig. 5a, the Fe 2p_{3/2} peak is separated into two peaks by the same peak fitting deconvolution technique. The peaks at 711.0 and 713.1 eV can be assigned to Fe²⁺ and Fe³⁺, respectively.¹⁹ The ratios of Fe²⁺/Fe³⁺ on the surface of MnFe (0), MnFe (0.05) and MnFe (0.15) were approximately 0.80, 0.82 and 0.83, respectively, indicating that the increasing content of Mn increased the content of Fe²⁺, which required higher reduction temperature than Fe³⁺.

As shown in Fig. 5b, two main peaks due to Mn 2p_{3/2} and Mn 2p_{1/2} can be observed from 642.5 eV to 653.9 eV. By performing a peak-fitting deconvolution, the Mn 2p_{3/2} spectra were separated into three peaks, Mn³⁺ (641.5 – 641.8 eV), Mn⁴⁺ (642.7 – 643.1 eV) and Mn nitrate (644.8 – 645.2 eV).³⁹ It could be clearly seen that the intensities of Mn⁴⁺ characteristic peaks increased with the addition of Mn, accompanied with a decrease of Mn³⁺ peaks. The ratios of Mn⁴⁺/Mn³⁺ on the surface of MnFe (0.05) and MnFe (0.15) were approximately 1.2 and 2.5, respectively. Furthermore, the surface atom concentrations of Mn, Fe, and O and the atomic

ratios of Mn/Fe were summarized in Table 2, the percent of O_{\square} on MnFe (0.15) fibers increased obviously with the increased Mn content, which were sure to increase the activity for NO oxidation to NO_2 and thereby enhance the “fast SCR” reaction activity ($4NH_3 + 2NO + 2NO_2 \rightarrow 4N_2 + 6H_2O$).⁴⁰ The O1s spectrum in Fig. 5c could be decomposed into two peaks, corresponding to various oxygen containing chemical bonds. According to the previous literature, the sub-bands at lower binding energy (530.0–530.4 eV) corresponded to the lattice oxygen (denoted as O_{β}), and the sub-bands at higher binding energy (532.2–532.5 eV) corresponded to the surface adsorbed oxygen (denoted as O_{α}), such as O_2^{2-} or O^- belonging to defect oxide or hydroxyl-like group.^{22,41} As listed in Table 2, with the increasing of Mn doping, the chemisorbed oxygen O_{α} content was gradually increased, the ratios of $O_{\alpha}/(O_{\alpha}+O_{\beta})$ over Fe_2O_3 , MnFe (0.05) and MnFe (0.15) nanofiber were 18.4 %, 27.0% and 37.5%, respectively. It may be related to the presence of the Mn^{3+} species could create a charge imbalance, vacancies, and unsaturated chemical bonds on the catalyst surface, which would lead to the increase of oxide defects or hydroxyl-like groups. As we all know, surface chemisorbed oxygen was thought as the most active oxygen and played an important role in oxidation reactions. This meant that the MnFe (0.15) nanofibers might have better activity for the oxidation of NO to NO_2 than pure Fe_2O_3 in the NH_3 -SCR process.

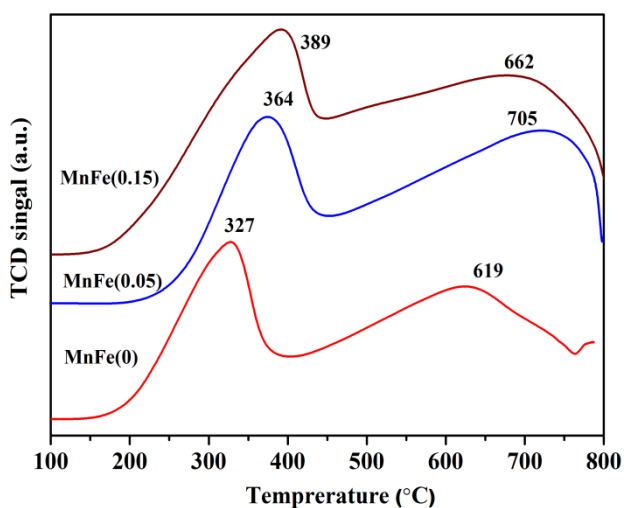


Fig. 4. H_2 -TPR profiles of MnFe hollow nanofibers.

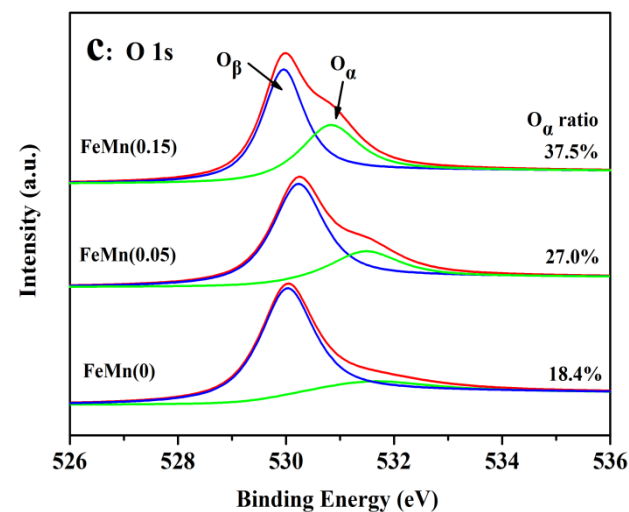
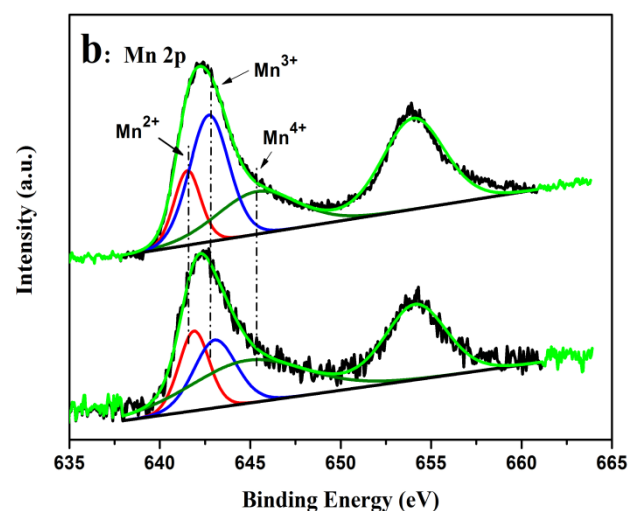
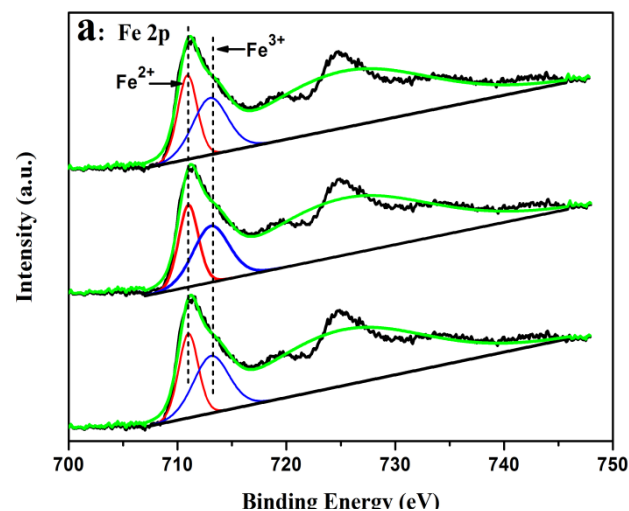


Fig. 5. (a) Fe 2p, (b) Mn 2p and (c) O1s from XPS spectra of MnFe nanofiber.

Table 2. XPS Results of Various Catalysts

Hollow fibers	Surface Atomic Concentration (%)				
	Fe	Mn	O _a	O _β	O _{total}
Fe ₂ O ₃	29.3	0	13.01	57.69	70.7
MnFe (0.05)	24.41	2.48	19.74	53.37	73.11
MnFe (0.15)	17.95	6.47	28.34	47.74	75.58

3.3 Low-temperature catalytic performance

The NO_x conversions, N₂ selectivities, and N₂O formations of the Mn-Fe catalysts with different molar ratios of Fe/Mn were shown in Fig. 6. Experimental results showed that there was only 38-80% NO_x conversion when pure Fe₂O₃ was used as SCR catalyst at 100-300 °C, the addition of Mn content could significantly increase NO_x conversion below 250 °C. It was found that the NO_x conversion was greatly improved from 38 to 100% with an increase of Mn/ Fe molar ratio from 0 to 0.2 at 150 °C, the N₂ selectivity decreased with an increase of Mn/ Fe molar ratio (as shown in Fig. 6b). For the MnFe (0.15) catalyst, the NO_x conversion was approximately 100% at 150 °C, and the amount of N₂O formed was below 20 ppm at 150 °C, indicating its promising N₂ selectivity.

The influences of 200 ppm SO₂ and 8 vol% H₂O on the performance of the MnFe (0.15) catalyst were investigated at 150 °C and the results were illustrated in Fig. 6c. It could be seen that a slight NO conversion decline occurred during 200 ppm SO₂ was added and then became stable, after removing SO₂ the conversion recovered to 92%. When 8 vol% H₂O was introduced into the stream, the NO conversion declined and kept at about 96%, after stopping H₂O the conversion restored to 99%. When the 200 ppm SO₂ and 8 vol% H₂O were injected into the feed gases at the same time, NO conversion decreased a little more, but the NO conversion still maintained at about 82%. The above results suggested that the catalyst had certain SO₂/H₂O durability.

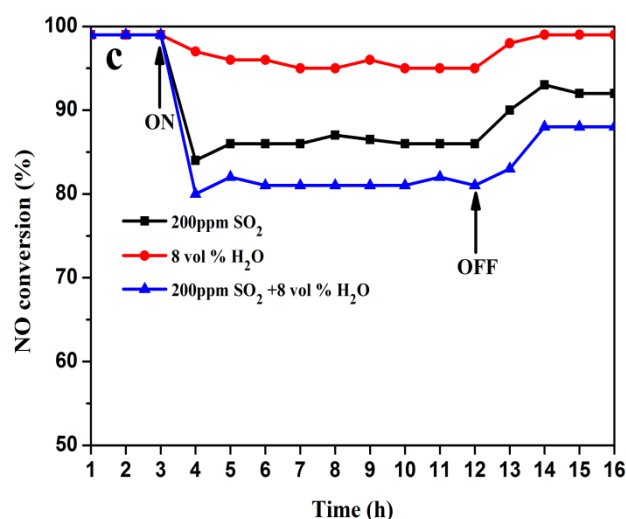
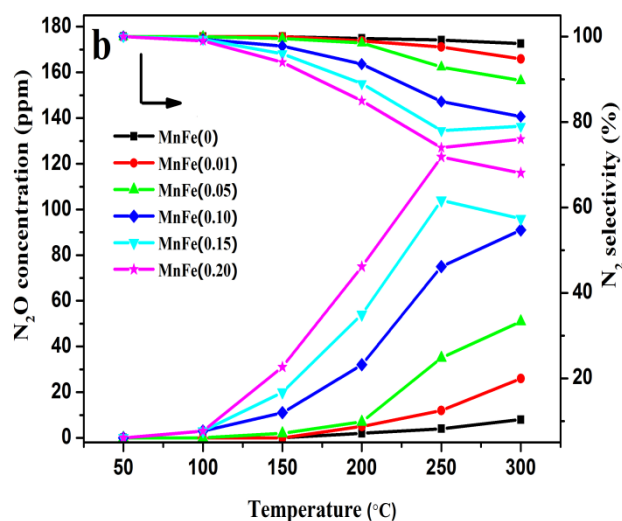
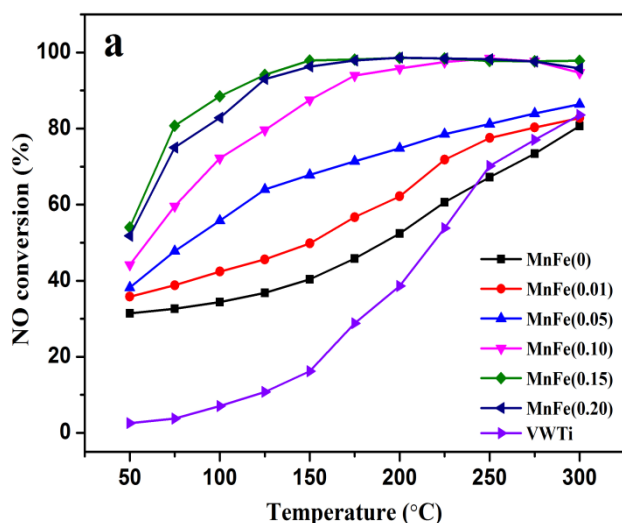


Fig. 6 (a) NO_x conversion using MnFe (x) hollow fibrous catalyst and VWTi catalyst; (b) N₂ selectivity and N₂O concentration in the SCR reaction; (c) Influence of H₂O and SO₂ on NO conversion in the SCR reaction over MnFe (0.15) catalyst at 150 °C. Reaction conditions: [NO] = 500 ppm, [NH₃] = 500 ppm, [SO₂] = 200 ppm, [H₂O] = 8%, [O₂] = 5%, GHSV = 50,000 h⁻¹.

3.4 In situ FT-IR analysis

To investigate detailed reaction mechanism, the in situ DRIFTS experiment of reaction between NH₃ and pre-adsorbed NO + O₂ species at 150 °C was carried out and the results are shown in Fig. 7. In this experiment, the hollow nanofibers was first treated with NO+O₂ /Ar for 1 h and then purged with Ar for 30 min. When NH₃ was introduced at 150 °C, the DRIFT spectra could be recorded as a function of time (Fig. 7a). After NH₃ passed over the NO + O₂ pretreated catalyst, the band at 1610 cm⁻¹ due to NO₂⁴¹ decreased and after 1min, the bidentate nitrate species (1580 cm⁻¹)³⁰ on manganese oxides gradually disappear. After NH₃ was introduced for 10min, the band at 1580cm⁻¹ disappeared, indicating that bidentate nitrate had participated in the reaction process, the band at 1550 cm⁻¹ appeared, which could be assigned

to the intermediate of oxidation of ammonia.^{42,43} As already noted, the intensity of the band at 1240 cm^{-1} due to bridged nitrate increases obviously, and its position shifted to 1260 cm^{-1} , which could be ascribed to the deformation nitrate species.⁴⁴ Meanwhile, the IR bands attributed to coordinated NH_3 (1260 and 1602 cm^{-1}) on the Lewis acid sites, ionic NH_4^+ (1440 cm^{-1}) on Brønsted-acid sites appeared, and the bands in the region of 3700-3000 cm^{-1} attributed to N-H stretching vibration could also be observed.⁴⁵ After the catalyst was purged with NH_3 for 10 min, both adsorbed NH_3 and NO_x species could be observed on the catalyst surface. These results indicated that only the reaction between NO_2 and ammonia had occurred, not others. Furthermore, the coexistence of ammonia and nitrate adspecies showed that NH_3 and NO_x could be adsorbed over different active sites of catalyst surface.

In this experiment, the reactants were introduced to the $\text{MnFe}(0.15)$ catalyst in the reversed order (as shown in Fig. 7b). After the $\text{MnFe}(0.15)$ catalyst was first purged with NH_3 for 30 min, the catalyst surface was mainly covered by coordinated NH_3 (1207, 1230, 1440, 1602 and 1640 cm^{-1}).⁴⁵ When $\text{NO} + \text{O}_2$ was introduced for 2 min, the bands due to adsorbed NH_3 species decrease slightly and totally disappear after 10 min. At the same time, the nitrate species begin to form on the catalyst surface. However, bands at 1560 cm^{-1} increased a bit, which could also prove oxidation of ammonia such as nitrate or nitrite.⁴¹ After the catalyst was purged with $\text{NO} + \text{O}_2$ for 20 min, the catalyst surface was mainly covered by monodentate nitrate (1365 cm^{-1} and 1560 cm^{-1}).^{30,46} On the basis of the above results, it can be concluded that coordinate NH_3 played important roles in reducing NO_x in SCR reaction.

In general, when the SCR reaction happened at 150 $^\circ\text{C}$, both adsorbed NH_3 and NO_x species were considered to be involved in the SCR reaction. Besides, the coordinated NH_3 as well as in situ formed NO_2 species were considered to be involved in the NH_3 -SCR reaction following an L-H mechanism.^{47,48}

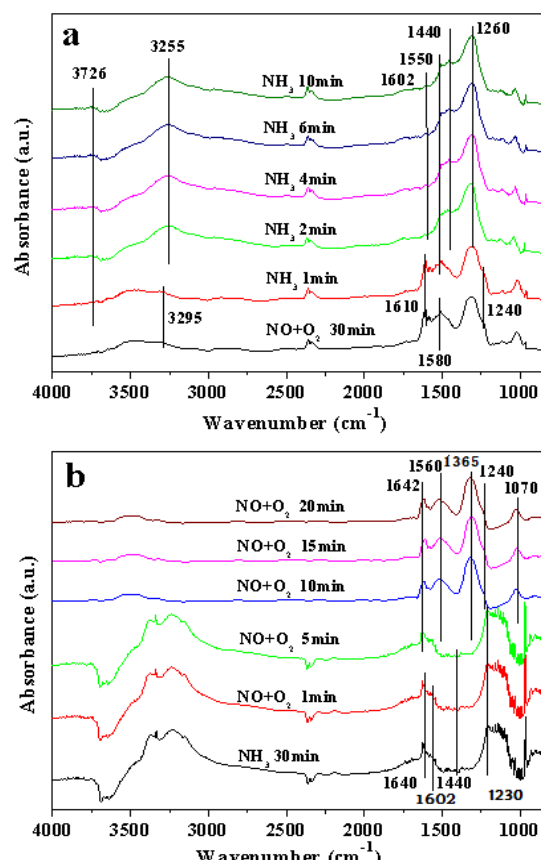


Fig. 7. In situ DRIFT spectra of $\text{MnFe}(0.15)$ catalyst for the reaction between (a) NH_3 and adsorbed NO_x at 150 $^\circ\text{C}$, (b) $\text{NO} + \text{O}_2$ and adsorbed NH_3 species at 150 $^\circ\text{C}$.

40 Conclusions

In this paper, hollow MnFe nanofibers with different Mn doping content were prepared by the electrospinning method, which were highly active for the low temperature selective catalytic reduction (SCR) of NO with NH_3 . The $\text{MnFe}(0.15)$ hollow fibers showed the highest activity and 100% NO_x conversion at 150 $^\circ\text{C}$ with a space velocity of 50,000 h^{-1} . In addition, the large BET surface areas present in the catalyst also contributed to facilitate the SCR reaction. Based on in situ DFTIR analysis, more surface acidity, the formation of the intermediate, and the better low temperature reducibility properties, would be the main reasons for the high low-temperature catalytic activity.

Acknowledgements

The authors gratefully acknowledge the financial support of national natural foundation of china (21377061), Asia Research Center in Nankai University (AS1326), Natural Science Foundation of Tianjin (12JCQNJC05800), Key Technologies R&D Program of Tianjin (13ZCZDSF00300) and the assistance of Dr. Raymond Seekell (University of Notre Dame) in manuscript preparation and discussion.

Notes and references

^a College of Environmental Science and Engineering, Key Laboratory of Environmental Pollution Process and Environmental Criteria, Nankai

- University, Tianjin 300071, P. R. China; E-mail: sihuizhan@nankai.edu.cn or jkcs66902@163.com, Tel/Fax: +86-22-23502756.
- ^b Department of Chemistry, Tianjin University, Tianjin 300072, P. R. China, E-mail: liyi@tju.edu.cn
- 1 K. Mathisen, D.G. Nicholson and A.N. Fitch, *J. Mater. Chem.*, 2005, **1**, 204-217.
- 2 R. M. Tost, J.S. Gonzalez and P. M. Torres, *J. Mater. Chem.*, 2002, **11**, 3331-3336.
- 3 Z.B. Wu, B.Q. Jiang, Y. Liu, W.R. Zhao and B.H. Guan, *J. Hazard. Mater.*, 2007, **145**, 488-494.
- 4 C.C. Zhou, Y.P. Zhang, X.L. Wang, H.T. Xu, K.Q. Sun and K. Shen, *J. Colloid. Interface. Sci.*, 2013, **392**, 319-324.
- 5 E. James, II. Parks, *Science*, 2010, **26**, 1584-1585.
- 6 X.Y. Shi, F.D. Liu, L.J. Xie, W.P. Shan and H. He, *Environ. Sci. Technol.*, 2013, **47**, 3293-3298.
- 7 Y. Li, J.H. Peng, X. Huang, X. Li, W.K. Su, X.X. Sun, D.Z. Wang and J.M. Hao, *Environ. Sci. Technol.*, 2014, **48**, 4515-4520.
- 8 Q. Li, H.S. Yang, F.M. Qiu and X.B. Zhang, *J. Hazard. Mater.*, 2011, **192**, 915-921.
- 9 J. Li, H. Chang, L. Ma, J. Hao and R.T. Yang, *Catal. Today*, 2011, **175**, 147-156.
- 10 M.S. Maqbool, A.K. Pullura and H. P. Ha, *Appl. Catal. B.*, 2014, **152-153**, 28-37.
- 11 Y. Peng, J. Li, W. Shi, J. Xu and J. Hao, *Environ. Sci. Technol.*, 2012, **46**, 12623-12629.
- 12 R.H. Gao, D.S. Zhang, X.G. Liu and L.Y. Shi, *Catal. Sci. Technol.*, 2013, **1**, 191-199.
- 13 F.D. Liu, H. He, C.B. Zhang, W.P. Shan and X.Y. Shi, *Catal. Today*, 2011, **175**, 18-25.
- 14 L. Chen, J.H. L and M.F. Ge, *Chem. Engineer. J.*, 2011, **170**, 531-537.
- 15 J. Chen, M. Shen, X. Wang, G. Qi, J. Wang, W. Li., *Appl. Catal.*, 2013, **134-135**, 251-257.
- 16 P. Fabrizioli, T. Burgi and A. Baiker, *J. Catal.*, 2002, **206**, 143-154.
- 17 M.A. Larrubia, G. Ramis and G. Busca, *Appl. Catal. B: Environ.*, 2001, **30**, 101-110.
- 18 Y.J. Kim, H.J. Kwon, I.S. Nama, J.W. Choung, J.K. Kil, H.J. Kim, M.S. Cha and G.K. Yeo, *Catal. Today*, 2010, **151**, 244-250.
- 19 S. Roy, B. Viswanath, M.S. Hegde and G. Madras, *J. Phys. Chem. C.*, 2008, **112**, 6002-6012.
- 20 Z.L. Liu, Y. Yi, S.X. Zhang, T.L. Zhu, J.Z. Zhu and J.G. Wang, *Catal. Today*, 2013, **216**, 76-81.
- 21 W. Tian, H. Yang, X. Fan and X. Zhang, *J. Hazard. Mater.*, 2011, **188**, 105-109.
- 22 Z. Chen, F. Wang, H. Li, Q. Yang, L. Wang and X. Li, *Ind. Engin. Chem. Res.*, 2012, **51**, 202-212.
- 23 H. Li, D. Zhang, P. Maitarad, L. Shi, R. Gao, J. Zhang and W. Cao, *Chem. Commun.*, 2012, **48**, 10645-10647.
- 24 J. Shan, Y. Zhu, S. Zhang, T. Zhu, S. Rouvimov and F. Tao, *J. Phys. Chem. C.*, 2013, **117**, 8329-8335.
- 25 S. Yang, J. Li, C. Wang, J. Chen, L. Ma, H. Chang, L. Chen, Y. Peng and N. Yan, *Appl. Catal. B: Environ.*, 2012, **117-118**, 73-80.
- 26 H.Q. He, J. Yin, Y.X. Li, Y. Zhang, H.S. Qiu and J.B. Xu, *Appl. Catal. B: Environ.*, 2014, **156-157**, 35-43.
- 27 S. Kim, S.K. Lim, *Appl. Catal. B: Environ.*, 2008, **84**, 16-20.
- 28 C. Wessel, R. Ostermann, R. Dersch and B.M. Smarsly, *J. Phys. Chem. C.*, 2011, **115**, 362-372.
- 29 D. Ma, Y.J. Xin, M.C. Gao and J. Wu, *Appl. Catal. B: Environ.*, 2014, **147**, 49-57.
- 30 S.J. Yang, C.Z. Wang, J.H. Li, N.Q. Yan, L. Ma and H.Z. Chang, *Appl. Catal. B: Environ.*, 2011, **110**, 71-80.
- 31 X.C. Li, V.T. John, J.J. Zhan, G.H. He, J.B. He and L. Spinu, *Langmuir*, 2011, **27**, 6252-6259.
- 32 Y. Wan, W. Zhao, Y. Tang, L. Li, H. Wang, Y. Cui, J. Gu, Y. Li and J. Shi, *Appl. Catal. B: Environ.*, 2014, **148-149**, 114-122.
- 33 C.R. Gong, D.R. Chen, X.L. Jiao and Q.L. Wang, *J. Mater. Chem.*, 2002, **12**, 1844-1847.
- 34 S.H. Zhan, J.Y. Yang, Y. Liu, N. Wang, J.J. Dai, H.B. Yu, X.C. Gao and Y. Li, *J. Colloid. Interface. Sci.*, 2011, **355**, 328-333.
- 35 G. Giecko, T. Borowiecki, W. Gac and J. Kruk, *Catal. Today*, 2008, **137**, 403-409.
- 36 M.R. Morales, B.P. Barbero and L.E. Cadus, *Appl. Catal. B: Environ.*, 2007, **74**, 1-10.
- 37 C. Wang, S. Yang, H. Chang, Y. Peng and J. Li, *J. Mol. Catal. A: Chem.*, 2013, **376**, 13-21.
- 38 B. Thirupathi, P.G. Smirniotis, *J. Catal.*, 2012, **288**, 74-83.
- 39 D.A. Peña, B.S. Uphade and P.G. Smirniotis, *J. Catal.*, 2004, **221**, 421-431.
- 40 Y.J. Kim, H.J. Kwon, I. Heo, I.S. Nam, B.K. Cho, J.W. Choung, M.S. Cha and G.K. Yeo, *Appl. Catal. B.*, 2012, **126**, 9-21.
- 41 Y. Shu, H. Sun, X. Quan and S. Chen, *J. Phys. Chem. C.*, 2012, **116**, 25319-25327.
- 42 L. Chen, J. Li and M. Ge., *Environ. Sci. Technol.* 2010, **44**, 9590-9596.
- 43 Y. Shu, H. Sun, X. Quan and S. Chen., *J. Phys. Chem. C.*, 2012, **116**, 25319-25327.
- 44 M. Casapu, O. Krocher, M. Mehring, M. Nachtegaal, C. Borca, M. Harfouche and D. Grolimund, *J. Phys. Chem. C.*, 2010, **114**, 9791-9801.
- 45 G. Ramis, M.A. Larrubia, *J. Mol. Catal. A.* 2004, **215**, 161-167.
- 46 A. Karami, V. Salehi, *J. Catal.*, 2012, **292**, 32-43.
- 47 H.J. Chae, S.T. Choo, H. Choi and I.S. Nam, *Ind. Eng. Chem. Res.*, 2000, **39**, 1159-1170.
- 48 A. Shi, X. Wang, T. Yua and M. Shen. *Appl. Catal.*, 2011, **106**, 359-369.

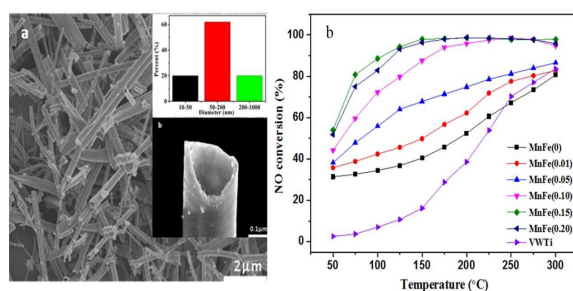
Table of Contents

Facile preparation of MnO₂ doped Fe₂O₃ hollow nanofibers for low temperature SCR of NO with NH₃

Sihui Zhan,^{*a} Mingying Qiu, ^{*a} Shanshan Yang^a, Dandan Zhu,^a Hongbing Yu^a and Yi Li^{*b}

^a College of Environmental Science and Engineering, Key Laboratory of Environmental Pollution Process and Environmental Criteria, Nankai University, Tianjin 300071, P. R. China; E-mail: sihui-zhan@nankai.edu.cn, Tel/Fax: +86-22-23502756.

^b Department of Chemistry, Tianjin University, Tianjin 300072, P. R. China, E-mail: liy@tju.edu.cn



MnO₂ doped Fe₂O₃ hollow nanofibers were successfully synthesized by electrospinning method, which exhibit superior catalytic activity for low temperature NH₃-SCR.