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Binary Mn-FeOx nanoflakes supported on CNT by an one-step redox method for low temperature NO reduction with NH3

Yanbing Zhang, Yingzan Chen, Jinhe Huang, Chengjian Song, Xianglong Cheng, Haibo Ren and Xie Wang

1 College of Materials and Chemical Engineering, Henan University of Urban Construction, Pingdingshan 467000, People’s Republic of China
2 College of Chemistry and Chemical Engineering, Anqing Normal University, Anqing 246011, People’s Republic of China

E-mail: zyb481428@163.com (Y Zhang), 602989941@qq.com and anhuiss@sina.com

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Abstract

Binary Mn–FeOx/CNT-OSR catalysts were prepared by an one-step redox method, and showed 44%–83.7% NO conversion at 80 °C–180 °C. The catalytic activity of the 0.06 Mn–FeOx/CNT-OSR catalyst is optimum and reaches 65.9%–83.7% at 80 °C–180 °C, resulting from the generation of high valence of MnO2 and Fe2O3 with weak crystallinity.

1. Introduction

The emission of nitrogen oxides (NOx) from the stationary sources automotive exhaust gases has aroused a series of environmental issues including ozone deplete, greenhouse effect, photochemical smog, and acid rain [1, 2]. Give this, many technologies have been adopted to decompose the NOx. Note that selective catalytic reduction of NO with NH3 (SCR), as a mature denitration technology, has been used in practical application due to its excellent comprehensive properties [3, 4]. Nevertheless, the V2O5-WO3/MoO3/TiO2 catalyst, as the core of SCR technology, still has some disadvantages such as the toxicity of V-based and high working temperature window (300 °C–400 °C) [5, 6]. Thus, how to resolve the above questions of commercial V-base catalyst is important.

In light of the environmental friendliness and outstanding low temperature SCR activity, Manganese oxides (MnO2) and iron oxides (Fe2O3) have been roused great concern in low temperature NO reduction with NH3 [6, 7]. Zhang et al fabricated the Fe-doped manganese oxide octahedral molecular sieve (OMS-2), and the Fe-OMS-2 catalyst displays outstanding low temperature catalytic activity and alkali tolerance [8]. Ren et al found that the introduce of Fe could increase the relative ratios of Mn4+/Mn3+ and the amount of surface active sites, and thus, improved the SCR activity [9]. It is noteworthy that the above single MnO2 and binary Mn–Fe catalysts are possessed of admirable denitration activity, but the preparation methods generally involve the high temperature calcination treatment or the high pressure hydrothermal procedure. Hence, the development of a mild one-step redox method is key for the fabrication of binary Mn–Fe catalyst with excellent low temperature SCR activity.

In view of an unique one-dimension tubular structure, electronic transmission, physical and chemical performances, Carbon nanotubes (CNT), as the catalytic supports, have been applied in low temperature NO reduction with NH3 [7, 10]. Wu et al investigated the properties of CuAl-LDO/CNT (LDO, layered double oxide) catalysts, and found that the NO conversion and N2 selectivity of the catalyst surpass 80% and 90% within 180 °C–300 °C, respectively [10]. Li et al prepared a series of Fe/Mel@ZSM-5 by an induced growth method, and the catalysts presents excellent denitration activity and N2 selective at 300 °C because of the high dispersion of iron nanoparticles [6]. It should be note that though the above catalysts possess admirable denitration activity, the working temperature window is between 180 °C and 300 °C, which will inhibit their application in plants of steel, cement, glass and other industries where the flue gas temperature is usually at 100 °C–200 °C [11, 12].

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Therefore, the SCR catalyst with excellent catalytic activity below 200 °C should be developed to meet the needs of various application fields.

1.1. XRD patterns
XRD was applied to analyse the crystalline state. Noticeably, the characteristic diffraction peaks were seen at 26.2°, 43.0°, 53.7°, and 77.8°, respectively, which were ascribed to the graphite peaks [13]. With the addition of MnOx and FeOx active components, the weak diffraction peak attributing to MnO2 was found in the Mn-FeOx/CNT-OSR catalysts prepared by the one-step redox method, meaning the generation of the weakly crystalline MnO2 active components. It is known that high valence state and weakly crystalline state of MnO2 are normally favor for the low temperature SCR activity [14]. It is notable that the typical diffraction peaks corresponding to the FeOx was not be detected by XRD, which might be the formation of weakly crystalline and amorphous FeOx. Usually, weak crystalline and amorphous active component is conducive to the low temperature denitrification activity [15].

As for the Mn-FeOx/CNT-TIM catalyst, a series of diffraction peaks due to the Mn3O4 were detected in figure 1-(7), indicating the formation of Mn3O4. The crystalline property of Mn3O4 over the Mn-FeOx/CNT-TIM catalyst is better than that of MnO2 over the Mn-FeOx/CNT-OSR catalysts. To our knowledge, the low temperature SCR activity of Mn3O4 with high crystallinity and low valence state is weaker than that of MnO2 with weakly crystallinity and high valence state [16]. Plus, the diffraction peaks intensities due to the graphite peaks were declined gradually with the introduction of active components, suggesting the presence of interaction between the CNT and the active components [5, 17].

1.2. TEM and HRTEM images
The micromorphology of the 0.06 Mn-FeOx/CNT-OSR and the Mn-FeOx/CNT-TIM catalysts were studied by TEM and HR-TEM. Based on figure 2(a), highly dispersed nanosheets were seen from the 0.06 Mn-FeOx/CNT-OSR catalyst, meaning that the active components have been successfully supported on the surface of the CNT. In light of the HR-TEM image (figure 2(b)), a series of nanoflakes were found on the surface of the CNTs, further proving the formation of the Mn-FeOx/CNT-OSR catalyst. It is worth noting that the above results are relevant to the conclusions of XRD. Additionally, the apparent lattice fringe attributing to the MnOx and FeOx was not be detected from figure 2(b), demonstrating the generation of the weakly crystalline active components, which is connected with the results of XRD. Again, it is apparent that the elements signals of the Mn and Fe were found in EDX spectrum (figure 2(d)), further proving the formation of the Mn-FeOx/CNT-OSR catalyst, which is also in connection with the conclusion of XRD and FESEM (ESI, figure S1 (available online at stacks.iop.org/MRX/8/055004/mmedia)).

For the Mn-FeOx/CNT-TIM catalyst (figure 2(c)), some nanoparticles ascribing to active components were found on the surface of the CNT. Note that a part of nanoparticles are agglomerate, which is generally bad for the...
catalytic activity. As for HR-TEM image, a lattice fringe of 0.248 nm corresponding to the crystal face of (211) of Mn$_3$O$_4$ is obviously detected in the Mn-FeO$_x$/CNT-TIM catalyst, which is in accordance with the result of XRD. The above result presents that the high crystallinity and low valence state of Mn$_3$O$_4$ were formed in the Mn-FeO$_x$/CNT-TIM catalyst, which are normally bad for the SCR activity compared to the low crystallinity and high valence state of MnO$_2$.

1.3. HAADF-STEM images

HAADF-STEM was further used to investigate the micromorphology of the 0.06 Mn-FeO$_x$/CNT-OSR catalyst. It is clear from figure 3 that a series of bright spots corresponding to the heavy element signal could be seen on the surface of the CNT, demonstrating that the 0.06 Mn-FeO$_x$/CNT-OSR catalyst have been successfully prepared via the one-step redox method. Again, EDX mappings present that the signals of Mn, Fe, O, and C were well dispersed with a series of cylindrical distribution, indicating the existence of the Mn, Fe, O, and C elements on the CNT. The above conclusions are all relevant to the results of XRD and TEM/HR-TEM.

1.4. XPS analysis

XPS was applied to analyse the relative contents and the oxidation state of elements near the surface of the resultant catalysts. For the full XPS spectrum (figure 4(A)), the signals of the Fe, Mn, O, and C elements were discovered in the 0.06 Mn-FeO$_x$/CNT-OSR catalyst, proving the existence of the Fe, Mn, O, and C elements, which is in line with the conclusions of the FESEM (ESI, figure S1) and TEM/HR-TEM. As for Mn 2p spectrum (figure 4(B)), two typical peaks were seen at 653.8 eV and 642.2 eV, attributing to the Mn 2p$_{1/2}$ and Mn 2p$_{3/2}$, respectively, demonstrating the formation of the MnO$_2$ in the 0.06 Mn-FeO$_x$/CNT-OSR catalyst [18]. In addition, the energy gap of 11.6 eV between Mn 2p$_{1/2}$ and Mn 2p$_{3/2}$ further indicates the presence of the MnO$_2$.

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Figure 2. TEM and HR-TEM images: (a) and (b) 0.06 Mn-FeO$_x$/CNT-OSR catalyst; (c) and (d) Mn-FeO$_x$/CNT-TIM catalyst; as well as (e) EDX spectrum of the 0.06 Mn-FeO$_x$/CNT-OSR catalyst from the red circle region of figure 3(b).
which is in agreement with the conclusion of XRD. It should be specified that the MnO₂ is normally possessed of the first-rate low temperature SCR activity among all the manganese oxides, which is conducive to the SCR activity [14, 19].

Based on the Fe 2p spectrum of the 0.06 Mn-FeOₓ/CNT-OSR catalyst (figures 4(C)–(e)), apparently, two typical peaks along with a satellite at 718.8 eV could be seen at 724.6 eV and 710.7 eV ascribing to the Fe 2p 3/2 and the Fe 2p 1/2, respectively, indicating the formation of the Fe₂O₃ in the 0.06 Mn-FeOₓ/CNT-OSR catalyst [20, 21]. Plus, the energy separation of 13.9 eV is presence between the Fe 2p 3/2 and the Fe 2p 1/2, further revealing the generation of the Fe₂O₃ in the 0.06 Mn-FeOₓ/CNT-OSR catalyst [22]. On basis of the Fe 2p spectrum of the Mn-FeOₓ/CNT-TIM catalysts (figures 4(C)–(f)), two representative peaks corresponding to the Fe 2p 3/2 and the Fe 2p 1/2 could be found, whereas the satellite peak could not be detected, denoting the generation of the Fe₂O₃ in the Mn-FeOₓ/CNT-TIM catalyst [23, 24]. It should be pointed out that the SCR activity of the Fe₂O₃ is generally better than that of the Fe₃O₄ [25].
As shown in figure 4(D), the O 1 s spectra were separated into two peaks performed peak-fitting deconvolutions. Among them, the peaks located at around 531.4 eV were attributed to the surface oxygen (denoted as O\(_{α}\)), and the peaks at 529.8 eV were ascribed to the lattice oxygen (labeled as O\(_{β}\)) [8, 26]. By the calculation, the relative content of the surface oxygen in the 0.06 Mn-FeO\(_x\)/CNT-OSR catalyst (52.0%) is higher than that over the Mn-FeO\(_x\)/CNT-TIM catalyst (41.7%). It should be mentioned that the surface oxygen is generally more active than lattice oxygen due to its high reactivity [9, 27].

1.5. NO conversion

Figure 5 shows the NO conversion as a function of the temperature for the two catalysts. Clearly, the NO conversion of the two catalysts was raised with the increase of the temperature between 80 °C–180 °C. For the Mn-FeO\(_x\)/CNT-OSR catalysts, the catalysts possess admirable low temperature SCR activity, and the NO conversion reaches 44.0%–83.7% at 80 °C–180 °C. It is notable that the 0.06 Mn-FeO\(_x\)/CNT-OSR catalyst exhibits the optimum catalytic activity among all the catalysts, and the NO conversion attains 65.9%–83.7% at 80 °C–180 °C. Regarding the Mn-FeO\(_x\)/CNT-TIM catalyst, it only presents 39.1%–55.9% NO conversion at 80 °C–180 °C, which is lower than that of the 0.06 Mn-FeO\(_x\)/CNT-OSR catalyst. The above results indicated that the one-step redox method is helpful for the preparation of outstanding low temperature SCR catalyst compared to the traditional impregnation method. Again, the 0.06 Mn-FeO\(_x\)/CNT-OSR catalyst possesses higher BET surface, which is usually conducive to the catalytic activity (ESI, table S1). In light of the pore diameter distribution (ESI, figure S2), it is clear that the 0.06 Mn-FeO\(_x\)/CNT-OSR catalyst presents mesoporous structure. Plus, the 0.06 Mn-FeO\(_x\)/CNT-OSR catalyst displays excellent cyclic and long period properties (ESI, figure S3), which are due to its outstanding structural performance (ESI, figure S4 and figure S5).

To sum up, Mn-FeO\(_x\)/CNT-OSR catalysts with outstanding low temperature denitration activity were prepared via the one-step redox method. The NO conversion of the as-synthesized catalysts attains 44%–83.7% between 80 °C and 180 °C. the 0.06 Mn-FeO\(_x\)/CNT-OSR catalyst exhibits the optimal denitration activity at 80 °C–180 °C (65.9%–83.7%), which might be due to the formation of high valence state and weak crystallinity of MnO\(_2\), Fe\(_2\)O\(_3\), as well as high BET surface of the catalyst.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).
ORCID iDs

Yanbing Zhang  https://orcid.org/0000-0003-3756-4830

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