Manganese oxide nanorod catalysts for low-temperature selective catalytic reduction of NO with NH₃

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MnOₓ nanorod catalysts were successfully synthesized by two different preparation methods using porous SiO₂ nanorods as the template and investigated for the low-temperature selective catalytic reduction (SCR) of NO with NH₃. The catalysts were characterized by scanning electron microscopy, transmission electron microscopy, nitrogen adsorption, X-ray diffraction, X-ray photoelectron spectroscopy, and NH₃ temperature-programmed desorption. The results show that the obtained MnOₓ-P nanorod catalyst prepared by redox precipitation method exhibits higher NO removal activity than that prepared by the solvent evaporation method in the low temperature range of 100–180 °C, where about 98% NO conversion is achieved over MnOₓ(0.36)-P nanorods. The reason is mainly attributed to MnOₓ(0.36)-P nanorods possessing unique flower-like morphology and mesoporous structures with high pore volume, which facilitates the exposure of more active sites of MnOₓ and the adsorption of reactant gas molecules. Furthermore, there is a lower crystallinity of MnOₓ, higher percentage of Mn⁴⁺ species and a large amount of strong acid sites on the surface. These factors contribute to the excellent low-temperature SCR activity of MnOₓ(0.36)-P nanorods.

1. Introduction

Nitrogen oxides (NOₓ) are considered to be one of the main air pollutants, which can cause great harm to the ecological environment and human health. Therefore, it is urgent to control the emissions of NOₓ. The selective catalytic reduction (SCR) of NO with NH₃ has been proven to be the most effective technology for the removal of NOₓ. Commercial SCR catalysts, V₂O₅–WO₃/TiO₂ and V₂O₅–MoO₃/TiO₂ catalysts have shown high activity of NO removal, and these catalysts must be used in the temperature range of 350–450 °C.¹,² To satisfy the high operating temperature, the SCR unit needs to be placed upstream of the electrostatic precipitator and desulfurization devices, resulting in the deactivation of catalysts because of high concentration of dust and SO₂ in the flue gases. In order to overcome the disadvantages of these V₂O₅/TiO₂ based catalysts, researchers have paid much attention to developing efficient low-temperature SCR catalysts, which can be placed downstream of the desulfurizer and electrostatic precipitators without the need for reheating of flue gases.³–⁵

Various transition metal oxide catalysts have been found to be active in the NH₃-SCR reaction. Among them, manganese oxide (MnOₓ) catalysts exhibit excellent low temperature-SCR activities due to their variable valence states and high redox properties.⁶–⁷ In addition, it has been demonstrated that the specific surface area and crystallinity of MnOₓ have also great influence on their SCR activities.⁸ Furthermore, it has been reported that the morphologies of the catalysts significantly influence their properties and catalytic performance.⁹–¹¹ Recently, mesoporous materials have attracted extensive attention owing to their large specific surface area, highly ordered mesoporous structure, which are advantageous to the generation of abundant active sites and mass transport of gas molecules. In particular, mesoporous metal oxides combine the advantages of both metal oxides and mesoporous structure in comparison with nanoparticles, which have found applications in various fields, such as electrode materials, gas sensors and adsorption, catalysis, etc.¹²–¹⁴ For instance, Gao et al.¹⁵ reported a three-dimensional (3D) mesoporous MnO₂ prepared using KIT-6 as a template, which showed much higher SCR activity than mesoporous MnO₂ templated from SBA-15 or MCM-41, maintaining NO conversion of 100% in the temperature range of 75–275 °C, because of the special 3D mesostructure. Tian et al.¹⁶ studied MnO₂ nanorods exhibited higher NO conversion than MnO₂ nanotubes and nanoparticles, and found that the higher SCR activity of MnO₂ nanorods may be mainly attributed to lower crystallinity, more lattice oxygen, higher reducibility, and more amount of strong acid sites. Therefore, controlled synthesis of MnO₂ catalysts with different morphologies is very effective way to improve their SCR activities. However, there are still many challenges.
In this work, we synthesized a series of MnO₂ nanorods catalysts using porous SiO₂ nanorods as template through two different preparation methods. The activities of these MnO₂ nanorods catalysts for SCR of NO at low temperatures were evaluated. The effect of Mn loading on SCR activities of MnO₂ nanorods catalysts at different temperatures were also investigated. The catalysts were characterized to understand the structure and morphologies of MnO₂ nanorods catalysts as well as their relationship with catalytic activity. The results are of importance for better understanding of low temperature SCR reaction on nanostructured MnO₂ catalysts and beneficial to promote the development of NO removal technology from flue gases.

2. Experimental

2.1 Catalyst preparation

All the chemical reagents used were analytical grade. MnO₂ nanorods catalysts were prepared by two-step process. Firstly, the porous SiO₂ nanorods template was synthesized according to the previously reported procedure. Secondly, MnO₂ nanorods catalysts were prepared by two different methods using the porous SiO₂ nanorods as template. Detailed preparation methods were the following:

2.1.1 Redox precipitation method (P). A series of MnO₂ nanorods catalysts were synthesized by the redox precipitation method using KMnO₄ as oxidant and manganese acetate as reductant, respectively. In a typical synthesis, a certain amount of the as-synthesized porous SiO₂ nanorods was initially dispersed in 50 mL deionized water by ultrasonic treatment, subsequently appropriate amount of manganese acetate was slowly added to the above solution. After stirring for 6 h, the solution of KMnO₄ containing 40 mL deionized water was slowly added to the above mixture, and continuously stirred for 12 h. The main reaction between Mn(CH₃COO)₂ and KMnO₄ is expressed by the following equation: (3Mn²⁺ + 2MnO₄⁻ + 2H₂O → 5MnO₂ + 4H⁺). Then, the obtained product was collected by filtration, and washing several times with deionized water, and then drying at 110 °C for 12 h. Finally, the SiO₂@MnO₂ was treated with 2 M NaOH solution at 80 °C to remove the SiO₂ nanorods template, followed by centrifugation and washing with deionized water several times and drying at 110 °C for 12 h. The resultant catalysts are labeled as MnO₂(y)-E nanorods, where y represents the mass ratio of Mn to SiO₂ nanorods template, and E represents the solvent evaporation method.

2.1.2 Solvent evaporation method (E). For comparison, the MnO₂ nanorods catalysts were also synthesized by the solvent evaporation method using manganese acetate as the precursor. A certain amount of the as-synthesized porous SiO₂ nanorods was initially dispersed in 40 mL ethanol by ultrasonic treatment. Subsequently, appropriate amount of manganese acetate was slowly added to the above solution, and stirred for 2 h. Then, the mixture was heated up to 50 °C to evaporate the ethanol. The obtained powder was dried at 80 °C for 12 h, followed by calcination at 400 °C for 3 h in air atmosphere. Finally, the SiO₂ nanorods template was removed with 2 M NaOH solution at 80 °C, then centrifugation, washing with deionized water several times and drying at 110 °C for 12 h. The resultant catalysts are labeled as MnO₂(y)-E nanorods, where y represents the mass ratio of Mn to SiO₂ nanorods template, and E represents the solvent evaporation method.

2.2 Activity test

NO removal activity tests were carried out in a fixed-bed reactor with a diameter of 8 mm. The gas mixture consisted of 500 ppm NO, 500 ppm NH₃, 5.0 vol% O₂ and balance N₂. In all experiments, the total gas flow rate was maintained at 500 mL min⁻¹, corresponding to a gas hourly space velocity (GHSV) of 62 000 h⁻¹. The reaction temperatures were controlled regulated from 100 to 300 °C. The concentrations of NO and O₂ in the inlet and outlet gases were continually measured on-line by a flue gas analyzer (MRU VARIO PLUS, Germany).

2.3 Characterization

The morphologies and microstructures of the samples were examined using scanning electron microscope (SEM, FEI Nova NanoSEM 450) and transmission electron microscopy (TEM, JEOL JEM-2100F). The pore structure was measured at 77 K using a Quadrasorb SI analyzer (Quantachrome Instrument Crop) and the corresponding pore size distribution was obtained by the density functional theory (DFT model). X-ray diffraction (XRD) measurements were recorded on a Rigaku D/max 2550 diffractometer using Cu Kα radiation. X-ray photoelectron spectroscopy (XPS) measurements were carried out on an Axis Ultra DLD spectrometer with Al Kα radiation. NH₃-temperature programmed desorption (NH₃-TPD) was performed on a TP-5080 adsorption analyzer (Xianquan Co.) with a thermal conductivity detector (TCD). Before the NH₃-TPD experiment, 0.1 g sample was pretreated in He flow at 300 °C for 30 min, followed by cooling down to 100 °C. Afterwards, the He flow was switched to a stream containing 5 vol% NH₃/He to adsorb NH₃ for 60 min at 100 °C and then purged with He at the same temperature. Finally, the temperature was increased to 800 °C in He flow at a heating rate of 10 °C min⁻¹.

3. Results and discussion

3.1 Morphological characterization

Fig. 1 shows SEM images of the porous SiO₂ nanorods. As can be observed in Fig. 1, the obtained SiO₂ nanorods shows one-
dimensional rod-like structure. These nanorods are nearly uniform with lengths in the range of 300–400 nm and diameters of about 100–200 nm. Furthermore, all SiO$_2$ nanorods are almost monodispersed without aggregation.

The morphologies and microstructures of MnO$_x$ nanorods catalysts prepared by different methods are characterized by SEM. The results in Fig. 2 indicate the different morphology can be clearly observed over MnO$_x$,(0.36)-E and MnO$_x$,(0.36)-P nanorods. After the loading of MnO$_2$ and etching by the NaOH solution, the morphology of MnO$_x$,(0.36)-E nanorods is mainly one-dimensional rod-like structure, which does not change much compared with that of SiO$_2$ nanorods. These indicate that MnO$_x$ is uniformly distributed in the rod-like structure, favoring to the enhancement of SCR activity. Additionally, a small amount of nanoparticles and nanosheets MnO$_x$ are observable on the surface of the rod-like structure, which may be caused by the unloaded MnO$_x$ on the SiO$_2$ nanorods because of the precipitation and crystallization of partial manganese precursor during the solvent evaporation process. The SEM image of MnO$_x$,(0.36)-P nanorods is clearly different from that of MnO$_x$,(0.36)-E nanorods. Flower-like structure is observed, which is assembled by numerous manganese oxide nanosheets (Fig. 2c and d). After the careful observation, it is found that a certain amount of loose macroporous structure is also formed on the surface of the catalyst, due to the accumulation of MnO$_x$ nanosheets. These macroporous structure could facilitate the adsorption and desorption of reactant gas molecules on the active sites of catalyst surface, which is advantageous to NH$_3$-SCR reaction.

The detailed morphologies and microstructures of MnO$_x$ nanorods catalysts obtained by different methods are further characterized by TEM. From Fig. 3a, it is observed that MnO$_x$,(0.36)-E nanorods still maintains one-dimensional rod-like structure, agreeing well with the SEM results. It is worth noting that the inter center of MnO$_x$,(0.36)-E nanorods is not completely hollow structure. Since the porous SiO$_2$ nanorods has abundant mesoporous structures, it is reasonable to expect the manganese precursor easily fills the mesoporous template including the edge and inner pores of SiO$_2$ nanorods during the MnO$_2$ impregnation process. Thus, the inner partially hollow structure is formed after the further etching of SiO$_2$. In addition, there exists unloaded nanoparticles and nanosheets MnO$_x$ near the rod-like structure, in accordance with the SEM results (Fig. 2a and b). Compared to TEM image of MnO$_x$,(0.36)-E nanorods, MnO$_x$,(0.36)-P nanorods is mainly composed of nanorods, with a diameter about 100–200 nm and length about 300–500 nm (Fig. 3c), which is similar with the size of the SiO$_2$ nanorods. And it can also be seen that MnO$_x$ nanosheets are deposited on the surface of the nanorods, suggesting that the flower-like MnO$_x$ is assembled by these MnO$_x$ nanosheets. Meanwhile, many porous structures in the inner space of nanorods are also observed, which is explained because the MnO$_x$ nanosheets are self-assembled randomly and not parallel to each other, leading to the formation of the porous structure. Such results are good agreement with the SEM observation (Fig. 2c and d).

The HRTEM images of the two catalysts are shown in Fig. 3b and d. The HRTEM image of MnO$_x$,(0.36)-E nanorods reveals the visible lattice fringes with an interplanar spacing of 0.214, 0.289 and 0.493 nm, which can be assigned to the (015) plane of birnessite-type MnO$_2$ (δ-MnO$_2$), (200) and (101) planes of Mn$_3$O$_4$, respectively. These data suggests that Mn$_3$O$_4$ and δ-MnO$_2$ coexist on the surface of MnO$_x$,(0.36)-E nanorods. However, for MnO$_x$,(0.36)-P nanorods, the lattice fringes with an interplanar spacing of 0.241 and 0.717 nm can be observed, which can be assigned to the (101) and (003) crystal planes of δ-MnO$_2$, respectively.

**3.2 NO removal activities**

Fig. 4 exhibits the NO removal activities of MnO$_x$ nanorods catalysts obtained by the two different methods. It can be seen that the catalysts preparation method has significant effect on the NO removal activity. As shown in Fig. 4a, MnO$_x$,(0.36)-P and MnO$_x$,(0.72)-P nanorods catalysts exhibit higher NO removal activities.
activity, above 94% of NO conversions can be achieved at temperatures of 100–200 °C. Especially in the low temperature range of 100–180 °C, they maintain about 98% NO conversions. For MnO_x(0.18)-P nanorods, it shows relatively low NO removal activity, but the maximum NO conversion is still up to 92% at 160 °C. From Fig. 4b, it can be observed that MnO_x(0.18)-E and MnO_x(0.36)-E nanorods catalysts exhibit relatively high NO removal activity. NO conversions of the two catalysts at 100 °C is approximately 70%, and they reach more than 90% in the temperature range of 140–240 °C. For MnO_x(0.72)-E nanorods, it shows relatively low NO removal activity below 200 °C, but it reaches a maximum value (above 90%) at 240 °C. From Fig. 4b, it can be observed that MnO_x(0.18)-E and MnO_x(0.36)-E nanorods catalysts exhibit relatively high NO removal activity. NO conversions of the two catalysts at 100 °C is approximately 70%, and they reach more than 90% in the temperature range of 140–240 °C.

3.3 XRD

To further investigate the crystal phase composition of MnO_x nanorods catalysts obtained by different methods, XRD patterns were characterized, and the results are shown in Fig. 5. The XRD pattern of MnO_x(0.36)-E nanorods displays the characteristic diffraction peaks located at 2θ = 18.0°, 28.9°, 32.4°, 36°, 44.4°, 58.5°, 59.9° and 64.7°, which can be indexed as the (101), (112), (103), (211), (220), (321), (224) and (400) crystal planes of Mn_3O_4 with a spinel structure (JCPDS card no. 24-0734), respectively. And it can also be observed that the diffraction peaks at 12.3°, 24.8°, 36.9° and 42.2° are ascribed to the (003), (006), (101), and (015) crystal planes of δ-MnO_2 (JCPDS card no. 52-0556), respectively. For MnO_x(0.36)-P nanorods, the diffraction peaks at 12.3°, 24.8°, 36.9°, 42.2°, and 66.3° are assigned to the (003), (006), (101), (015), and (113) planes of δ-MnO_2 crystalline phase. These data is consistent with the observation using HRTEM. It is worth noting that the diffraction peaks of MnO_x on MnO_x(0.36)-P nanorods become broader and the intensities of the peaks become much weaker than those of MnO_x(0.36)-E nanorods, suggesting the smaller size of crystal particle and lower crystallinity of MnO_x. It has been widely demonstrated that amorphous phase of manganese oxides usually exhibits higher catalytic activity for SCR of NO.
than crystal manganese oxides. Based on these results, it can be concluded that the improved dispersion of MnO₂ species is obtained by the redox precipitation method, which contributes to the excellent SCR activity of MnO₂(0.36)-P nanorods, as evidenced by the results of activity evaluation presented in Fig. 4.

3.4 Pore structure analysis

The pore structure characterizations of the MnO₂ nanorods catalysts obtained by different methods are analyzed by N₂ adsorption–desorption isotherms. As presented in Fig. 6a, MnO₂(0.36)-E nanorods exhibits a typical type-IV isotherm with a hysteresis loop at the relative pressure (P/P₀) of 0.4–0.9, indicating the presence of mesopores. For MnO₂(0.36)-P nanorods, the isotherm still belongs to the type-IV isotherm with an obvious hysteresis loop at P/P₀ of 0.8–1.0, suggesting that the catalyst has characteristic of mesoporous material (Fig. 6c). Their pore sizes are further analyzed, as shown in Fig. 6b and d, respectively. The pore size distribution curve of MnO₂(0.36)-E nanorods shows the coexistence of micropores and mesopores, and its pore size distributes in the range of 0.6–4 nm. MnO₂(0.36)-P nanorods exhibits a wider pore size distribution and a larger number of mesopores in the range of 4–28 nm can be also observed. Moreover, the pore parameters of the samples are listed in Table 1. It can be observed that the Soret for MnO₂(0.36)-P and MnO₂(0.36)-E nanorods is 151 m² g⁻¹ and 272 m² g⁻¹, respectively. The Soret values of these MnO₂ nanorods catalysts are much larger than those of carrier-free MnO₂-based catalysts as previously reported, as which may result from the highly porous structure of SiO₂ nanorods template and/or the accumulation of the nanoparticles. It is worth pointing out that the V₅₀⁰ of MnO₂(0.36)-P nanorods (0.61 cm³ g⁻¹) is significantly higher than that of MnO₂(0.36)-E nanorods (0.31 cm³ g⁻¹), which may be due to its flower-like structure, as demonstrated by the SEM results (Fig. 2c and d). Additionally, the pore volume of MnO₂(0.36)-P nanorods at smaller pore sizes (<4 nm) decreases obviously, and the pore volume at larger pore sizes (5–28 nm) increases greatly, indicating that there exists more mesoporous structure in MnO₂(0.36)-P nanorods. Thus, such rich mesoporous structure with high pore volume of MnO₂(0.36)-P nanorods may be favorable for exposure of more active sites of MnO₂ and the adsorption of reactant molecules, leading to the excellent SCR activity at the low temperatures (below 200 °C).

3.5 XPS characterization

To further determine the surface chemical states of elements in MnO₂ nanorods catalysts, the XPS measurement was carried out and the results are presented in Fig. 7. The relative atomic ratios of Mn and O elements are summarized in Table 2. As displayed in Fig. 7a, the Mn 2p spectrum of MnO₂(0.36)-E nanorods exhibits two main peaks with binding energies of 653.8 eV and 642.3 eV, which represents Mn 2p₁/₂ and Mn 2p₃/₂, respectively. The Mn 2p₃/₂ spectrum can be fitted into three characteristic peaks at 641.0–642.0 eV, 642.2–642.5 eV and 642.9–643.7 eV, corresponding to Mn⁴⁺, Mn³⁺, and Mn²⁺, respectively. These data suggest that Mn⁴⁺, Mn³⁺ and Mn²⁺ manganese oxide phases coexist on the surface of MnO₂(0.36)-E nanorods. For MnO₂(0.36)-P nanorods, the binding energies of Mn 2p₁/₂ and Mn 2p₃/₂ are located at 653.9 eV and 642.2 eV, respectively. The binding energy separation between these two peaks is 11.7 eV, which is in accordance with previously reported results of MnO₂, indicating that the valence of Mn element is very close to 4 in MnO₂(0.36)-P nanorods. Moreover, the Mn 2p₃/₂ spectrum is fitted into two peaks, which are attributed to Mn⁴⁺ (642.1 eV) and Mn⁴⁺ (643.5 eV), respectively. These results further demonstrate that MnO₂ is the main manganese oxide in MnO₂(0.36) nanorods, which is in accordance with the XRD result. The relative ratio of different oxidation state of manganese species can be calculated by the area ratio of Mn²⁺, Mn³⁺, and Mn⁴⁺ species, as shown in Table 2. The percentage of Mn⁴⁺/Mn³⁺ on MnO₂(0.36)-P nanorods (50.8%) is greatly higher than that on MnO₂(0.36)-E nanorods (35.7%). As literature reported, manganese species with higher oxidation state are preferable for oxidation reactions over the manganese-based catalysts. It has been confirmed that Mn⁴⁺ species are beneficial to promote the low-temperature SCR activity, due to the enhancement of oxidation of NO to NO₂. Therefore, the higher percentage of Mn⁴⁺ on MnO₂(0.36)-P nanorods results in the increased SCR activity at the low temperatures of 100–160 °C.

As shown in Fig. 7b, the O 1s XPS spectra can be fitted into two peak. The peak located at 529.5–530.2 eV can be assigned to the lattice oxygen (O²⁻) (denoted as Oₐ), while the peak located at 531.2–532.0 eV is assigned to the chemisorbed oxygen, such as O²⁻ or O₂⁻ (denoted as Oₐ). The relative concentrations of Oₐ and Oₐ can be determined from the area ratio of Oₐ/(Oₐ + Oₐ) and Oₐ/(Oₐ + Oₐ), respectively. As illustrated by Table 2, the ratio of Oₐ/(Oₐ + Oₐ) is 49.3% and 38.6% for MnO₂(0.36)-E and MnO₂(0.36)-P nanorods, respectively, which is higher than the data previously reported for MnO₂ nanorods (36.7%) and MnO₂/TiO₂-GE (19.9%). It has been widely reported that the surface chemisorbed oxygen species (Oₐ) are more active than the lattice oxygen species (Oₐ) in oxidation reactions because of their higher mobility, which may easily exchange with oxygen in the gas phase or oxygen molecules absorbed on catalyst surface, thus acting as the supplement of lattice oxygen. Moreover,
the higher concentration of $O_b$ is advantageous to the improvement of oxidation of NO to NO$_2$, which facilitates the “fast SCR” reaction ($4\text{NH}_3 + 2\text{NO} + 2\text{NO}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$), resulting in the enhancement of catalytic activity. Thus, the relative high concentration of surface chemisorbed oxygen in MnO$_x$(0.36)-E and MnO$_x$(0.36)-P nanorods is favorable for achieving high SCR activity. The above XPS results demonstrate that the high concentration of Mn$^{4+}$ species plays an important role in the low-temperature SCR activity of MnO$_x$(0.36)-P nanorods.

3.6 NH$_3$-TPD

It is generally known that the adsorption and oxidation of NH$_3$ on the surface acid sites of catalyst are considered to be a key step in the NH$_3$-SCR reaction. NH$_3$-TPD experiments were performed to determine the surface acidity of the obtained catalysts, and the results are shown in Fig. 8 and Table 3. It is found...
NH₃ adsorption and oxidation on the catalyst surface, leading to strong acid sites on it, which contributes to enhancement of stronger surface acidity, especially there are more amount of nanorods.

Fig. 8 NH₃-TPD profiles of the different MnOₓ nanorods catalysts.

Table 2 The relative atomic ratios of the different MnOₓ nanorods catalysts

| Sample          | \(X_{\text{Mn}}\) (%) | \(X_{\text{O}}\) (%) |
|-----------------|----------------------|---------------------|
| \(\text{MnO}_x(0.36)-\text{P}\) | 0  49.2  50.8 | 61.4  38.6 |
| \(\text{MnO}_x(0.36)-\text{E}\) | 6.4  57.9  35.7 | 50.7  49.3 |

Table 3 The amount of surface acids over the different catalysts

| Sample          | \(T_1\) \(^{a}\) | \(T_2\) | \(T_3\) | \(S_1\) \(^b\) | \(S_2\) | \(S_3\) |
|-----------------|------------------|--------|--------|---------------|--------|--------|
| \(\text{MnO}_x(0.36)-\text{P}\) | 132  | 269  | 539  | 30.3  | 28.9  | 56.7  |
| \(\text{MnO}_x(0.36)-\text{E}\) | 116  | 278  | —     | 17.0  | 86.8  | —     |

\(^{a}\) The desorption peak at temperature. \(^{b}\) The area of desorption peak.

that MnOₓ(0.36)-E nanorods exhibits two obvious desorption peaks located at the temperature range of 50–180 °C (labeled as peak 1) and 190–400 °C (labeled as peak 2). And no visible desorption peaks above 400 °C can be observed. For MnOₓ(0.36)-P nanorods, besides the two desorption peaks located at 50–400 °C, another desorption peak at 410–690 °C (labeled as peak 3) is also observed. The peaks 1 and 2 are ascribed to NH₃ desorption from the weak acid sites, and peak 3 is assigned to the strong acid sites. It is generally accepted that the area of NH₃ desorption peak is proportional to the amount of acid sites. As listed in Table 3, the desorption peak area of strong acid sites over MnOₓ(0.36)-P nanorods significantly enhances compared with MnOₓ(0.36)-E nanorods, indicating that a large amount of strong acid sites exist on its surface. Based on the above results, MnOₓ(0.36)-P nanorods has stronger surface acidity, especially there are more amount of strong acid sites on it, which contributes to enhancement of NH₃ adsorption and oxidation on the catalyst surface, leading to the excellent low-temperature SCR activity of MnOₓ(0.36)-P nanorods.

4. Conclusions

A series of MnOₓ nanorods catalysts using porous SiO₂ nanorods as template were synthesized through two different preparation methods. The obtained MnOₓ-P nanorods catalyst prepared by redox precipitation method exhibits higher NO removal activity at low temperatures [lower than 200 °C] in comparison to MnOₓ-E nanorods. About 98% NO conversion is achieved over MnOₓ(0.36)-P nanorods in the low temperature range of 100–180 °C. The reason is mainly attributed to its unique flower-like morphology and mesoporous structures with high pore volume. Furthermore, there are the lower crystallinity of MnOₓ, higher percentage of Mn⁴⁺ species and a large amount of strong acid sites on the surface of MnOₓ(0.36)-P nanorods. These factors result in its excellent low-temperature SCR activity.

Conflicts of interest

There are no conflicts to declare.

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