available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Article (Special Issue on Environmental and Energy Catalysis)

Synthesis of novel $\text{MnO}_x/\text{TiO}_2$ core-shell nanorod catalyst for low-temperature NH_3 -selective catalytic reduction of NO_x with enhanced SO_2 tolerance

Zhongyi Sheng^{a,c}, Dingren Ma^a, Danqing Yu^b, Xiang Xiao^c, Bingjie Huang^a, Liu Yang^{a,*}, Sheng Wang^d

^a School of Environment, Nanjing Normal University, Nanjing 210023, Jiangsu, China

^b School of Chemical Engineering and Technology, Wuhan University of Science and Technology, Wuhan 430081, Hubei, China

^c Suzhou Industrial Technology Research Institute of Zhejiang University, Suzhou 215163, Jiangsu, China

^d State Power Environmental Protection Research Institute, Nanjing 210031, Jiangsu, China

ARTICLE INFO

Article history:

Received 19 February 2018

Accepted 12 March 2018

Published 5 April 2018

Keywords:

Low-temperature selective catalytic reduction

Core-shell

Nanorod

SO_2 resistance

MnO_x

ABSTRACT

In this study, a $\text{MnO}_x/\text{TiO}_2$ core-shell catalyst prepared by a two-step method was used for the low-temperature selective catalytic reduction of NO_x with NH_3 . The catalyst exhibits high activity, high stability, and excellent N_2 selectivity. Furthermore, it displays better SO_2 and H_2O tolerance than its MnO_x , TiO_2 , and $\text{MnO}_x/\text{TiO}_2$ counterparts. The prepared catalyst was characterized systematically by transmission electron microscopy, high-resolution transmission electron microscopy, X-ray diffraction, Raman, BET, X-ray photoelectron spectroscopy, NH_3 temperature-programmed desorption and H_2 temperature-programmed reduction analyses. The optimized $\text{MnO}_x/\text{TiO}_2$ catalyst exhibits an obvious core-shell structure, where the TiO_2 shell is evenly distributed over the MnO_x nanorod core. The catalyst also presents abundant mesopores, Lewis-acid sites, and high redox capability, all of which enhance its catalytic performance. According to the XPS results, the decrease in the number of Mn^{4+} active centers after SO_2 poisoning is significantly lower in $\text{MnO}_x/\text{TiO}_2$ than in $\text{MnO}_x/\text{TiO}_2$. The core-shell structure is hence able to protect the catalytic active sites from H_2O and SO_2 poisoning.

© 2018, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Selective catalytic reduction (SCR) processes are the state-of-the-art for NO_x abatement in coal-fired power plants [1–3]. However, the commercial catalytic ($\text{V}_2\text{O}_5\text{-WO}_3$ (MoO_3)/ TiO_2) system exhibits some typical disadvantages [4], such as the need for a high starting temperature, narrow reactive temperature window (280–350 °C), and the decay of the N_2

selectivity at high temperatures [5–7]. Therefore, the development of novel catalysts for low-temperature NH_3 -SCR remains a challenging task for industrial application. Recently, manganese oxide-based catalysts have attracted much attention for their superior activity in low-temperature SCR reactions [8–16]. However, they always suffer from severe SO_2 poisoning. Jin et al. [17] have reported that the NO conversion by Mn/TiO_2 catalysts decreases rapidly in the presence of SO_2 , although an

* Corresponding author. Tel./Fax: +86-25-85891455; E-mail: 15700079861@163.com

The work was supported by the National Natural Foundation of China (51508281, 41771498) and the Program of Natural Science Research of Jiangsu Higher Education Institutions of China (16KJD610001).

DOI: 10.1016/S1872-2067(18)63059-1 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 39, No. 4, April 2018

enhancement of the SO₂ tolerance during low-temperature SCR was achieved after Ce doping. Sheng et al. [18] have also proposed that the presence of high concentrations of SO₂ in the flue gas leads to prominent deactivation of a Mn-Ce/TiO₂ catalyst prepared by a co-precipitation method for low-temperature SCR of NO_x with NH₃. Therefore, many researchers are working toward the development of superior SCR catalysts with high activity and good SO₂ tolerance [19–22].

Core-shell nanostructures have been widely studied for their unique structure, which can effectively protect the active components from migrating and sintering [23,24]. Therefore, the design of a catalyst with a core-shell structure seems a promising approach to protect the active sites from SO₂ poisoning. It has been reported that ceria supported on titania nanotubes shows high activity for intermediate- and high-temperature NH₃-SCR [25–27]. Pappas et al. [28] designed a series of manganese oxide-confined titania nanotube catalysts with different morphological features and found that their remarkable low-temperature SCR activity was due to the abundance of surface Mn⁴⁺ species. However, most of the literature so far regarding core-shell nanostructures for SCR reactions have reported titania nanotubes or carbon nanotubes (CNTs) as the shell [29,30], while granular metal oxide@TiO₂ has seldom been used.

In this work, a novel MnO_x@TiO₂ core-shell nanorod catalyst was prepared by a two-step method, as shown in Fig. 1. MnO_x nanorods were first prepared by a hydrothermal method [31], and then a versatile kinetics-controlled coating method [32] was used to fabricate a series of MnO_x@TiO₂ nanorod catalysts, one of which presented a core-shell structure. The influence of the presence of SO₂ in the flue gas on the SCR activity of the core-shell catalyst was also investigated.

2. Experimental

2.1. Catalysts preparation

MnO_x@TiO₂ nanorod catalysts were prepared by a new two-step method. KMnO₄ (2 mmol) and MnSO₄·H₂O (3 mmol) were dissolved in deionized water (80 mL) at room temperature. After stirring ceaselessly for 20 min, the solution was transferred to a Teflon-lined stainless steel autoclave. The autoclave was maintained at 180 °C for 4 h and then cooled down

Fig. 1. Schematic illustration of the fabrication process of MnO_x@TiO₂ nanorods.

to ambient temperature. The resulting solid product was filtered, washed carefully with deionized water, and finally dried in an electric oven at 80 °C for 12 h [31]. The obtained powder was used as the MnO_x nanorod core. The TiO₂ shell material was prepared via a versatile kinetics-controlled coating method [32]. The MnO_x nanorod (0.5 mmol) core material was dispersed in ethanol (100 mL) and a concentrated ammonia solution (0.30 mL, 28 wt%) by ultrasonication for 30 min. Then, different molar amounts of tetrabutyl titanate were added dropwise and the reactions were allowed to proceed for 24 h at 45 °C under continuous mechanical stirring. The resultant products were separated, collected, and washed with deionized water and ethanol for several times. Finally, the obtained powders were dried in an electric oven at 100 °C for 12 h and calcined at 500 °C in air for 2 h [32]. The catalysts were denoted as MnO_x@TiO₂(*y*), where *y* refers to the Mn:Ti molar ratio, which were 1:4, 1:2, and 1:1 in this study.

The counterpart MnO_x/TiO₂ nanomaterial was also prepared by a hydrothermal method. KMnO₄ (2 mmol), MnSO₄·H₂O (3 mmol), and an appropriate amount of tetrabutyl titanate were mixed in deionized water. Then, the mixture was sealed in a Teflon-lined stainless steel autoclave at 180 °C for 4 h after further magnetic stirring. The sediment was then centrifuged, washed with deionized water and ethanol, dried at 100 °C for 12 h, and finally calcined in air at 500 °C for 2 h. The catalyst was denoted as MnO_x/TiO₂. MnO_x nanorods were prepared using the first step of the MnO_x@TiO₂ synthesis, and TiO₂ nanoparticles were prepared using a similar hydrothermal method as that employed for the MnO_x/TiO₂ catalyst.

2.2. Catalyst characterization

The morphological features of all the prepared catalysts were characterized by transmission electron microscopy (TEM), high-resolution TEM (HR-TEM), and element mapping using a FEI TECNAI G2 F20 instrument operated at 200 kV. The crystalline structure of the samples was examined by X-ray diffraction (XRD) using a Bruker D8 Advance diffractometer. Raman spectra were recorded on an SPEX-1403 Laser Raman Spectrometer at room temperature with a resolution of about 0.6 cm⁻¹. An Ar-ion laser with a wavelength of 514.5 nm in backscattering configuration was used to excite the crystals. The surface area and pore distribution of the catalysts were calculated with the Brunauer-Emmett-Teller (BET) equation using Micromeritics ASSP 2020 equipment at -196 °C by N₂ physisorption. The surface atomic states of the catalysts were analyzed by X-ray photoelectron spectroscopy (XPS) on a Thermo Escalab 250Xi instrument. H₂ temperature-programmed reduction (H₂-TPR) experiments were performed on a Tianjin XQ TP5080 auto adsorption apparatus. Prior to the H₂-TPR measurements, 50 mg of the catalysts were pretreated under N₂ at a total flow rate of 30 mL·min⁻¹ at 300 °C for 0.5 h, and then cooled down to room temperature under N₂ atmosphere. The temperature was then raised to 600 °C at a constant heating rate of 10 °C·min⁻¹ under H₂ (5 vol%)/N₂ flow (30 mL·min⁻¹). The H₂ consumption during the experiment was monitored by a thermal conductivity detector (TCD). NH₃ tem-

perature-programmed desorption (NH₃-TPD) was performed on the same apparatus. Before the NH₃-TPD experiments, the catalysts (150 mg) were purged at 300 °C under a N₂ flow (30 mL·min⁻¹) for 0.5 h and cooled to 100 °C under N₂ flow. The samples were then exposed to a flow of NH₃ at 100 °C for 1 h, followed by N₂ purging for 0.5 h. Finally, the temperature was raised to 800 °C under N₂ flow at a constant heating rate of 10 °C·min⁻¹.

2.3. Activity tests

The SCR activity was measured in a fixed-bed reactor where the samples (4 mL) were loaded. The temperature was raised from 60 to 260 °C. The typical reactant gas consisted of 500 ppm NO, 500 ppm NH₃, 200 ppm SO₂ (if added), 10% H₂O (if added), 5 vol% O₂, and balance N₂ with a gas hourly space velocity (GHSV) of 24000 h⁻¹. Water vapor was generated by passing N₂ through a heated bottle containing deionized water. The NO, NO₂, SO₂, and O₂ content was measured on a flue gas analyzer (MRU Vario Plus, Germany), and N₂O was measured on a different gas analyzer (G200). The NO_x conversion and N₂ selectivity were calculated as follows:

$$\text{NO}_x \text{ conversion (\%)} = \frac{C_{\text{NO}_x}^{\text{in}} - C_{\text{NO}_x}^{\text{out}}}{C_{\text{NO}_x}^{\text{in}}} \times 100$$

$$\text{N}_2 \text{ selectivity (\%)} = \frac{C_{\text{NO}_x}^{\text{in}} + C_{\text{NH}_3}^{\text{in}} - C_{\text{NO}_2}^{\text{out}} - 2C_{\text{N}_2\text{O}}^{\text{out}}}{C_{\text{NO}_x}^{\text{in}} + C_{\text{NH}_3}^{\text{in}}} \times 100$$

3. Results and discussion

3.1. Microstructure and morphology

The morphology of MnO_x, TiO₂, MnO_x/TiO₂, and MnO_x@TiO₂ at different Mn:Ti molar ratios was investigated by TEM, and the images are shown in Fig. 2(a)–(f). From Fig. 2(a), it can be

seen that the MnO_x nanorods are well formed, being thus good precursors for core-shell structures. From Fig. 2(b), it is clear that a large number of homogeneous TiO₂ nanoparticles were successfully synthesized by the hydrothermal method, with a particle diameter ranging from 5 to 15 nm. Fig. 2(c) shows that the MnO_x and TiO₂ materials are present in MnO_x/TiO₂ as nanorods and nanoparticles, respectively, and that they are randomly agglomerated. Catalysts at different Mn:Ti molar ratios (1:4, 1:2, and 1:1) were prepared to explore the effect of the Mn loading on the formation of core-shell nanorods and their TEM images are shown in Fig. 2(d)–(f). As shown in Fig. 2(d), some TiO₂ nanoparticles are attached to the MnO_x nanorods, although most of them appear aggregated. When the Mn:Ti ratio was increased to 1:1, almost no TiO₂ nanoparticles were observed adhered to the MnO_x nanorods; both nanomaterials are well-shaped but show no interaction. However, an obvious core-shell structure is observed in the case of MnO_x@TiO₂(1:2) (Fig. 2(e)). Abundant TiO₂ nanoparticles are evenly distributed on the surface of the MnO_x nanorods. The HR-TEM, selected area electron diffraction, and element mapping results (Fig. 2(g) and (h)) also confirmed the core-shell nanorod structure. It can be seen in the HR-TEM image (Fig. 2(g)) that the spacing distances between the lattice planes are 0.240, 0.515, and 0.352 nm, corresponding to the (101) and (200) crystal planes of MnO_x, and the (101) plane of anatase TiO₂, respectively, in agreement with the diffraction pattern (inset in Fig. 2(g)). These results also indicate that the shell of the MnO_x@TiO₂(1:2) catalyst was successfully fabricated in the form of anatase TiO₂. From Fig. 2(h), the Ti and Mn element mappings confirm that Ti completely covers the Mn core. All these experimental results support the formation of a core-shell structure.

3.2. XRD analysis and Raman spectra of the catalysts

The XRD patterns of the catalysts with different structures

Fig. 2. TEM images of MnO_x (a), TiO₂ (b), MnO_x/TiO₂ (c), and MnO_x@TiO₂ at different molar ratios: Mn:Ti = 1:4 (d), Mn:Ti = 1:2 (e), and Mn:Ti = 1:1 (f); HR-TEM image and selected area electron diffraction (g); element mapping for MnO_x@TiO₂(1:2) (h).

Fig. 3. XRD patterns (a) and Raman spectra (b) of the catalysts ($\text{MnO}_x\text{@TiO}_2$ refers to the catalyst with $\text{Mn}:\text{Ti} = 1:2$).

are shown in Fig. 3(a). The reflections of the TiO_2 nanoparticle catalyst correspond to the typical diffraction pattern for anatase TiO_2 . The MnO_x nanorod catalyst was assigned as cryptomelane-type $\alpha\text{-MnO}_2$ [JCPDS 44-0141, tetragonal, $I4/m$, $a = b = 0.978$ nm, $c = 0.286$ nm] [33,34]. The diffraction peaks of $\text{MnO}_x/\text{TiO}_2$ were ascribed to anatase TiO_2 , while no obvious signals for manganese oxides were found. This observation suggests that the manganese oxides are well dispersed on the TiO_2 support [35]. $\text{MnO}_x\text{@TiO}_2(1:2)$ presents peaks for both anatase TiO_2 and cryptomelane-type $\alpha\text{-MnO}_2$, consistent with the electron diffraction image in Fig. 2(g), revealing the good crystallinity of both anatase TiO_2 and $\alpha\text{-MnO}_2$. However, the peak intensity of anatase TiO_2 and $\alpha\text{-MnO}_2$ has diminished, possibly due to the excellent dispersion of anatase TiO_2 on the catalyst surface.

Raman spectroscopy measurements were conducted to obtain more information on the crystalline structure of the catalysts [36]. As shown in Fig. 3(b), $\text{MnO}_x/\text{TiO}_2$ presents bands located at 142, 395, 515, and 638 cm^{-1} , which are typical of the anatase TiO_2 phase [37,38], in agreement with the XRD analysis in Fig. 3(a). Many researchers have reported that the vibrational features of MnO_2 exhibit low Raman activity [39,40], and only the stretching vibrations of $[\text{MnO}_6]$ octahedra have been proven to appear in the region of 500–700 cm^{-1} [41]. $\text{MnO}_x\text{@TiO}_2$ presents lower-intensity bands in the Raman spectrum. The peaks at 577 and 675 cm^{-1} are assigned to the stretching vibrations of Mn-O-Mn and Mn-O , respectively [42], consistent with the bands for $\alpha\text{-MnO}_2$. No obvious TiO_2 phase is observed, due to the porous TiO_2 coverage of the MnO_x nanorod surface. This result is in good agreement with the previous XPS results. The XPS and Raman results thus support the presence of MnO_2 in $\text{MnO}_x\text{@TiO}_2(1:2)$, which is crucial for excellent SCR performance.

3.3. BET surface area and pore structure

N_2 adsorption-desorption measurements were performed to determine the specific surface area and porous structure of

the catalysts. As illustrated in Fig. 4, the isotherm of $\text{MnO}_x\text{@TiO}_2(1:2)$ reveals a typical type-IV curve, indicating the presence of mesopores according to the definition of the International Union of Pure and Applied Chemistry. It can be seen that $\text{MnO}_x\text{@TiO}_2(1:2)$ and $\text{MnO}_x/\text{TiO}_2$ present H3-type and H2-type hysteresis loops, respectively, also indicative of their mesoporous nature. $\text{MnO}_x/\text{TiO}_2$ displays a higher absorption at relatively high pressures compared to $\text{MnO}_x\text{@TiO}_2(1:2)$, suggesting that its mean pore size is larger than that of $\text{MnO}_x\text{@TiO}_2(1:2)$. From the inset in Fig. 4, the pore size distribution of both $\text{MnO}_x\text{@TiO}_2(1:2)$ and $\text{MnO}_x/\text{TiO}_2$ indicates a pore size of around 10 nm, which means that these two catalysts are typically mesoporous. A rich mesoporous structure provides channels for the reactant gases to contact the inner surface of the catalyst.

3.4. Catalytic activity

The activity of the catalysts at different temperatures is presented in Fig. 5(a). It can be seen that the NO_x conversion

Fig. 4. N_2 adsorption-desorption isotherms and pore size distribution curves (inset) of the catalysts ($\text{MnO}_x\text{@TiO}_2$ refers to the catalyst with $\text{Mn}:\text{Ti} = 1:2$).

Fig. 5. (a) NH₃-SCR activity of all the catalysts; (b) N₂ selectivity of MnO_x@TiO₂(1:2) and MnO_x/TiO₂; (c) stability test for MnO_x@TiO₂(1:2) at 150 °C (MnO_x@TiO₂ refers to the catalyst with Mn:Ti = 1:2). Reaction conditions: 500 ppm NO, 500 ppm NH₃, 5% O₂, and balance N₂, GHSV = 24,000 h⁻¹.

over the different catalysts increased with the temperature. MnO_x/TiO₂ and MnO_x@TiO₂(1:2) exhibit higher catalytic activity than the other two catalysts for the SCR of NO_x with NH₃. MnO_x/TiO₂ presents better catalytic activity at temperatures below 90 °C, while the NO_x conversion reached 100% rapidly over MnO_x@TiO₂(1:2) at higher temperatures. The plot of the N₂ product selectivity over these two catalysts as a function of the temperature is shown in Fig. 5(b). The N₂ selectivity of these two catalysts increased with the temperature, although the N₂ selectivity of MnO_x@TiO₂(1:2) was always higher than that of MnO_x/TiO₂, reaching 100% at 130 °C. The stability of MnO_x@TiO₂(1:2) at 150 °C is shown in Fig. 5(c). Full NO_x conversion was reached rapidly and remained stable for more than 10 h. Therefore, it can be concluded that MnO_x@TiO₂(1:2) presents good stability, high N₂ selectivity, and high SCR activity.

3.5. Influence of H₂O and SO₂ on the catalyst performance

It has been reported that H₂O and SO₂ in exhaust fume can induce the deactivation of catalysts [43]. The effects of H₂O and SO₂ on the NO_x conversion over the MnO_x@TiO₂(1:2) and MnO_x/TiO₂ catalysts at 160 °C are illustrated in Fig. 6. The catalytic activity of both catalysts decreased in the presence of H₂O but recovered quickly the original value once H₂O was removed from the flue gas. This result indicates that the activity decay

induced by H₂O may be due to competitive adsorption with the reactant on the active sites of the catalyst surface [44]. However, when 200 ppm SO₂ was introduced in the reaction system, the NO_x conversion over MnO_x@TiO₂(1:2) and MnO_x/TiO₂ decreased from 100% to 37.3% and 14.0%, respectively, after 5 h at 160 °C, confirming that SO₂ has a poisoning effect on the SCR activity at low temperatures. Upon removal of SO₂, the NO_x conversion over MnO_x@TiO₂(1:2) gradually increased to 40.1% within 2 h with relative stability, while the NO_x conversion over MnO_x/TiO₂ remained almost constant at about 14.0%. When H₂O and SO₂ were introduced in the system together, the NO_x conversion over both catalysts decreased rapidly. After removal of the two poisoning agents, the NO_x conversion over MnO_x@TiO₂(1:2) was still maintained at 22.3%, while the MnO_x/TiO₂ catalyst was completely deactivated, demonstrating that MnO_x@TiO₂(1:2) has better resistance to SO₂ than MnO_x/TiO₂. Considering the similarities between the raw materials, composition, and preparation method, the difference between their SO₂ tolerance must originate from the core-shell structure: the TiO₂ shell protects the MnO_x active core from SO₂ poisoning.

3.6. XPS analysis

The atomic concentration and chemical state of each ele-

Fig. 6. H₂O, SO₂, and H₂O + SO₂ tolerance of MnO_x@TiO₂(1:2) (a) and MnO_x/TiO₂ (b) at 160 °C. Reaction conditions: 500 ppm NO, 500 ppm NH₃, 5% O₂, and balance N₂, with 200 ppm SO₂ and/or 10% H₂O, GHSV = 24,000 h⁻¹.

Fig. 7. XPS high-resolution scans of the Mn 2p (a), Ti 2p (b), O 1s (c), and S 2p (d) peaks for the catalysts. (1) $\text{MnO}_x/\text{TiO}_2$; (2) $\text{MnO}_x@\text{TiO}_2(1:2)$; (3) $\text{MnO}_x/\text{TiO}_2$ after SO_2 ; (4) $\text{MnO}_x@\text{TiO}_2(1:2)$ after SO_2 .

ment on the surface of $\text{MnO}_x/\text{TiO}_2$ and $\text{MnO}_x@\text{TiO}_2(1:2)$ before and after SO_2 deactivation were investigated by XPS measurements. Fig. 7 shows the obtained XPS spectra for Mn 2p, Ti 2p, O 1s, and S 2p, and the corresponding surface atomic concentrations and relative concentration ratio of the different oxidation states are summarized in Table 1.

As shown in Fig. 7(a), the Mn 2p_{3/2} spectra could be deconvoluted into two characteristic peaks attributed to Mn^{3+} (641.60 eV) and Mn^{4+} (643.40 eV) [45], while the Mn 2p_{1/2} peak was centered at 653.44 eV (Mn^{4+}) [5]. As listed in Table 1, the Mn atomic content of $\text{MnO}_x/\text{TiO}_2$ is much higher than that of $\text{MnO}_x@\text{TiO}_2(1:2)$, which is ascribed to the core-shell structure of $\text{MnO}_x@\text{TiO}_2(1:2)$. It is also well known that manganese species in higher oxidation state are more active for the SCR reaction over manganese-based catalysts, since Mn^{4+} ions can promote the oxidation of nitric oxide to NO_2 [46]. Therefore, the higher $\text{Mn}^{4+}/\text{Mn}^{3+}$ ratio in $\text{MnO}_x@\text{TiO}_2(1:2)$ (59.62%) is more suitable for low-temperature SCR and may be one of the reasons behind its higher SCR activity compared to $\text{MnO}_x/\text{TiO}_2$. Furthermore, the Mn atomic content of $\text{MnO}_x@\text{TiO}_2(1:2)$ slightly increased after SO_2 poisoning, while in the case of $\text{MnO}_x/\text{TiO}_2$, the Mn atomic content decreased dramatically to less than half the original value, suggesting that sulfation of

$\text{MnO}_x@\text{TiO}_2(1:2)$ mainly occurs on the TiO_2 shell rather than on the MnO_x core active sites and that corrosion of the shell leads to an increased Mn atomic content on the catalyst surface. The protection of the MnO_x core active sites by the TiO_2 shell is the main reason behind the superior SO_2 resistance of the $\text{MnO}_x@\text{TiO}_2(1:2)$ catalyst.

The Ti 2p spectra shown in Fig. 7(b) reveals that the titanium centers in $\text{MnO}_x@\text{TiO}_2(1:2)$ are mostly in the highest oxidation state (IV) and that there is no obvious difference on the Ti oxidation state after SO_2 poisoning. However, it can be clearly seen that the peaks attributed to Ti^{3+} (at around 643.0 eV [47] and 457.4 eV [48]) are present in $\text{MnO}_x/\text{TiO}_2$ before and after SO_2 deactivation. Owing to the absence of Ti^{3+} on the surface of $\text{MnO}_x@\text{TiO}_2(1:2)$, the Ti 2p_{1/2} and Ti 2p_{3/2} peaks shift to lower binding energies, suggesting that $\text{MnO}_x@\text{TiO}_2(1:2)$ has better stability than $\text{MnO}_x/\text{TiO}_2$. It can also be observed that the Ti atomic percentage in $\text{MnO}_x@\text{TiO}_2(1:2)$ is almost twice that in $\text{MnO}_x/\text{TiO}_2$, possibly due to the good coating of the TiO_2 shell over the MnO_x active center core, in agreement with the TEM and XRD results.

The O 1s peak (Fig. 7(c)) was well fitted as a combination of two kinds of surface oxygen. The peak at ~530.9 eV corresponds to chemisorbed oxygen or hydroxyl groups (O_α), as

Table 1

Atomic surface composition of the catalysts as determined by XPS.

Samples	Atomic composition (%)				Relative atomic ratio (%)			
	Mn	Ti	O	S	Mn		O	
					Mn ⁴⁺	Mn ³⁺	O _α	O _β
MnO _x /TiO ₂	18.13	11.42	55.91	—	57.83	42.17	62.54	37.46
MnO _x @TiO ₂ (1:2)	8.17	22.25	56.98	—	59.62	40.38	15.80	84.20
MnO _x /TiO ₂ after SO ₂	8.75	17.98	56.94	2.40	53.50	46.50	14.46	85.54
MnO _x @TiO ₂ (1:2) after SO ₂	9.10	18.28	56.87	2.26	57.72	42.28	29.81	70.19

cribed to Ti–OH or adsorbed H₂O on the catalyst surface, while the peak at ~529.2 eV is assigned to lattice oxygen (O_β), attributed to Ti–O in the TiO₂ crystal lattice [49]. It can be clearly seen that the binding energies of O_α and O_β over MnO_x@TiO₂(1:2) are shifted to higher values (O_α: 0.6 eV, O_β: 0.6 eV) compared to those for the MnO_x/TiO₂ sample. A higher binding energy indicates new stable covalent bonding [50]. Furthermore, it has been reported that a higher concentration of O_α species is beneficial to the NH₃-SCR of NO [50]. The relative concentration ratio of O_α species in MnO_x/TiO₂ is higher than that in MnO_x@TiO₂(1:2), which may result in higher catalytic activity at lower temperatures. However, the concentration of O_α species in MnO_x@TiO₂(1:2) is higher than in MnO_x/TiO₂ after SO₂ deactivation, which is one of the reasons behind the higher SO₂ tolerance of MnO_x@TiO₂(1:2).

Sulfur species are observed on both MnO_x/TiO₂ and MnO_x@TiO₂(1:2) after SO₂ poisoning, attributed to the sulfur atoms in HSO₄[−] (168.0 eV) and SO₄^{2−} (169.5 eV) [51], suggesting that the components of both catalysts react with SO₂ to form sulfate species. The S atomic content of MnO_x@TiO₂(1:2) is only slightly lower than that of MnO_x/TiO₂ after SO₂ poisoning, indicating that a similar amount of sulfates is formed on both catalysts. However, the great difference between the variation in the Mn content for both samples, which suggests that the sulfates formed on the surface of MnO_x/TiO₂ and MnO_x@TiO₂(1:2) are mainly Mn(SO₄)_x and Ti(SO₄)_y species, respectively, further confirms that the core-shell structure effectively protects the active core of the catalyst.

3.7. NH₃-TPD analysis

It has been proposed that the adsorption of NH₃ on the surface of the catalyst plays a crucial role in the SCR reaction [52]. The adsorption of NH₃ is associated with the surface acidity of the material. Thus, ammonia temperature-programmed desorption measurements were performed in order to investigate the surface acidity of the catalysts before and after SO₂ poisoning. The results are shown in Fig. 8. One broad weak peak ranging from 100 to 300 °C is observed for all samples due to the desorption of NH₃ from weak and medium acidic sites [53]. The strong peak observed at around 710 °C is probably due to the desorption of N₂ [54]. For MnO_x/TiO₂, the desorption peak at 342 °C corresponds to the release of NH₄⁺ from Brønsted acid sites and the peaks at 543 and 592 °C correspond to the desorption of NH₃ from Lewis acid sites [55]. In contrast, the broad weak peak at ~380 °C in the desorption curve of

MnO_x@TiO₂(1:2) can be ascribed to desorption from Brønsted acid sites and the sharp peak at ~648 °C to desorption from Lewis acid sites. The peaks for MnO_x@TiO₂(1:2) are comparatively shifted to higher temperatures, suggesting the presence of stronger Lewis acid sites in MnO_x@TiO₂(1:2) than in MnO_x/TiO₂ [56]. It is well known that Lewis acid sites exert a major influence in SCR systems, which might be key for the higher SCR activity of MnO_x@TiO₂(1:2) compared to that of MnO_x/TiO₂.

After SO₂ poisoning, the peak associated with the Brønsted acid sites of MnO_x/TiO₂ shifts to 377 °C and the peak attributed to Lewis acid sites to 611 °C, suggesting that the adsorption on Lewis acid sites becomes stronger after SO₂ poisoning. The possible reason behind this observation is that the original Lewis acid sites are damaged by SO₂, but the presence of SO₂ enhances the adsorption on Lewis acid sites. In the case of MnO_x@TiO₂(1:2), the peak corresponding to Brønsted acid sites remains almost unchanged and the peak of Lewis acid sites shifts to a lower temperature (640 °C), from which it can be deduced that the Lewis acid sites are also damaged by SO₂ and that SO₂ adsorption is concentrated on the TiO₂ shell, resulting in the higher tolerance of MnO_x@TiO₂(1:2) toward SO₂.

3.8. H₂-TPR analysis

In order to investigate the redox capability of the catalysts, hydrogen temperature-programmed reduction experiments

Fig. 8. NH₃-TPD profiles of the catalysts (MnO_x@TiO₂ refers to the catalyst with Mn:Ti = 1:2).

Fig. 9. H₂-TPR profiles of the catalysts (MnO_x@TiO₂ refers to the catalyst with Mn:Ti = 1:2).

were carried out. As illustrated in Fig. 9, MnO_x/TiO₂ shows three distinctive peaks at 340, 480, and 513 °C, corresponding to the stepwise reduction of MnO₂ to Mn₂O₃, Mn₂O₃ to Mn₃O₄, and Mn₃O₄ to MnO, respectively [30]. For MnO_x@TiO₂(1:2), the corresponding temperature of the first peak shifts to 345 °C, suggesting that the wrapping effect of TiO₂ slightly weakens the oxidation ability of MnO₂. However, the latter two peaks shift to lower temperatures (380 and 410 °C), indicating an enhancement of the oxidation capability of the surface Mn species [57,58].

The three distinct reduction peaks for MnO_x/TiO₂ and MnO_x@TiO₂(1:2) after SO₂ poisoning are clearly seen in Fig. 9. All these three peaks shift to higher temperatures after poisoning, indicating that SO₂ has reacted with MnO_x and destroyed some active centers that could interact with NO_x.

3.9. Discussion

A novel MnO_x@TiO₂ core-shell nanorod catalyst with high NH₃-SCR catalytic activity was successfully fabricated via a new two-step method (a hydrothermal process followed by a versatile kinetics-controlled coating method), in which abundant TiO₂ nanoparticles are evenly distributed on the surface of MnO_x nanorods. At the same time, no core-shell structure was observed for the counterpart MnO_x/TiO₂ catalyst. Based on the catalytic activity and XPS analyses, the lower catalytic activity of MnO_x@TiO₂(1:2) below 90 °C may be attributed to fewer O_α species, as mentioned in the discussion of Fig. 7(c). However, the higher catalytic activity of MnO_x@TiO₂(1:2) compared to that of MnO_x/TiO₂ with the increasing temperature (>90 °C) is the result of a larger number of strong Lewis acid sites and higher redox capacity, as proven by the NH₃-TPD and H₂-TPR results.

Moreover, MnO_x@TiO₂(1:2) shows higher enhanced SO₂ and H₂O tolerance. As mentioned before, considering the similarities between the two samples, the reason behind MnO_x@TiO₂(1:2) exhibiting a higher SO₂ resistance than MnO_x/TiO₂ may be the result of its unique core-shell structure.

Fig. 10. Mechanism of the SCR of NO_x with NH₃ over MnO_x@TiO₂(1:2) in the presence of SO₂.

The concentration of O_α species and Mn atomic content in MnO_x@TiO₂(1:2) slightly increased after exposure to SO₂. The content of sulfur in MnO_x@TiO₂(1:2) was almost that in MnO_x/TiO₂ after SO₂ poisoning. All these results suggest that sulfation of MnO_x@TiO₂(1:2) occurs mainly on the TiO₂ shell rather than on the MnO_x core active sites, and that the corrosion of the shell leads to an increase of the Mn atomic content on the surface of the catalyst. According to the NH₃-TPD results, the Lewis acid sites on MnO_x@TiO₂(1:2) are damaged by SO₂, but SO₂ is effectively isolated on the TiO₂ shell, affording the observed higher tolerance of MnO_x@TiO₂(1:2) toward SO₂. The uniform distribution of the MnO_x core and the protection of the TiO₂ shell minimize the poisoning of surface active sites by SO₂, resulting in high stability and improved SO₂ tolerance.

Fig. 10 presents a schematic of the composition changes in the MnO_x@TiO₂(1:2) catalyst in the presence of SO₂. The presence of a TiO₂ shell inhibits the formation of MnSO₄ and hinders the reaction of SO₂ with the active material, thus protecting the Mn-related active sites. This is an important factor to explain the higher SO₂ tolerance of MnO_x@TiO₂(1:2) compared to that of catalysts lacking a core-shell structure.

4. Conclusions

In summary, a novel MnO_x@TiO₂ core-shell nanorod catalyst with high NH₃-SCR catalytic activity was successfully fabricated via a new two-step method. The catalyst exhibits high activity, excellent N₂ selectivity, high stability, and enhanced SO₂ and H₂O tolerance for the low-temperature SCR of NO_x with NH₃. The uniform distribution of the MnO_x core and protection of the TiO₂ shell minimize the exposure of surface active sites to SO₂, reducing the formation of byproducts such as (NH₄)₂SO₃ and NH₄HSO₄, which hence affords high stability and improved SO₂ tolerance. Our study provides a novel method to solve the SO₂ poisoning problem of low-temperature SCR catalysts.

References

- [1] N. Z. Yang, R. T. Guo, W. G. Pan, Q. L. Chen, Q. S. Wang, C. Z. Lu, *Fuel*, **2016**, 169, 87–92.
- [2] M. Casapu, O. Kröcher, M. Mehring, M. Nachtegaal, C. Borca, M.

Graphical Abstract

Chin. J. Catal., 2018, 39: 821–830 doi: 10.1016/S1872-2067(18)63059-1

Synthesis of novel $\text{MnO}_x/\text{TiO}_2$ core-shell nanorod catalyst for low-temperature NH_3 -selective catalytic reduction of NO_x with enhanced SO_2 tolerance

Zhongyi Sheng, Dingren Ma, Danqing Yu, Xiang Xiao, Bingjie Huang, Liu Yang *, Sheng Wang
 Nanjing Normal University; Wuhan University of Science and Technology;
 Suzhou Industrial Technology Research Institute of Zhejiang University;
 State Power Environmental Protection Research Institute

This work reports a novel $\text{MnO}_x/\text{TiO}_2$ core-shell nanorod catalyst, which exhibits high activity and enhanced SO_2 tolerance for the low-temperature selective catalytic reduction of NO_x with NH_3 due to the protective effect of the TiO_2 shell.

- Harfouche, D. Grolimund, *J. Phys. Chem. C*, **2010**, 114, 9791–9801.
- [3] T. Zhang, R. Y. Qu, W. K. Su, J. H. Li, *Appl. Catal. B*, **2015**, 176–177, 338–346.
- [4] T. Boningari, P. R. Ettireddy, A. Somogyvari, Y. Liu, A. Vorontsov, C. A. McDonald, P. G. Smirniotis, *J. Catal.*, **2015**, 325, 145–155.
- [5] A. Y. Zhou, D. Q. Yu, L. Yang, Z. Y. Sheng, *Appl. Surf. Sci.*, **2016**, 378, 167–173.
- [6] M. Shelef, *Chem. Rev.*, **1995**, 95, 209–225.
- [7] K. Cheng, T. Zhang, J. M. Li, Y. C. Wei, G. Y. Jiang, A. J. Duan, J. Liu, Z. Zhao, *J. Environ. Sci.*, **2014**, 26, 2106–2113.
- [8] M. Stanculescu, G. Caravaggio, A. Dobri, J. Moir, R. Burich, J. P. Charlard, P. Bultink, *Appl. Catal. B*, **2012**, 123–124, 229–240.
- [9] B. Thirupathi, P. G. Smirniotis, *J. Catal.*, **2012**, 288, 74–83.
- [10] Y. Li, Y. P. Li, Y. Wan, S. H. Zhan, Q. X. Guan, Y. Tian, *RSC Adv.*, **2016**, 6, 54926–54937.
- [11] K. Zhuang, J. Qiu, F. S. Tang, B. L. Xu, Y. N. Fan, *Phys. Chem. Chem. Phys.*, **2011**, 13, 4463–9.
- [12] S. J. Yang, F. H. Qi, S. C. Xiong, H. Dang, Y. Liao, P. K. Wong, J. H. Li, *Appl. Catal. B*, **2016**, 181, 570–580.
- [13] Z. B. Wu, R. B. Jin, Y. Liu, H. Q. Wang, *Catal. Commun.*, **2008**, 9, 2217–2220.
- [14] Z. B. Wu, B. Q. Jiang, Y. Liu, H. Q. Wang, R. B. Jin, *Environ. Sci. Technol.*, **2007**, 41, 5812–7.
- [15] J. Liu, X. Y. Li, R. Y. Li, Q. D. Zhao, J. Ke, H. N. Xiao, L. D. Wang, S. M. Liu, M. Tade, S. B. Wang, *Appl. Catal. A*, **2018**, 549, 289–301.
- [16] R. T. Guo, P. Sun, W. G. Pan, M. Y. Li, S. M. Liu, X. Sun, S. W. Liu, J. Liu, *Ind. Eng. Chem. Res.*, **2017**, 56, 12566–12577.
- [17] R. B. Jin, Y. Liu, Y. Wang, W. L. Cen, Z. B. Wu, H. Q. Wang, X. L. Weng, *Appl. Catal. B*, **2014**, 148–149, 582–588.
- [18] Z. Y. Sheng, Y. F. Hu, J. M. Xue, X. M. Wang, W. P. Liao, *J. Rare Earths*, **2012**, 30, 676–682.
- [19] X. Xiao, S. C. Xiong, Y. J. Shi, W. P. Shan, S. J. Yang, *J. Phys. Chem. C*, **2016**, 120, 1066–1076.
- [20] B. Q. Jiang, Z. B. Wu, Y. Liu, S. C. Lee, W. K. Ho, *J. Phys. Chem. C*, **2010**, 114, 4961–4965.
- [21] Z. G. Huang, Z. P. Zhu, Z. Y. Liu, Q. Y. Liu, *J. Catal.*, **2003**, 214, 213–219.
- [22] L. Zhang, D. S. Zhang, J. P. Zhang, S. X. Cai, C. Fang, L. Huang, H. R. Li, R. H. Gao, L. Y. Shi, *Nanoscale*, **2013**, 5, 9821–9829.
- [23] G. D. Li, Z. Y. Tang, *Nanoscale*, **2014**, 6, 3995–4011.
- [24] Z. Ma, S. Dai, *ACS Catal.*, **2011**, 1, 805–818.
- [25] H. Q. Wang, X. B. Chen, X. L. Weng, Y. Liu, S. Gao, Z. B. Wu, *Catal. Commun.*, **2011**, 12, 1042–1045.
- [26] X. B. Chen, S. Cao, X. L. Weng, H. Q. Wang, Z. B. Wu, *Catal. Commun.*, **2012**, 26, 178–182.
- [27] X. B. Chen, H. Q. Wang, G. Shan, Z. B. Wu, *J. Colloid Interf. Sci.*, **2012**, 377, 131–136.
- [28] D. K. Pappas, T. Boningari, P. Boolchand, P. G. Smirniotis, *J. Catal.*, **2016**, 334, 1–13.
- [29] J. M. Sun, X. H. Bao, *Chem. Eur. J.*, **2008**, 14, 7478–7488.
- [30] W. Chen, X. L. Pan, X. H. Bao, *J. Am. Chem. Soc.*, **2007**, 129, 7421–7426.
- [31] X. Zhang, W. S. Yang, J. J. Yang, D. G. Evans, *J. Cryst. Growth*, **2008**, 310, 716–722.
- [32] W. Li, J. P. Yang, Z. X. Wu, J. X. Wang, B. Li, S. S. Feng, Y. H. Deng, F. Zhang, D. Y. Zhao, *J. Am. Chem. Soc.*, **2012**, 134, 11864–11867.
- [33] S. H. Liang, F. Teng, G. Bulgan, R. L. Zong, Y. F. Zhu, *J. Phys. Chem. C*, **2008**, 112, 5307–5315.
- [34] Y. Dai, J. H. Li, Y. Peng, X. F. Tang, *Acta Phys. Chim. Sin.*, **2012**, 28, 1771–1776.
- [35] S. C. Xiong, Y. Liao, H. Dang, F. H. Qi, S. J. Yang, *RSC Adv.*, **2015**, 5, 27785–27793.
- [36] P. L. Wang, H. Q. Wang, X. B. Chen, Y. Liu, X. L. Weng, Z. B. Wu, *J. Mater. Chem. A*, **2014**, 3, 680–690.

- [37] L. Qian, Z. L. Du, S. Y. Yang, Z. S. Jin, *J. Mol. Struct.*, **2005**, 749, 103–107.
- [38] D. Salinas, P. Araya, S. Guerrero, *Appl. Catal. B*, **2012**, 117, 260–267.
- [39] F. Kapteijn, A. D. Vanlangeveld, J. A. Moulijn, A. Andreini, M. A. Vuurman, A. M. Turek, J. M. Jehng, I. E. Wachs, *J. Catal.*, **1994**, 150, 94–104.
- [40] D. Gosztola, M. J. Weaver, *J. Electroanal. Chem.*, **1989**, 271, 141–154.
- [41] C. M. Julien, *Solid State Ionics*, **2006**, 177, 11–19.
- [42] Y. J. Xie, Y. Y. Yu, X. Q. Gong, Y. Guo, Y. L. Guo, Y. Q. Wang, G. Z. Lu, *CrystEngComm*, **2015**, 17, 3005–3014.
- [43] K. Skalska, J. S. Miller, S. Ledakowicz, *Sci. Total Environ.*, **2010**, 408, 3976–3989.
- [44] X. N. Lu, C. Y. Song, S. H. Jia, Z. S. Tong, X. L. Tang, Y. X. Teng, *Chem. Eng. J.*, **2015**, 260, 776–784.
- [45] Z. H. Chen, Q. Yang, H. Li, X. H. Li, L. F. Wang, S. C. Tsang, *J. Catal.*, **2010**, 276, 56–65.
- [46] X. F. Tang, J. H. Li, J. M. Hao, *Catal. Commun.*, **2010**, 11, 871–875.
- [47] D. Gonbeau, C. Guimon, G. Pfister-Guillouzo, A. Levasseur, G. Meunier, R. Dormoy, *Surf. Sci.*, **1991**, 254, 81–89.
- [48] F. Werfel, O. Brümmer, *Phys. Scr.*, **1983**, 28, 92–96.
- [49] Z. B. Wu, Z. Y. Sheng, Y. Liu, H. Q. Wang, J. S. Mo, *J. Hazard. Mater.*, **2011**, 185, 1053–1058.
- [50] B. X. Shen, Y. Yao, J. H. Chen, X. P. Zhang, *Microporous Mesoporous Mater.*, **2013**, 180, 262–269.
- [51] H. B. Fu, X. Wang, H. B. Wu, Y. Xin, J. M. Chen, *J. Phys. Chem. C*, **2007**, 111, 6077–6085.
- [52] N. Y. Topsøe, *Science*, **1994**, 265, 1217–9.
- [53] F. Lonyi, J. Valyon, J. Engelhardt, F. Mizukami, *J. Catal.*, **1996**, 160, 279–289.
- [54] Y. Wang, *Acta Chim. Sin.*, **2006**, 64, 1611–1614.
- [55] D. Wang, Y. Jangjou, Y. Liu, M. K. Sharma, J. Y. Luo, J. H. Li, K. Kamasudram, W. S. Epling, *Appl. Catal. B*, **2015**, 165, 438–445.
- [56] X. Xiao, Z. Y. Sheng, L. Yang, F. Dong, *Catal. Sci. Technol.*, **2015**, 6, 1507–1514.
- [57] B. Thirupathi, P. G. Smirniotis, *Appl. Catal. B*, **2011**, 110, 195–206.
- [58] B. Thirupathi, P. G. Smirniotis, *J. Catal.*, **2012**, 288, 74–83.

低温 NH_3 -SCR 新型 $\text{MnO}_x/\text{TiO}_2$ 纳米棒核壳结构催化剂的合成及抗 SO_2 性能研究

盛重义^{a,c}, 麻丁仁^a, 俞丹青^b, 肖 香^c, 黄冰洁^a, 杨 柳^{a,*}, 王 圣^d

^a南京师范大学环境学院, 江苏南京210023

^b武汉科技大学化学工程与技术学院, 湖北武汉430081

^c浙江大学苏州工业技术研究院, 江苏苏州215163

^d国电环境保护研究院, 江苏南京210031

摘要: 氮氧化物 (NO_x) 是造成大气污染的主要来源之一, 严重威胁人类的身体健康. 选择性催化还原 (SCR) 技术由于其独特的优势而受到青睐. 但 SCR 催化剂容易受到 SO_2 的侵蚀而失活, 使用寿命降低. 开发具有抗硫能力强的高活性催化剂已成为脱硝技术研究的热点. 核壳结构催化剂由于其独特的外壳结构能有效地减少活性物质与 SO_2 的接触, 减少催化剂中毒, 延长催化剂的使用寿命. 而水热合成法能有效控制催化剂的外形结构, 动力学外裹法能将物质均匀分布在被包裹物质的表面, 两者结合有利于核壳结构催化剂的合成.

本文采用两步法 (水热法 + 动力学外包裹法) 制备的 $\text{MnO}_x/\text{TiO}_2$ 纳米棒核壳结构低温脱硝催化剂具有高活性、高稳定性和优异的 N_2 选择性. 此外, 与 MnO_x , TiO_2 和 $\text{MnO}_x/\text{TiO}_2$ 等纳米材料相比, $\text{MnO}_x/\text{TiO}_2$ 具有更好的 SO_2 和 H_2O 抗性, 表明 $\text{MnO}_x/\text{TiO}_2$ 具备良好的运用前景. 采用 TEM, HR-TEM, XRD, Raman, BET, XPS, NH_3 -TPD 和 H_2 -TPR 等方法对催化剂进行了系统的表征. TEM 和 HR-TEM 结果表明, $\text{MnO}_x/\text{TiO}_2$ 表现出明显的核壳结构, 且 TiO_2 颗粒均匀分布在 MnO_x 纳米棒上. XRD 和 Raman 结果发现 $\text{MnO}_x/\text{TiO}_2$ 中含有 MnO_2 , 从而保证了 $\text{MnO}_x/\text{TiO}_2$ 具有良好的脱硝活性. 同时, BET, NH_3 -TPD 和 H_2 -TPR 等结果表明, $\text{MnO}_x/\text{TiO}_2$ 具有丰富的中孔结构和路易斯酸位点, 以及强氧化还原能力, 因而其催化性能提高. 根据 SO_2 侵蚀后的 XPS 结果, $\text{MnO}_x/\text{TiO}_2$ 与 $\text{MnO}_x/\text{TiO}_2$ 相比, 两者中的 S 元素含量差异小, 但前者中的 Mn^{4+} 降低量远少于后者. 表明 $\text{MnO}_x/\text{TiO}_2$ 的核壳结构可以在 SO_2 存在条件下有效地保护活性位点, 因而具有更强的 SO_2 抗性.

关键词: 低温选择性催化还原; 核壳结构; 纳米棒; 二氧化硫抗性; 锰氧化物

收稿日期: 2018-02-19. 接受日期: 2018-03-12. 出版日期: 2018-04-05.

*通讯联系人. 电话/传真: (025)85891455; 电子邮箱: 15700079861@163.com

基金来源: 国家自然科学基金 (51508281, 41771498); 江苏省高校自然科学研究面上项目 (16KJD610001).

本文的电子版全文由Elsevier出版社在ScienceDirect上出版 (<http://www.sciencedirect.com/science/journal/18722067>).