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Article

Effects of surface physicochemical properties on NH₃-SCR activity of MnO₂ catalysts with different crystal structures

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ABSTRACT

α -, β -, δ -, and γ -MnO₂ nanocrystals are successfully prepared. We then evaluated the NH₃ selective catalytic reduction (SCR) performance of the MnO₂ catalysts with different phases. The NO_x conversion efficiency decreased in the order: γ -MnO₂ > α -MnO₂ > δ -MnO₂ > β -MnO₂. The NO_x conversion with the use of γ -MnO₂ and α -MnO₂ catalysts reached 90% in the temperature range of 140–200 °C, while that based on β -MnO₂ reached only 40% at 200 °C. The γ -MnO₂ and α -MnO₂ nanowire crystal morphologies enabled good dispersion of the catalysts and resulted in a relatively high specific surface area. We found that γ -MnO₂ and α -MnO₂ possessed stronger reducing abilities and more and stronger acidic sites than the other catalysts. In addition, more chemisorbed oxygen existed on the surface of the γ -MnO₂ and α -MnO₂ catalysts. The γ -MnO₂ and α -MnO₂ catalysts showed excellent performance in the low-temperature SCR of NO to N₂ with NH₃.

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1. Introduction

Nitrogen oxides (NO_x) such as NO, NO₂, and N₂O are major air pollutants that cause adverse environmental effects, including photochemical smog, acid rain, and ozone depletion [1,2]. Nitrogen oxides also cause harm to the human body [3,4]. Technologies based on NH₃ selective catalytic reduction (SCR) are among the most effective methods of dealing with nitrogen oxides and have been widely applied [5]. The general reaction is as follows [6]:

The catalyst WO₃-V₂O₅/TiO₂ is the most widely used commercially owing to its high activity [7–9]. However, this catalyst is only active within a narrow temperature range of 300–400 °C. Thus, it cannot be applied to kiln tail gas treatments, because the exhaust gas temperature of cement kiln is between

80 and 200 °C [10]. For this reason, there has been strong interest in developing more active catalysts for low-temperature SCR [11,12].

Great efforts have recently been made to develop efficient catalysts for low-temperature SCR of NO by NH₃, and manganese oxide-based catalysts are among the most active catalysts [13–17]. Manganese oxides have attracted interest for applications to low-temperature SCR catalysts because they feature various labile oxygen sites, which are necessary to complete the catalytic cycle [18]. Pena et al. [19] studied the catalytic activity of the first-row transition metals, i.e., V, Cr, Mn, Fe, Co, Ni, and Cu, supported on TiO₂, and found that the activities followed the order: Mn > Cu > Cr > Co > Fe > V ≥ Ni. Kapteijn et al. [20] intensively investigated the catalytic activities and selectivities of pure manganese oxides in SCR. These results suggested that MnO₂ exhibited the best catalytic activity, followed by Mn₅O₈,

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Mn₂O₃, Mn₃O₄, and MnO. In recent years, our group has also performed a number of studies into the catalytic principle of manganese oxides [21–23].

MnO₂ exists in different phases, including α -, β -, δ - and γ -MnO₂ phases, in which MnO₆ octahedral units are linked in different ways [24–28]. The phase structure can considerably influence the catalytic activity of MnO₂ [29–31]. Carefully designed crystal forms of MnO₂ can exhibit good catalytic performance, particularly for electrocatalysis and CO catalysis, and have attracted considerable attention and research interest [32–37]. However, few studies have focused on the SCR performance of NO with NH₃ and the reaction mechanisms over different MnO₂ nanocrystals [38,39]. The α -, β -, δ -, and γ -MnO₂ oxides feature different catalytic functionalities, and the relationship between different crystal forms of MnO₂ and its catalytic activities in SCR have yet to be revealed.

In this study, different MnO₂ crystals, including α -, β -, δ -, and γ -MnO₂, were successfully prepared. The effects of the different MnO₂ crystals on NH₃-SCR are investigated. X-ray diffraction (XRD) together with various characterization methods, including Raman spectroscopy, scanning electron microscopy (SEM), thermogravimetric analysis (TGA), temperature-programmed reduction by H₂ (H₂-TPR), temperature-programmed desorption of NH₃ (NH₃-TPD), and X-ray photoelectron spectroscopy (XPS), were used to elucidate the factors affecting the catalytic properties of different MnO₂ crystals.

2. Experimental

2.1. Catalyst preparation

In a typical synthesis of the α -MnO₂ crystals, 10 mmol KMnO₄ and 10 mmol MnSO₄·H₂O were mixed in distilled water (100 mL) and magnetically stirred for 20 min to form a homogeneous mixture. The resulting mixture was transferred into a Teflon-lined stainless-steel autoclave (150 mL) and heated at 180 °C for 24 h. The reactor was cooled to room temperature, and the products washed several times with distilled water and ethanol, dried at 110 °C for 24 h, and heated at 350 °C for 5 h [40]. The β -MnO₂ crystals were obtained from thermal decomposition of Mn(NO₃)₂. A 10-mL portion of 50 wt% Mn(NO₃)₂ was transferred into a crucible, which was then heated to 350 °C for 5 h [41]. Similarly, δ -MnO₂ was prepared by thermal decomposition of KMnO₄. The KMnO₄ powder was heated at 350 °C for 5 h and then allowed to cool naturally. The obtained product was washed with deionized water several times and dried at 80 °C overnight. These samples were also heated at 350 °C [42]. The γ -MnO₂ crystals were obtained from the reaction of MnCl₂·4H₂O (6 mmol) and (NH₄)₂S₂O₈ (12 mmol), which were dissolved in 100 mL distilled water to form a homogeneous solution. Then, the mixed solution was transferred into a 150 mL Teflon-lined stainless-steel autoclave and heated at 90 °C for 24 h. The product was filtered, washed with distilled water and ethanol, and dried at 60 °C for 6 h. Finally, the samples were heated at 350 °C for 5 h [43].

2.2. Characterization

Powder XRD patterns were used to identify the phase structures of the obtained catalysts. Patterns were obtained with a D8 Advance diffractometer (Bruker, German) with Cu K α radiation (λ = 0.15406 nm) over a 2θ range from 10° to 80°. The crystalline phases were identified by comparison with reference data from the International Center for Diffraction Data (ICDD) files. Raman spectroscopy was used to characterize the structures, obtained with a Renishaw Raman spectrometer, which was equipped with a 632.8 nm laser, and the scanning range was 1000–100 cm⁻¹. High-resolution SEM (JSM-5610LV, Japan) was used to observe the micro-morphology of the catalysts (acceleration voltage 0.5–30 kV). A thermogravimetric analysis-mass spectrometer (TG, STA449, NETZSCH Analyzing and Testing, Germany) was used to measure TGA profiles for different series of catalysts in N₂ to prevent oxidation; the heating rate was 10 °C/min between 50 and 900 °C.

NH₃-TPD data were measured with an automated catalyst characterization system (Thermo, USA). Approximately 150 mg of finely ground sample was pretreated by heating in 20 mL/min of pure He from ambient to 300 °C at 20 °C/min, with a 60-min hold, after which the sample temperature was lowered to room temperature. Next, 10% NH₃/90% He was passed over the sample for 30 min, until the adsorption of NH₃ on the catalyst surface was saturated, and then the sample was heated with He to remove the adsorbed NH₃ at a rate of 10 °C/min up to 350 °C.

H₂-TPR experiments were performed on an automated catalyst characterization system (TPDRO1100, Thermo, USA) with a thermal conductivity detector (TCD). Prior to the H₂-TPR measurements, all samples were pretreated at 200 °C for 1 h in nitrogen (20 mL/min) and then cooled to 40 °C. During H₂-TPR, a flow of 5% H₂/95% N₂ was fed to approximately 50 mg of MnO₂ at a rate of 30 mL/min, and the MnO₂ was tested by increasing the temperature from 100 to 800 °C at a rate of 10 °C/min. The temperature was maintained at 800 °C for 30 min to allow the signal intensities of the hydrogen to return to their initial values. The amount of H₂ consumed by MnO₂ over a given temperature range was calculated by TCD.

To determine the surface atomic concentration and characterize the chemical states of the catalysts, XPS was implemented with a surface analysis system (VG Multilab 2000) operating at 10⁻⁹ Pa with Al K α radiation (1486.6 eV). The observed spectra were corrected with the use of the C 1s line at 284.6 eV as a standard.

2.3. Catalytic activity

The activity measurements were performed in a self-designed reactor containing a special glass tube (internal diameter (i.d.) = 20 mm), a temperature programming controller, and the feed gas mixture system. Prior to the SCR performance, about 2000 mg of the catalyst was pressed into tablets (i.d. 5 mm). The typical reaction conditions were as follows: [NO] = 720 ppm, [NH₃] = 800 ppm, [O₂] = 3 vol%, N₂ balance, and gas hourly space velocity (GHSV) of 30 000 h⁻¹. In addition, the reaction system was maintained at each reaction temperature for 30 min to achieve a steady state at reaction temperatures

ranging from 80 to 200 °C. The concentrations of feed gases were analyzed continuously with an off-gas analysis spectrometer (Gasboard-3800P). The N_2 and N_2O in the effluent were separated at 80 °C with a HeySep D column and their concentrations were analyzed with a thermal conductive detector (TCD) fitted to a gas chromatograph (Hewlett-Packard, HP 5890). The conversion of NO_x was calculated as $([NO]_{in} - [NO]_{out})/[NO]_{in}$ to evaluate the activity of each catalyst, and the N_2 selectivity was calculated as $(1 - 2[N_2O]_{out}/([NO]_{in} - [NO]_{out}))$.

3. Results and discussion

3.1. Structure characterization (XRD and Raman)

Figure 1 shows XRD patterns of the different MnO_2 crystals. The pattern in Figure 1(1) was indexed to the pure MnO_2 tetragonal phase. The lattice constants were in good agreement with those of α - MnO_2 (JCPDS 44-0141) [40], and the diffraction peaks at $2\theta = 12.8^\circ, 18.1^\circ, 28.7^\circ, 37.6^\circ, 41.9^\circ, 49.8^\circ, 56.4^\circ, 60.4^\circ$, and 69.5° could be exclusively indexed to the (110), (200), (310), (211), (301), (411), (600), (521), and (541) planes, respectively. The XRD patterns in Figure 1(2), (3) and (4) also corresponded well to those for the crystal structures of β - MnO_2 (JCPDS 24-0735), δ - MnO_2 (JCPDS 80-1098), and γ - MnO_2 (JCPDS 44-0412), respectively [45–50]. The diffraction peaks of β - MnO_2 at $28.7^\circ, 37.4^\circ, 41.1^\circ, 42.8^\circ, 56.8^\circ, 59.4^\circ$, and 65.1° could be exclusively indexed to the (110), (101), (200), (111), (211), (220), and (002) planes, respectively. The diffraction peaks of δ - MnO_2 at $12.3^\circ, 24.8^\circ$, and 36.4° corresponded well to the (001), (002), and (111) planes, respectively. Similarly, the diffraction peaks of γ - MnO_2 at $29.1^\circ, 37.4^\circ, 42.8^\circ$, and 56.8° could be exclusively indexed to (120), (131), (300), and (160) planes, respectively. The β - MnO_2 , δ - MnO_2 , and γ - MnO_2 structures were respectively a tetragonal phase, rhombic system, and monoclinic system. It has been reported that α - MnO_2 features a (2×2) tunnel structure. β - MnO_2 has an anatase structure with square symmetry, which is relatively stable. The structure of δ - MnO_2 is layered with large amounts of metal ions, hydroxyl, and water molecules between layers. γ - MnO_2 has a single bond (1×1) and

double bond (1×2) alternating structure, which is unstable and collapses easily [46–48].

Raman spectroscopy can be used to further identify the crystal structure of MnO_2 . The Raman spectra of four different MnO_2 crystals are shown in Figure 2. Raman peaks of α - MnO_2 were observed at 182, 573, and 646 cm^{-1} , while only a single distinct Raman peak was found for β - MnO_2 , δ - MnO_2 , and γ - MnO_2 at 664, 643, and 642 cm^{-1} , respectively [33]. Some references indicate that the Raman peak at 182 cm^{-1} is the deformation vibration of the M–O–M bond, and the peaks at 664, 643, and 642 cm^{-1} are lattice vibrations of the M–O bond [47]. Figure 2 clearly shows that the M–O bond vibration was observed in all four samples, which further indicated that the materials were MnO_2 . These results also verify the conclusions from our XRD analysis.

3.2. Catalytic performance

The SCR activities of the α -, β -, δ -, and γ - MnO_2 oxides were tested. Their different catalytic activities are clearly shown in Figure 3. Here, we only discuss the catalytic activity at low temperatures (80–200 °C). From Figure 3(a), the γ - and δ - MnO_2 catalysts showed almost the same catalytic activities, and the NO_x conversion was approximately 50% (i.e., the NO_x of the conversion on the α - MnO_2 catalyst reached 56%) at temperatures in the range of 80–100 °C. Above 140 °C, the catalytic activities reached 90%, with the best catalytic activity at 180 °C (approximately 95%). The activities remained stable to further increases of temperature. The two catalysts exhibited minor differences in NO_x conversion, and the activity of α - MnO_2 was 4% lower than that of γ - MnO_2 at the same temperature. The δ - MnO_2 catalytic activity was lower, achieving 79% at 160 °C and then gradually decreasing. The β - MnO_2 showed the lowest catalytic activity, of 10% from 80 to 120 °C and 40% at 200 °C.

The SCR activities of the MnO_2 , determined by normalization by surface area (specific activity), are shown in Figure 3(b). The specific activity followed the opposite trend to that of the conversion, as shown in Figure 3(a). Although, the specific activity of β - MnO_2 was better than those of the other three MnO_2 nanocrystals, its low surface area resulted in poor conversion.

Fig. 1. XRD patterns of four different MnO_2 nanocrystals. (1) α - MnO_2 ; (2) β - MnO_2 ; (3) δ - MnO_2 ; (4) γ - MnO_2 .

Fig. 2. Raman profiles of four different MnO_2 nanocrystals. (1) α - MnO_2 ; (2) β - MnO_2 ; (3) δ - MnO_2 ; (4) γ - MnO_2 .

Fig. 3. (a) NO_x conversion, (b) specific activity and (c) N₂ selectivity of four different MnO₂ nanocrystals at different temperatures. (1) α -MnO₂; (2) β -MnO₂; (3) δ -MnO₂; (4) γ -MnO₂.

Figure 3(c) shows that the N₂ selectivity on γ -MnO₂ was the best, followed by α - and δ -MnO₂. As the temperature was increased, the N₂ selectivity on all the catalysts decreased, indicating that at higher temperatures a higher proportion of N₂O was present in the products.

3.3. Microstructure analysis and specific surface area (SEM and BET)

SEM images of the four MnO₂ samples, examined at different magnification levels, are shown in Figure 4. The α - and γ -MnO₂ samples appeared as nanowires. Furthermore, the β -MnO₂ catalyst featured a bulk nanostructure and δ -MnO₂ featured a globular structure with many side outgrowths. According to the activity results, the nanowire structures of MnO₂ (γ -MnO₂ and α -MnO₂) showed the best catalytic activities, followed by the globular structure with the outgrowths (δ -MnO₂). The bulk nanostructure (β -MnO₂) featured the lowest catalytic activity.

Catalytic activity depends on the active center of the catalyst, and active sites are generally considered to be uniformly distributed over the surface of the catalyst. Thus, a larger over-

all surface area can provide more active catalyst centers, leading to higher catalytic activity [48]. The BET data in Table 1 show that γ -MnO₂ had the largest specific surface area, followed by α -MnO₂, δ -MnO₂, and β -MnO₂. In addition, the pore volume decreased in the order: γ -MnO₂ > α -MnO₂ > δ -MnO₂ > β -MnO₂. These physical properties were in accordance with the observed catalytic activities. Table 1 indicates that γ -MnO₂ featured the largest specific surface of 103.98 m²/g, while that of α -MnO₂ was 82.69 m²/g. Thus, more active sites were dispersed on their surfaces, which increased the probability of NH₃ contact with active sites and NO_x conversion. In addition, β -MnO₂ had the lowest specific surface area among the four different MnO₂ crystals, which might explain its low catalytic activity. Noticeably, the specific surface area of α -MnO₂ was approximately two times greater than that of δ -MnO₂, whereas NO_x conversion on α -MnO₂ and δ -MnO₂ did not show the same trend, and featured no major differences below 100 °C and differences of only 5%–15% in the range of 100–200 °C. This result implies that the specific surface area is one factor leading to the distinctive catalytic activity of the different MnO₂ nanocrystals, but not the main reason.

Fig. 4. SEM images of four different MnO₂ nanocrystals examined under different magnifications. (a) α -MnO₂; (b) β -MnO₂; (c) δ -MnO₂; (d) γ -MnO₂. (1) $\times 20\,000$; (2) $\times 40\,000$.

Table 1Physical properties of α -, β -, δ -, and γ -MnO₂.

Catalyst	$A_{\text{BET}}/(\text{m}^2/\text{g})$	$V_{\text{F}}/(\text{cm}^3/\text{g})$
α -MnO ₂	82.67	0.18
β -MnO ₂	3.28	0.016
δ -MnO ₂	49.45	0.093
γ -MnO ₂	103.97	0.23

The SEM images indicated that γ - and α -MnO₂ formed well-dispersed nanowire structures. The surface areas of γ -MnO₂ and α -MnO₂ were also reasonably large, which provided more active sites to promote the adsorption and transformation of gases; together these factors likely contributed to the high catalytic activity of these catalysts. The surface area of γ -MnO₂ was also larger than that of α -MnO₂. The β -MnO₂ catalyst showed agglomeration, which reduced its surface area. Furthermore, some nanospheres with outgrowths on their surfaces were found in δ -MnO₂. These outgrowths were responsible for the slightly higher surface area of δ -MnO₂ compared with that of β -MnO₂. The spherical structures with outgrowths might have contributed to the higher catalytic activity of δ -MnO₂ than that of β -MnO₂.

3.4. TGA

TGA profiles are shown in Figure 5. The initial mass loss below 250 °C is generally attributed to the loss of physically and chemically adsorbed water, including loosely bound and tightly bound (interlayer) H₂O molecules [49]. The initial mass losses of α -MnO₂, β -MnO₂, δ -MnO₂, and γ -MnO₂ were 0.98%, 0.17%, 4.49%, and 2.18%, respectively. The water loss of δ -MnO₂ was much larger than those of the other three structures, suggesting the existence of many water molecules remaining between the layers even after the heat treatment. Only minimal water losses were found for β -MnO₂, owing to the long high-temperature calcination. Hydroxyl groups (interlayer water) are Brönsted acid sites, which can promote NH₃ adsorption on the

Fig. 5. TGA profiles of four different MnO₂ nanocrystals. Heating rate was 10 °C/min, and in a N₂ stream. ΔM_{X1} : loss of physically and chemically adsorbed water; ΔM_{X2} : loss of chemical oxygen; ΔM_{X3} and ΔM_{X4} : transformations of MnO₂ to Mn₂O₃, then to Mn₃O₄, respectively.

catalyst surface in the form of NH₄⁺ [50], leading to different catalytic activities for δ -MnO₂ and β -MnO₂. The mass loss in the temperature range of 250–540 °C is considered to derive from the loss of chemical oxygen [51,52]. Subsequent mass losses were attributed to the transformations of MnO₂ to Mn₂O₃, then to Mn₃O₄ in the temperature range of 550–800 °C [53].

3.5. Surface acidity (NH₃-TPD)

NH₃-TPD experiments were performed to demonstrate the adsorption capability and acidity of the four MnO₂ crystals, and the results are shown in Figure 6. The NH₃ desorption peak was found in the range of 100–300 °C. Desorption of coordinated NH₃ bound to Lewis acid sites and residual NH₄⁺ strongly bound to hydroxyls can occur [54]. Roy et al [55] suggested that the NH₃ desorption in this range can be mainly attributed to the NH₃ adsorption at Brönsted acid sites and that these sites play an important role in the low-temperature activity of these catalytic materials. In any case, the two theories indicate that the peak area of the NH₃-TPD relates to the number of acidic sites on the catalyst surface [54,55]. Larger peak areas indicate greater amounts of adsorbed NH₃ and more acid sites on the catalyst, which lead to better catalytic activity. Figure 6 shows that α -MnO₂, δ -MnO₂, and γ -MnO₂ featured a wide NH₃ desorption peak at different temperatures. The NH₃ desorption temperatures were 206 °C for α -MnO₂ and 196 °C for δ -MnO₂. The NH₃ desorption temperature (248 °C) for γ -MnO₂ was higher than that for α -MnO₂ and δ -MnO₂, indicating that γ -MnO₂ featured stronger acidic surface sites, followed by α -MnO₂ and δ -MnO₂. Strong acidic sites improve the adsorption of active gases. Although the three MnO₂ structures showed a considerable amount of NH₃ desorption, the calculated results (Table 2) showed differences in the peak areas reflecting a decrease in peak size in the order: γ -MnO₂ > α -MnO₂ > δ -MnO₂.

The NH₃-TPD results showed that γ -MnO₂ featured the largest amount of and strongest acid sites, followed by α -MnO₂ and δ -MnO₂. These results agreed with the BET results. More and stronger acid sites can contribute to NH₃ adsorption and promote the catalytic reaction. Thus, γ -MnO₂ and α -MnO₂ have the best catalytic activities, which are consistent with the pre-

Fig. 6. NH₃-TPD profiles of four different MnO₂ nanocrystals. (1) α -MnO₂; (2) β -MnO₂; (3) δ -MnO₂; (4) γ -MnO₂.

Table 2

Data for the acidity (position of the desorption peaks and NH₃ desorption amount) of α -, β -, δ -, and γ -MnO₂.

Catalyst	Temperature (°C)	Peak area ($\mu\text{mol/g}$)
α -MnO ₂	206	37.31
β -MnO ₂	203	5.74
δ -MnO ₂	196	31.62
γ -MnO ₂	248	45.84

vious catalytic results. Furthermore, β -MnO₂ showed a small NH₃ desorption peak, revealing that its acidity was weak and the amount of NH₃ adsorbed on its surface was small, which could also explain its low NO_x conversion. On the basis of the above analysis, we believe that the number of acidic sites on the surface is a major factor leading to the different catalytic activities of the MnO₂ catalysts.

The γ -MnO₂ catalyst presented a single bond (1 $\times$ 1) and double bond (1 $\times$ 2) alternating structure, which could easily collapse, resulting in a large number of point defects and vacancies. Thus, a large number of defect-sites/active-sites for oxidation and a large surface area might be expected for the γ -MnO₂ catalyst. The δ -MnO₂ catalyst has a layered structure, which also features a large number of defect-/active-sites. Although β -MnO₂ has an anatase structure with square symmetry, the structure is relatively stable. Therefore, it has fewer defect-/active-sites. Materials with more vacancies and point defects are likely to show higher catalytic activity for oxidation reactions because more active sites for reduction/oxidation are present in the material [56]. Consequently, γ -MnO₂ showed the highest catalytic activity.

3.6. XPS analysis

XPS experiments were performed to study the surface electronic state of the catalysts and the results are shown in Figure 7. Figure 7(a) shows the Mn 2p_{3/2} peak located at 640.88 eV, indicating that the main oxidation state of Mn in all of the MnO₂ crystals was Mn⁴⁺ [57]. These results also supported the TGA and XRD results. The O 1s spectra (Figure 7(b)) showed two surface oxygen species. The binding energy at 528–529 eV is characteristic of lattice oxygen (denoted as O_l), and the binding

energy at 530–531 eV can be attributed to defect oxide or low-coordination surface oxygen ions (denoted as O_β) [58]. The surface chemisorbed oxygen O_β is reported to be highly active in oxidation reactions because of its higher mobility than lattice oxygen O_l [59,60]. A high relative concentration ratio of O_β/(O_β+O_l) on the catalyst surface correlated with a high SCR activity [61]. The presence of O_β can promote oxidation of NO to NO₂ and H-abstraction from adsorbed NH₃, which are both expected to be important processes in low-temperature NH₃-SCR [51]. The corresponding concentrations of O_β/(O_β+O_l) were 19.34%, 9.26%, 13.52%, and 30.96% for the α -, β -, δ -, and γ -MnO₂ nanocrystals, respectively. The γ -MnO₂ catalyst featured a greater capacity for activating NH₃, which is shown by the NH₃-TPD (Figure 5) and NO_x conversion results. The XPS results indicate that the surface oxygen content is a major factor that influences the activity of the different MnO₂ nanocrystals. The NO_x conversion was greater when the catalyst featured more surface chemisorbed oxygen, agreeing well with the TGA and SCR activity results. Surface-active oxygen can promote activation of the gas molecules and the reaction on γ -MnO₂ and α -MnO₂, causing both catalysts to have good catalytic activities. The β -MnO₂ catalyst featured very little surface-active oxygen, which is not conducive to the catalysis of gas molecules, hence, it showed lower NO_x conversion. Surface-active oxygen is another major factor affecting the catalytic activity of MnO₂ catalysts.

3.7. Reducibility (H₂-TPR)

H₂-TPR tests were used to characterize the redox ability of the catalysts. All H₂ consumption peaks in Figure 8 can be attributed to reduction of different MnO₂ crystals. H₂ can react with O₂, which is released from the MnO₂ conversion processes to generate water. Thus, the MnO₂ transformation path is determined by the consumption of H₂.

For the γ -MnO₂ crystal, two H₂ consumption peaks were observed at 360 and 499 °C, and the ratio of the lower to the higher temperature peak was approximately 2. From the theoretical value of H₂ consumption (Equation 1), we can expect a ratio of 2:1 when MnO₂ generates MnO via Mn₃O₄ [20, 62–64].

Fig. 7. Mn 2p (a) and O 1s (b) XPS spectra of the four different MnO₂ nanocrystals. (1) α -MnO₂; (2) β -MnO₂; (3) δ -MnO₂; (4) γ -MnO₂.

Fig. 8. H₂-TPR profiles of four different MnO₂ nanocrystals. (1) α -MnO₂; (2) β -MnO₂; (3) δ -MnO₂; (4) γ -MnO₂.

The TPR profile of the β -MnO₂ crystal was similar to that of the γ -MnO₂ crystal; however, both reduction peaks were slightly shifted to higher temperatures. This result suggested that the low-temperature oxidation performance of γ -MnO₂ was better than that of β -MnO₂ [53]. Furthermore, the ratio of the two reduction peaks was approximately 1:1; hence, the lower temperature peak could be attributed to the reduction of MnO₂ to Mn₂O₃, whereas the higher temperature peak could be attributed to the reduction of Mn₂O₃ to MnO [65]. However, the TPR profiles of the α -MnO₂ and δ -MnO₂ nanocrystals were largely different from those of the β -MnO₂ and γ -MnO₂ nanocrystals. For δ -MnO₂ and α -MnO₂, two almost overlapping peaks were observed. The main reduction peak of α -MnO₂ corresponded to 365 °C, while that of δ -MnO₂ was 374 °C, indicating that the redox ability of α -MnO₂ was stronger than that of δ -MnO₂. Furthermore, the light-off temperatures of the four different MnO₂ nanocrystals were quite different. For γ -MnO₂ and α -MnO₂, the starting redox temperatures were relatively low, at 138 and 206 °C, respectively, followed by δ -MnO₂ at 218 °C and β -MnO₂ at 271 °C. Together with the activity results, we suggest that the catalyst displayed efficient reactivity when the light-off temperature was relatively low. The main reduction product of the different MnO₂ nanocrystals was MnO, as indicated by the green appearance of the catalysts after the H₂-TPR experiment [53]. According to the H₂-TPR results for MnO₂, the redox ability of the four different MnO₂ crystals at low temperatures decreased in the order: γ -MnO₂ > α -MnO₂ > δ -MnO₂ > β -MnO₂. From previous analysis (Figure 3), γ -MnO₂ and α -MnO₂ showed better catalytic activities, which is consistent with the H₂-TPR testing. All these results indicate that the redox properties of the different MnO₂ crystals are the main factors leading to their different catalytic activities. The γ -MnO₂ and α -MnO₂ catalysts showed a reduction peak at lower temperature and possessed many mobile oxygen species at their surfaces [30]. The high oxygen mobility promoted adsorption of oxygen and its further excitation to active oxygen, which then became involved in the SCR reaction and consequently improved catalytic activity. While the reduction ability of β -MnO₂ was weak, a small amount of chemical oxygen was released.

The reduction reaction is not easily performed at low temperatures, and this eventually resulted in lower catalytic activity.

3.8. Catalytic activity and phase structure of MnO₂

The α -, β -, δ -, and γ -MnO₂ nanocrystals showed different catalytic performances. The NO_x adsorption over the α -, β -, δ -, and γ -MnO₂ nanocrystals and the activities of the catalysts correlated with their different phase structures. The α -, β -, δ -, and γ -MnO₂ structures are all constructed from chains of MnO₆ octahedra, which link in different ways. All the material featured channels of different dimensions. The crystal structure of α -MnO₂ consists of one-dimensional channels with relative dimensions (2×2) and (1×1) that extend along the *c*-axis of a tetragonal unit cell. These channels are formed by double chains of edge-sharing MnO₆ octahedra [66]. The structure of β -MnO₂ has a rutile-type structure with tetragonal symmetry. The MnO₆ units build up strings of edge-sharing octahedral extending along the crystallographic *c*-axis. These chains are linked with neighboring chains by sharing common corners, resulting in the formation of (1×1) channels in the β -MnO₂ structure [66,67]. The structure of γ -MnO₂ is considered to be a random intergrowth of ramsdellite (2×1 channels) and pyrolusite (1×1 channels) structures [68]. The crystal structure of ramsdellite is very similar to that of pyrolusite except that single chains of octahedra in pyrolusite are replaced by double chains in ramsdellite. The structure of δ -MnO₂ is made up from sheets of edge-sharing MnO₆ octahedra, which are separated by layers of water molecules or hydroxide anions (OH⁻). The oxygen atoms form a slightly distorted hexagonal closely packed array in the sheets of MnO [66].

The α -, β -, δ -, and γ -MnO₂ nanocrystals are channels structures with different channels sizes. The channels structures of MnO₂ are reported to have molecular sieve properties, thus, different channel sizes have different adsorption capacities for gas molecules. The channel size of β -MnO₂ is small at approximately 0.23 nm × 0.23 nm [66], making it is difficult for gas molecules to enter the tunnel. Furthermore, β -MnO₂ has strong thermal stability (TGA results), high crystallinity, and fewer structural defects. The number of exposed acid sites in β -MnO₂ is low (TPD data); hence, the activity and gas adsorption capacity are low. The low number of surface defects in β -MnO₂ and the low percentage of its surface capable of chemisorbing oxygen (XPS data) are likely to limit activation of reactant gas molecules. Therefore, the NH₃-SCR activity of β -MnO₂ was low. The channel size of α -MnO₂ is two times as large as that of β -MnO₂ [66,67]. During the reaction, NH₃ molecules can enter the tunnel structure more easily, which is beneficial for the adsorption of NH₃ on α -MnO₂. Furthermore defects in the α -MnO₂ crystal, including acidic sites (TPD, data) and chemisorbed oxygen, are beneficial for the catalytic reaction. The channel size of γ -MnO₂ is 0.46 nm × 0.23 nm [66,68], and it shows a good adsorption capacity for NH₃. Furthermore, the crystallinity of γ -MnO₂ was low, with more defects and a larger specific surface area, which contributed to the better catalytic activity. The main exposed face of the δ -MnO₂ catalyst was the (001) lattice plane, where the Mn ion is in a saturation state; thus, the δ -MnO₂ surface has

fewer acidic sites than the α - and γ -MnO₂ catalysts. The structure of the MnO sheets in δ -MnO₂ is also denser than that of α -MnO₂. Therefore, the reducibility of δ -MnO₂ (release lattice oxygen) is lower than that of the α -MnO₂, which is reflected by their lower catalytic activity.

4. Conclusions

The α -, β -, δ -, and γ -MnO₂ nanocrystals all form infinite channels with different dimensions. The different crystal structures lead to considerable differences in their surface acidity, surface active oxygen, and specific surface area, resulting in different catalytic activities. XPS results showed that γ -MnO₂ and α -MnO₂ contained more surface-active oxygen, which promoted activation of gas molecules and reactions on the catalyst surface, causing both catalysts to have good catalytic activities. The surface area of β -MnO₂ was low and its redox ability was weak, owing to fewer active oxygen and acidic sites on its surface, resulting in low catalytic activity. Although δ -MnO₂ had a relatively small surface area, the NH₃-TPD results suggested that more acid sites were dispersed on its surface, which improved its catalytic activity. In summary, the reduction ability and the specific surface area are important factors contributing to differences of MnO₂ activity; however, these are not the main factors. We suggest that surface site acidity and the amount of surface-active oxygen sites have the most important effects on the NH₃-SCR activity of MnO₂ catalysts.

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Graphical Abstract

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Effects of surface physicochemical properties on NH₃-SCR activity of MnO₂ catalysts with different crystal structures

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Surface-active oxygen can promote activation of gas molecules and reaction on γ -MnO₂ and α -MnO₂, giving both catalysts good catalytic activities. High specific surface area and reduction ability also contribute to catalytic activity.

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表面物理化学性质对不同晶型MnO₂的NH₃-SCR活性影响

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摘要: 氮氧化物(NO_x)是主要的大气污染物之一, 给环境和人类健康带来巨大危害。NH₃选择性催化还原(NH₃-SCR)技术是处理氮氧化物最有效的方法之一, 现已被广泛用于氮氧化物的处理, 其中SCR催化剂是该技术的核心。

锰基催化剂具有相对较好的低温催化活性, 而其中MnO₂的催化活性最为突出。二氧化锰可以形成多种晶型, 如α, β, δ和γ。晶相结构可显著影响催化活性, 不同晶型的MnO₂具有不同的催化性能, 其在电化学催化和CO催化方面已经得到广泛应用和研究。然而对于不同晶型MnO₂的NH₃低温选择催化还原NO_x的催化活性和催化机理的研究特别少。α-, β-, γ-和δ-MnO₂具有不同的晶型尺寸, 并在气体吸附、气体扩散和催化反应过程中表现出较大差异。因此, 有必要揭示不同MnO₂晶型表面物理化学性质与SCR催化活性之间的关系。

本文成功制备出四种不同晶型的纳米MnO₂ (α, β, δ和γ型)催化剂, 并测试了其NH₃低温选择催化活性。此外, 对催化剂进行了XRD, SEM, Raman, TG, BET, NH₃-TPD, XPS和H₂-TPR等一系列测试表征, 探究了导致不同晶型MnO₂的NH₃催化还

原 NO_x 差异的主要原因。结果表明, 四种不同晶型纳米 MnO_2 的 NH_3 -SCR催化活性顺序为 $\gamma\text{-MnO}_2 > \alpha\text{-MnO}_2 > \delta\text{-MnO}_2 > \beta\text{-MnO}_2$ 。 $\gamma\text{-MnO}_2$ 和 $\alpha\text{-MnO}_2$ 上的 NO_x 转化率在140–200 °C范围内可达90%以上, 但 $\beta\text{-MnO}_2$ 在200 °C只有40%的 NO_x 转化率。分析表明, $\gamma\text{-MnO}_2$ 和 $\alpha\text{-MnO}_2$ 的纳米线形貌具有较好的分散性, 导致它们的比表面积较高, 这为活性位点提供了更多的分散空间, 有利于活性气体分子的吸附和催化过程的进行。 H_2 -TPR和 NH_3 -TPD结果显示, $\gamma\text{-MnO}_2$ 和 $\alpha\text{-MnO}_2$ 比其他两种晶型的 MnO_2 催化剂具有较好的可还原性和更多更强的酸性位点。 XPS分析结果表明, 在 $\gamma\text{-MnO}_2$ 和 $\alpha\text{-MnO}_2$ 表面存在更多的化学吸附氧。基于上述这些有利的物理化学性质, $\gamma\text{-MnO}_2$ 和 $\alpha\text{-MnO}_2$ 催化剂显示出较好的低温 NH_3 -SCR活性。 尽管 $\delta\text{-MnO}_2$ 的比表面积较小, 但是 NH_3 -TPD结果显示其层状形貌的纳米晶体表面分散有较多的酸性位点, 从而有效提升了其催化效果, 同时其较好的氧化还原性能也有助于催化性能的改善。

关键词: MnO_2 ; 晶体结构; 表面活性氧; 选择催化还原; 物理化学性质

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《催化学报》进入中科院 JCR 期刊分区工程技术大类2区

近日, 中国科学院文献情报中心发布 2016 年版中科院JCR期刊分区, *Chinese Journal of Catalysis* (《催化学报》) 在工程技术类 1845 种期刊中排名第 354 位, 居工程技术大类2区。中科院 JCR 期刊分区按照学术影响力作为划分方式, 将每个学科的所有期刊按照学术影响力 (3年平均JCR影响因子 (IF)) 由高到低降序排列, 依次划分为4个区, 使每个分区期刊影响力总和相同。由于学科内期刊的3年IF的偏态分布, 这使得1区期刊数量极少。为保证期刊1区期刊数量, 1区期刊取整个学科数量总数的5%, 即3年平均IF最高的5%的期刊为1区期刊。2–4区期刊使用3年平均IF总和相同的方式划分 (分区方法详见<https://www.fenqubiao.com>)。

近年, 《催化学报》的学术质量及影响力不断提升, 这是中国化学会催化委员会委员、《催化学报》编委、审稿专家、作者和读者长期不懈努力和共同支持的结果。衷心感谢各位老师、在期刊宣传、投稿原创性高质量稿件、学术质量把关以及组约优秀稿件、组办高水平专刊等方面所给予的持续的、巨大的支持!

(《催化学报》编辑部)