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Article

The effects of Mn loading on the structure and ozone decomposition activity of MnO_x supported on activated carbon

Mingxiao Wang, Pengyi Zhang*, Jing Li, Chuanjia Jiang

State Key Joint Laboratory of Environment Simulation and Pollution Control, School of Environment, Tsinghua University, Beijing 100084, China

ARTICLE INFO

Article history:

Received 30 August 2013

Accepted 22 November 2013

Published 20 March 2014

Keywords:

Manganese oxide

Ozone decomposition

Activated carbon

Indoor air

Nanomaterial

ABSTRACT

Manganese oxide catalysts supported on activated carbon (AC, MnO_x/AC) for ozone decomposition were prepared by in situ reduction of the permanganate. The morphology, oxidation state, and crystal phase of the supported manganese oxide were characterized by scanning electron microscopy, X-ray photoelectron spectroscopy, X-ray diffraction, electron spin resonance, Raman spectroscopy, and temperature-programmed reduction. The supported MnO_x layer was distributed on the surface of AC with a morphology that changed from a porous lichen-like structure to stacked nanospheres, and the thickness of the MnO_x layer increased from 180 nm to 710 nm when the Mn loading was increased from 0.44% to 11%. The crystal phase changed from poorly crystalline $\beta\text{-MnOOH}$ to $\delta\text{-MnO}_2$ with the oxidation state of Mn increasing from +2.9–+3.1 to +3.7–+3.8. The activity for the decomposition of low concentration ozone at room temperature was related to the morphology and loading of the supported MnO_x . The 1.1% MnO_x/AC showed the best performance, which was due to its porous lichen-like structure and relatively high Mn loading, while 11% MnO_x/AC with the thickest MnO_x layer had the lowest activity owing to its compact morphology.

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1. Introduction

Ozone is a hazardous air pollutant even at the ppb level. Many studies have reported correlations between ozone concentration and diseases and mortality, which include respiratory-related hospital admissions, lost school days, restricted activity days, development of asthma in adult males, asthma related emergency visits, and premature mortality [1]. The permitted 1 h maximum ozone is 60 to 80 ppb in different countries [2]. The ozone concentration is often more than 200 ppb in the air in aircraft cabins during cross-continental flights [3]. In the office and printing shops, photocopiers, laser printers, and other modern office equipment produce ozone by co-

rona discharge processes [4]. In addition, exhaust gases from processing units for sterilization, deodorization, and wastewater treatment usually contain ozone of high concentrations [5]. In addition, catalytic ozonation, non-thermal plasmas, anion air purifiers, and 185 nm vacuum ultraviolet lights are widely used to remove pollutants in water and indoor air, such as toluene, VOCs, etc [6–9]. However, the residual ozone released in these processes limits their practical application. Thus, in recent years, the removal of gas phase ozone has been extensively studied. Catalytic decomposition is a promising technique for effective ozone removal [10–14].

Activated carbon (AC) can be used directly or as a catalyst support for ozone decomposition to remove ozone through

* Corresponding author. Tel: +86-10-62796840; Fax: +86-10-62797760; E-mail: zpy@tsinghua.edu.cn

This work was supported by the National High Technology Research and Development Program of China (863 Program, 2012AA062701) and the National Natural Science Foundation of China (21221004).

DOI: 10.1016/S1872-2067(12)60756-6 | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 35, No. 3, March 2014

both chemical interaction and catalytic conversion [15]. In addition, a variety of oxygen-containing functional groups on the surface of charcoal can easily be modified to contribute to ozone decomposition. Dhandapani and Oyama [5] reported that among the common metal oxides (with γ - Al_2O_3 as carrier or cordierite as matrix), MnO_2 possessed the highest activity in the catalytic decomposition of ozone. In addition, manganese oxides (MnO_x) have appreciable activity in the oxidation of alkenes, alcohols, and VOC mixtures [16–18]. The catalytic properties of MnO_x -based materials were attributed to the ability of manganese to form oxides with different oxidation states. Temperature-programmed reduction results showed that the catalytic activity of MnO_x is dependent on its reducibility [5]. Although MnO_x nanomaterials with various morphologies have been synthesized and intensively investigated for electrochemical materials, gas phase formaldehyde decomposition, and water treatment, there have been few reports on how the oxidation state, reducibility, morphology, and dispersion of manganese affect its catalytic activity for ozone decomposition, and on the key factors in decomposing ozone.

Here, we report the loading of MnO_x on an AC surface (MnO_x/AC) by the *in situ* reduction of permanganate by activated carbon, and the investigation of the effects of Mn loading on the morphology, dispersion, oxidation state, and crystal phase of the supported MnO_x and its activity for ozone decomposition. Our work provides insights into the nature of supported manganese oxides and their activities for ozone decomposition.

2. Experimental

2.1. Preparation of MnO_x/AC

Coal-based granular activated carbon (DX-09) from Shanxi Xinhua Chemical Plant of China was used. This comprised cylindrical rods with an average diameter of 0.9 mm and length of 2–3 mm. Its specific surface area was $957 \text{ m}^2/\text{g}$ and the pore volume was $0.565 \text{ cm}^3/\text{g}$ with the average pore size of 2.4 nm. Activated carbon supported manganese oxides (MnO_x/AC) with different nominal Mn loadings (0.44%, 1.1%, 5.5%, and 11%) were synthesized by *in situ* reduction of KMnO_4 with AC. The Mn loadings were calculated using the ratio of the Mn mass in the precursor solution to that of AC. First, the activated carbon was successively pretreated with 1 mol/L NaOH and 1 mol/L HNO_3 to remove the ash contents on the surface. Then, 2.0 g of the treated AC was immersed in 50 mL aqueous KMnO_4 solution (with different concentrations to give the different loadings), whereupon the permanganate was reduced by the carbon and MnO_x was deposited on the surface of the AC. When the purple color of KMnO_4 faded after 24 h, the turbid supernatant was decanted and the supported MnO_x on activated carbon was dried at 378 K for 1 h.

2.2. Characterization of MnO_x/AC

The surface and cross-sectional morphologies of MnO_x/AC were observed by scanning electron microscopy (SEM, S-5500,

Hitachi, Japan). Surface elemental analysis was carried out by energy dispersive X-ray spectroscopy (EDS) with the accelerating voltage of 7 kV and an analysis depth of 200 nm. The chemical state of the MnO_x on the AC surface was investigated by X-ray photoelectron spectroscopy (XPS, PHI-5300, ESCA). The oxidation state of Mn was determined from the width of the Mn 3s peak splitting (ΔE_s Mn 3s) and the deconvolution of the O 1s spectra.

The crystal phase of the MnO_x was studied by both Raman spectroscopy (RM2000, Renishaw, UK) and X-ray diffraction (XRD, D8 Advance, Bruker, Germany). The Raman scattering spectra were acquired between 100 and 1200 cm^{-1} with a spectral resolution of 2 cm^{-1} . The laser light source was an argon ion laser at the wavelength of 514.5 nm, and the power used was 0.235 mW. We used the surface of the catalysts rather than the ground powder of the MnO_x/AC samples for the Raman characterization, and so the signal reflects the structure of MnO_x on the outer surface.

Hydrogen temperature-programmed reduction (TPR) measurements were carried out with a U-shaped quartz microreactor (Autochem II 2920, Micromeritics, USA). Cylindrical MnO_x/AC was first ground and sieved through a 60 mesh screen. Then 100 mg of crushed catalyst was reduced in 5% H_2/Ar flow at a heating rate of 5 K/min. The hydrogen consumption was determined by a thermal conductivity detector (TCD).

Electron spin resonance (ESR) signals of the MnO_x/AC samples were recorded on a Bruker A-300 spectrometer at ambient temperature. Ground powder of MnO_x/AC was put in a 50 μL glass tube for the measurement. The microwave frequency was fixed at 9.44 GHz, and the magnetic sweep span was 0–5000 G. WinEPR Acquisition and WinEPR softwares were used for spectrometer control, data acquisition, and spectral analysis.

2.3. Catalytic activity test

The activity of MnO_x/AC for ozone decomposition was measured with a cylindrical fixed bed plug flow reactor made of stainless steel. Cylindrical catalyst (1.0 g) was used with a packed volume of 2.2 cm^3 . At a flow rate of 3.0 L/min, the space velocity was $8.2 \times 10^4 \text{ h}^{-1}$, and the corresponding residence time was 0.044 s, which is usual for practical indoor air purification. The inlet ozone was generated by a low pressure mercury ultraviolet lamp (UVCN HD212VH, Beijing Aerospace Hongda Optoelectronics Technology, China). The ozone concentration was monitored online with a UV photometric ozone analyzer (Model 49i, Thermo Scientific, USA). The inlet ozone concentration, reaction temperature, and room humidity were maintained at 43–48 mg/m^3 , 298 K, and 60%, respectively.

3. Results and discussion

3.1. Morphology and thickness of supported MnO_x

From the *in situ* reduction of permanganate on the surface of AC, MnO_x was accumulated and it formed films on the outer surface of the AC. Table 1 shows the thickness and actual load-

Table 1Thickness and actual Mn loadings of MnO_x/AC samples.

Nominal Mn loading (%)	Thickness (nm)	Actual Mn loading (%)
0.44	180–190	0.43
1.1	330–365	1.07
5.5	290–350	2.56
11	590–710	9.33

ings of MnO_x/AC for the different nominal Mn loadings. With the increase of nominal manganese loading, the actual loading also increased. Figure 1 shows the surface and cross-sectional morphologies of MnO_x with different nominal Mn loadings. When the nominal Mn loading was 0.44%, a porous lichen-like structure with a thickness of 180–190 nm, which was assembled from curled MnO_x nanobelts, was observed by SEM. When the Mn loading was increased to 1.1%, the lichen-like structure remained, but the MnO_x layer became denser and the thickness was increased to 330–365 nm. On the 5.5% MnO_x/AC sample, the loose lichen-like morphology had largely collapsed, and compact nanospheres were present on the surface with thickness of 290–350 nm. For the 11% MnO_x/AC, the lichen-like structure had completely disappeared, and on this catalyst, the MnO_x nanobelts were stacked into nanospheres with the thickness of the MnO_x layer increasing to 590–710 nm.

3.2. XPS analysis of the supported manganese

When the cylindrical AC was immersed in the permanganate solution, the permanganate was reduced by the AC to manganese oxides with different valence states, namely, Mn²⁺, Mn³⁺, and Mn⁴⁺, and subsequently, MnO_x layers were formed and deposited on the outer surface of AC. The Mn 3s splitting is widely used for calculating the manganese oxidation state by its satellite separation (ΔE_s). For Mn⁴⁺, Mn³⁺, and Mn²⁺ in manganese oxides, ΔE_s (Mn 3s) is 4.7–4.8, 5.3–5.4, and ~5.8, respectively [19–21]. Figure 2 shows the Mn 3s spectra of the samples. The ΔE_s of 0.44% and 1.1% MnO_x/AC were 5.4 and 5.3 eV respectively, which agreed well with the ΔE_s for Mn³⁺. The ΔE_s of the 5.5% and 11% MnO_x/AC were 4.9 and 5.0 eV, respectively. These values were between the typical ΔE_s for Mn⁴⁺ and Mn³⁺, which indicated the coexistence of Mn⁴⁺ and Mn³⁺ in 5.5%

Fig. 2. Mn 3s XPS spectra of the MnO_x/AC samples.

and 11% MnO_x/AC. Using the data from the samples tested in the literature above [20,21], the average oxidation state of the manganese was estimated and as +3.0 and +3.1 for the 0.44% and 1.1% MnO_x/AC samples, respectively, and +3.8 and +3.7 for the 5.5% and 11% MnO_x/AC samples.

In addition, the O 1s spectra were also used to estimate the manganese oxidation state. The O 1s spectra were asymmetrical and can be deconvoluted into three primary peaks assignable to Mn–O–Mn (529.3–530.5 eV), Mn–O–H (530.5–531.5 eV), and H–O–H (531.8–532.8 eV) [22,23]. The average manganese oxidation state was calculated from the intensities of the Mn–O–Mn and Mn–O–H peaks (i.e., $S_{\text{Mn-O-Mn}}$ and $S_{\text{Mn-O-H}}$) by the formula: oxidation state = $(4 \times (S_{\text{Mn-O-Mn}} - S_{\text{Mn-O-H}}) + 3 \times S_{\text{Mn-O-H}}) / S_{\text{Mn-O-Mn}}$ [24]. The deconvolution of the O 1s peak and calculated oxidation states are shown in Fig. 3. The results are consistent with the values calculated from the Mn 3s peak splitting.

3.3. XRD and Raman results

Figure 4 shows the XRD patterns of MnO_x/AC, with that of AC shown for comparison. The diffraction peaks at $2\theta = \sim 26.6^\circ$, 42.6° , and 79.0° were assigned to amorphous carbon. No

Fig. 1. Surface and cross-sectional morphologies of the MnO_x/AC samples with different nominal Mn loadings. (a,b) 0.44%; (c,d) 1.1%; (e,f) 5.5%; (g,h) 11%.

Fig. 3. O 1s XPS spectra of the MnO_x/AC samples (OS = oxidation state).

Fig. 4. X-ray diffraction patterns of the MnO_x/AC samples.

other peaks were observed when the Mn loading was lower than 5.5%, which indicated that there was poor crystallinity of supported MnO_x or that its actual content was too low to be detected by XRD. As the Mn loading increased, the amount of MnO_x on the support increased, and also the supported MnO_x aggregated from a porous lichen-like structure to larger nanospheres. The peaks at 36.8° and 65.7° observed with the 5.5% and 11% MnO_x/AC samples can be attributed to birnessite MnO_2 ($\delta\text{-MnO}_2$, JCPDS, 18-0802). $\delta\text{-MnO}_2$ is a layered manganese oxide with varying water and foreign cation contents, which is contained in a large number of natural manganese oxide deposits. Most of the materials have very poor crystallinity, as shown in Fig. 4. Typically, $\delta\text{-MnO}_2$ has four diffraction peaks at $2\theta = 12.2^\circ$, 24.7° , 36.8° , and 65.7° . $\delta\text{-MnO}_2$ can also be synthesized by the redox reaction of KMnO_4 with $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ [25]. As reported in the literature [26,27], the presence of excess K^+ ions is favorable for producing $\delta\text{-MnO}_2$, which exists as sheets of MnO_6 octahedrons with water or Na^+ . In this work, the EDS analysis showed that the ratio of K/Mn was 0.11 and 0.15 for 5.5% and 11% MnO_x/AC , respectively, while the amount of K^+ in 0.44% and 1.1% MnO_x/AC was very low. Due to strong interference from the carbon signals, the peaks at $2\theta = 12.2^\circ$ and 24.7° of MnO_x/AC were obscured by

the signals of amorphous carbon.

Figure 5 shows the Raman spectra of MnO_x/AC and AC. A broad peak at 800 cm^{-1} was observed with the AC sample, which can be attributed to surface oxygen-containing groups. For all four MnO_x/AC samples, three additional peaks were observed. Peaks at 495, 554, and 633 cm^{-1} for 0.44% MnO_x/AC and peaks at 492, 553, and 635 cm^{-1} for 1.1% MnO_x/AC were observed. Likewise, peaks at 494, 557, and 631 cm^{-1} for 5.5% MnO_x/AC and peaks at 495, 553, and 635 cm^{-1} for 11% MnO_x/AC were also clearly detected. The Raman spectra of all four MnO_x/AC samples were consistent with those of layered birnessite-type manganese oxide, and these three peaks can be attributed to the stretching vibrations in octahedral MnO_6 [28]. However, as indicated by the XPS analysis, the Mn oxidation states of 0.44% and 1.1% MnO_x/AC were +2.9 to +3.0 and +3.1, respectively, which is different from that of birnessite (+3.6 to +3.8) [29]. Therefore, the crystal phase of MnO_x in the 0.44% and 1.1% MnO_x/AC samples was considered to be Feitknechtite $\beta\text{-MnOOH}$, which has a hexagonal layered structure and can be transformed to birnessite $\delta\text{-MnO}_2$ by redox reactions without a significant change in the crystal structure [30].

3.4. TPR results and crystal formation

A three-step reduction profile of unsupported MnO_x was reported by Craciun et al. [31]. The first two peaks at 600 and 690 K were attributed to the two-step reduction of MnO_2 (MnO_2 to Mn_2O_3 , and Mn_2O_3 to Mn_3O_4), and the third peak at 783 K was due to the complete reduction of Mn_3O_4 to MnO . The reduction of MnO to Mn metal was not observed even up to 1223 K because of the large negative value of the reduction potential [32]. It is well known that the reduction profile of bulk MnO_x in hydrogen is due not only to the oxidation state but also to the crystallinity or defect concentration. The reduction of supported manganese oxide is more complicated than that of bulk MnO_x because of the additional influence of the support.

The TPR profiles of the different MnO_x/AC samples and AC are shown in Fig. 6. Activated carbon alone gave two small hydrogen consumption peaks at 723 and 928 K, which can be

Fig. 5. Raman spectra of the MnO_x/AC samples.

Fig. 6. H₂-TPR profiles of AC and the different MnO_x/AC samples.

attributed to the reduction of oxygen-containing groups on the carbon surface [33]. The TPR profile of 0.44% MnO_x/AC was similar to that of the AC support. However, a detailed inspection indicated that in the case of 0.44% MnO_x/AC, the hydrogen consumption amount was significantly increased, and the onset reduction temperature was decreased from 550 to 500 K. This increase in hydrogen consumption can be explained by the reduction of Mn³⁺ in the 0.44% MnO_x/AC sample. This peak was overlapped by that of the AC support, so no separate reduction peak was observed.

When the Mn loading was increased to 1.1%, the reduction started at a temperature lower than 500 K, and an obvious broad shoulder centered at 570 K appeared in the TPR profile, which can be attributed to a small amount of amorphous or poorly crystalline MnO₂ aggregates on the outer surface of the MnO_x layer. As the Mn loading was increased to 5.5% and 11%, the hydrogen consumption at temperatures below 600 K was significantly increased, which was attributed to the reduction of the δ-MnO₂ aggregates observed by SEM and which agreed with the XRD results. In the TPR profiles of all the MnO_x/AC samples, hydrogen consumption at temperatures above 800 K was significantly increased as compared to AC support, which was attributed to the Mn–O–C species. Similar results have been reported on AC supported metal catalysts by Calafat et al. [34].

Based on the above results, the evolution and structure of the supported MnO_x film on AC surface were deduced to be as follows.

It was reported that permanganate reacted with carbon to produce MnO₂ by the reaction given as $4\text{MnO}_4^- + 3\text{C} + \text{H}_2\text{O} \rightarrow 4\text{MnO}_2 + \text{CO}_3^{2-} + 2\text{HCO}_3^-$ [35–37]. However, this is not an elementary reaction. Here, we propose a two-step reaction pathway to produce MnO₂. First, AC as a reductant reacted with permanganate, and a large amount of Mn²⁺ was produced (Re-

action (1)), which was further oxidized by permanganate to form MnO₂ (Reaction (2)). The occurrence of Mn²⁺ in the reaction was confirmed by the ESR analysis. As shown in Fig. 7, 0.44% MnO_x/AC showed a broad Lorentzian-shaped signal with $g = 2.064$ and a well-resolved six line hyperfine structure, which can be attributed to Mn²⁺. The splitting constant A was in the range of 80–100 G, which meant that the manganese was in the environment of distorted octahedral symmetry [38–40].

As reported by Nesbitt et al. [41], precipitates of birnessite MnO₂ can be formed by the reaction of Mn²⁺ with an oxidant by two electron transfer steps, first from Mn²⁺ to Mn³⁺-oxyhydroxide (MnOOH), which is then oxidized to MnO₂. In addition, Elzinga [42] reported that the presence of Mn²⁺ caused the reductive transformation of birnessite into Feitknechtite (β-MnOOH) and manganite (γ-MnOOH) through an interfacial electron transfer from adsorbed Mn²⁺ to structural Mn⁴⁺, as shown in Reaction (3). Thus, in the case of low Mn loadings (0.44% and 1.1%), there were two possible reasons for the existence of MnOOH: the permanganate concentration was not high enough to oxidize the Mn²⁺ into MnO₂ or the MnO₂ formed was reduced back into MnOOH by Mn²⁺. Accordingly, β-MnOOH was the main MnO_x component on the 0.44% and 1.1% MnO_x/AC samples, as reported by Jiang et al. [43]. On the other hand, in the case of higher Mn loadings (5.5% and 11%), the excess permanganate can oxidize all Mn²⁺ into MnO₂ and prevent MnO₂ from being reversibly reduced by Mn²⁺. Thus, δ-MnO₂ was the main crystal phase of the MnO_x in the 5.5% and 11% MnO_x/AC samples. In addition, due to high Mn loading, it was not only the crystal phase that changed from β-MnOOH to δ-MnO₂, but also the morphology was changed from a porous lichen-like structure to compact nanospheres.

3.5. Activity for ozone decomposition

The activities of AC and the supported MnO_x catalysts with different Mn loadings for ozone decomposition at room temperature (298 K) and high room humidity (60%) were evaluated using a fixed bed plug flow reactor. The results are shown in Fig. 8. The ozone removal ratio by the AC decreased very fast to be less than 50% within 300 min, while all the supported MnO_x catalysts showed better performance. Due to the initial adsorption on the catalyst, the ozone removal ratio declined quickly within 150–200 min in the first stage. After that, the

Fig. 7. Mn²⁺ signal detected with the 0.44% MnO_x/AC sample by ESR.

Fig. 8. Performance for ozone decomposition by MnO_x/AC samples.

activities of all the supported MnO_x catalysts reached stable states during the test period of 24 h. The ozone removal ratios by 0.44% and 1.1% MnO_x/AC were 72% and 83%, respectively, which was consistent with the increased Mn loading. Likewise the removal ratio by 5.5% and 11% MnO_x/AC were 54% and 50%, respectively, which slightly decreased with the increase of Mn loading.

Because the activity test was conducted under the conditions of a high space velocity ($8.2 \times 10^4 \text{ h}^{-1}$) and short space time (0.044 s), which are usual values in practical use due to the use of a limited reaction volume and high flow rate, the catalytic decomposition of ozone mainly proceeded on the outer surface of the catalyst [44]. AC in the inner part of the catalyst may not get access to the ozone. Thus, the morphology and contents of MnO_x on the exterior surface were the crucial factors in ozone removal. Supported MnO_x showed a porous lichen-like structure for the 0.44% MnO_x/AC catalyst, which was beneficial for the gas-solid catalytic decomposition reaction of ozone and it showed good activity. The 1.1% MnO_x/AC still maintained the lichen-like structure while the MnO_x film became denser and thicker, thus, its activity was significantly increased. When the nominal Mn loading was increased to 5.5%, the porous morphology had largely collapsed to form compact nanospheres. Although the thickness of the MnO_x film was larger than that of 0.44% MnO_x/AC , its ozone removal ratio was significantly lower. For the same reason, the activity further decreased for the 11% MnO_x/AC catalyst because the MnO_x was completely composed of compact nanospheres. Although the effect of the crystal phase and oxidation state of Mn on the catalytic activity for ozone decomposition cannot be excluded, it seems that the morphology is the more important factor in this study. In addition, as compared with the activity of other catalysts reported in the literature, the 1.1% MnO_x/AC catalyst gave a similar activity to that of the supported fine powder catalyst, while the 1.1% MnO_x/AC is a particulate catalyst, which gives much lower air resistance in practical applications. For example, it was reported that under a space velocity of $5 \times 10^4 \text{ h}^{-1}$, the ozone removal ratio of MnO_x supported on $\text{TiO}_2\text{-Mg}$ silicate with a ratio of 7:3 was 88% [45]. In comparison, the ozone removal ratio by the 1.1% MnO_x/AC catalyst was 83% under a slightly higher space velocity of $8.1 \times 10^4 \text{ h}^{-1}$.

4. Conclusions

Manganese oxide supported on activated carbon (MnO_x/AC) was prepared by *in situ* reduction of permanganate with activated carbon. The effects of Mn loading on the morphology, oxidation state, and crystal phase of the supported MnO_x were investigated. When the nominal Mn loading was low at 0.44% and 1.1%, the supported MnO_x on the surface of activated carbon grew into a porous lichen-like morphology, the oxidation state of Mn was +2.9 to +3.1, and the phase was poorly crystallized $\beta\text{-MnOOH}$. When the nominal Mn loading was increased to 5.5% and 11%, the lichen-like structure collapsed, the MnO_x film mostly consisted of nanospheres, the oxidation state of Mn increased to +3.7 to +3.8, and $\delta\text{-MnO}_2$ appeared as the main crystal phase. Although the effect of the crystal phase on the activity cannot be excluded, the reason why the 1.1% MnO_x/AC catalyst showed the best activity was mainly due to its porous lichen-like structure and relatively high Mn content, while 11% MnO_x/AC showed the lowest activity due to its compact MnO_x layer even though it had the highest Mn loading. These findings throw light on how to synthesize manganese oxide catalysts with higher activity for ozone decomposition.

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Graphical Abstract

Chin. J. Catal., 2014, 35: 335–341 doi: 10.1016/S1872-2067(12)60756-6

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Tsinghua University

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锰负载量对活性炭载锰氧化物的结构及催化分解臭氧性能的影响

王鸣晓, 张彭义*, 李金格, 姜传佳

清华大学环境学院环境模拟与污染控制国家重点联合实验室, 北京100084

摘要: 将高锰酸钾与活性炭(AC)原位氧化还原制备的活性炭载锰氧化物(MnO_x/AC)用作臭氧分解的催化剂。采用扫描电镜、X射线光电子能谱、X射线衍射、电子自旋共振波谱、拉曼光谱以及程序升温还原研究了设计Mn负载量对负载锰氧化物性质(形貌、氧化态和晶体结构)的影响。结果表明, Mn负载量由0.44%增至11%, 负载锰氧化物在活性炭表面由疏松的地衣状变为堆叠的纳米球状体, 负载层的厚度由~180 nm增加至~710 nm, 结构由氧化态+2.9到+3.1的低结晶 $\beta\text{-MnOOH}$ 生长为由氧化态+3.7到+3.8的 $\delta\text{-MnO}_2$ 结晶。 MnO_x/AC 室温催化分解低浓度臭氧的活性与负载锰氧化物的形貌及含量密切相关。 Mn负载量为1.1%的 MnO_x/AC 具有疏松的地衣状形貌, 催化分解臭氧的性能最高, Mn负载量为11%的 MnO_x/AC 具有紧密的堆积结构,因而表现出最低的催化臭氧分解活性。

关键词: 锰氧化物; 臭氧分解; 活性炭; 室内空气; 纳米材料

收稿日期: 2013-08-30. 接受日期: 2013-11-22. 出版日期: 2014-03-20.

*通讯联系人. 电话: (010)62796840; 传真: (010)62797760; 电子信箱: zpy@tsinghua.edu.cn

基金来源: 国家高技术研究发展计划(863计划, 2012AA062701); 国家自然科学基金(21221004).

本文的英文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).