available at www.sciencedirect.com

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

Article

Low-temperature catalytic degradation of the odorous pollutant hexanal by γ -MnOOH: The effect of Mn vacancies

Shanhong Sui ^{a,b}, Pengyi Zhang ^{a,b,*}, Huiyu Zhang ^{a,b}, Ranran Cao ^{a,b}^a State Key Joint Laboratory of Environment Simulation and Pollution Control, School of Environment, Tsinghua University, Beijing 100084, China^b Beijing Key Laboratory for Indoor Air Quality Evaluation and Control, Beijing 100084, China

ARTICLE INFO

Article history:

Received 22 April 2019

Accepted 25 May 2019

Published 5 October 2019

Keywords:

 γ -MnOOH

Manganese vacancy

Hexanal degradation

Indoor air

Catalysis

ABSTRACT

Hexanal is a typical indoor odorant from wood-based products, which induces discomfort and irritation to human beings. The removal of hexanal has rarely been investigated. In this study, we found that the amount of Mn vacancies in γ -MnOOH significantly affects its catalytic activity toward hexanal degradation and transformation into CO_2 . The as-synthesized Mn vacancy-rich γ -MnOOH exhibited high efficiency toward hexanal removal, achieving 100% degradation of 15 ppm hexanal at 85 °C and complete transformation into CO_2 at 160 °C under the gas hourly space velocity of 240 L/(g·h); its activity could be completely regenerated by *in-situ* heat treatment at 180 °C. Moreover, it was found that the degradation of hexanal occurred in a stepwise manner, i.e., losing one CH_2 unit per step. Electron spinning resonance studies detected strong indicative signals for the presence of the superoxide anion radical ($\bullet\text{O}_2^-$) on Mn-vacancy-rich γ -MnOOH, which may act as active oxygen species for the hexanal degradation. Understanding the role of Mn-vacancy and the mechanism of hexanal degradation by γ -MnOOH are essential for developing efficient oxide catalysts for volatile organic compounds besides hexanal.

© 2019, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

In recent decades, with social development and rapid urbanization, indoor air pollution has become a topic of concern. Among various pollutants, volatile organic compounds (VOCs) including aromatic compounds and formaldehyde have attracted significant attention due to their complexity, irritation, and pathogenicity [1,2]. Undoubtedly, formaldehyde is the indoor air pollutant with the most concern. However, besides formaldehyde, there are numerous VOCs that cause indoor pollution [3]. For example, hexanal is often detected in indoor environments at relatively high concentrations [4,5]. It is re-

ported that sawdust and wood pellets emit many kinds of aldehydes, including hexanal [6,7]. Hexanal has also been identified as one of the major odorous compounds in oak wood [8]. Our recent research found that hexanal contributed significantly to the odor emitted from particleboard due to its very low odor-threshold ($1.25 \mu\text{g}/\text{m}^3$) and relatively high concentration [9]. Toxicological research indicates that the odor of hexanal partially impairs mouse maternal behavior and induces the neonatal death of mice [10]; moreover, the potential genotoxic and epigenetic effects of hexanal on the respiratory system were conceivable [11].

Thus far, many approaches have been explored for the re-

* Corresponding author. Tel: +86-10-62773720; Fax: +86-10-62796840; E-mail: zpy@tsinghua.edu.cn

This work was supported by National Natural Science Foundation of China (21677083) and Suzhou-Tsinghua Innovation Guiding Program (2016SZ0104).

DOI: S1872-2067(19)63415-7 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 40, No. 10, October 2019

removal of indoor VOCs, such as adsorption [12,13], plasma-assisted catalytic oxidation [14], photocatalytic degradation [15–17], and thermal catalytic oxidation [18,19]; however, few papers on the degradation of hexanal have been reported. Yao et al. [20] studied the removal of hexanal via a post-plasma catalysis system over a Co-Mn solid solution at ambient temperature and found that Co/Mn (9/1) was the most suitable for hexanal removal. Kolar et al. [21] used wood fly ash to catalytically oxidize hexanal and found that at 160 °C, nearly 90% of 400–600 ppm hexanal was converted under the gas-hourly space velocity (GHSV) of 12 L/(g·h). Li et al. [22] reported that 90% of hexanal could be degraded by Cu-Mn composite oxide supported on TiO₂ at a temperature as high as 225 °C. Xiang et al. [23] also reported that MnO_x/SBA-15 exhibited good synergistic effect with plasma in the catalytic oxidation of hexanal. Chen et al. [24] found that MnO_x supported on γ -Al₂O₃ showed a comparable efficiency to that of Pt/ γ -Al₂O₃ for the removal of hexanal by combination with non-thermal plasma.

Manganese oxides are recognized as efficient and environmentally friendly transition metal oxides that are employed in the catalytic removal of pollutants, such as CO, NO, ozone, and VOCs [25–27]. The effects of the crystal phase, morphology, crystal facets, and vacancies on their catalytic performance have been widely investigated. For example, Wang et al. [28] found that the presence of Mn vacancies in birnessite-type MnO₂ facilitated the formation of active oxygen species, and accordingly, improved the activity for HCHO oxidation. Kwon et al. [29,30] also reported that Mn vacancies significantly reduced the band-gap of hexagonal birnessite-type MnO₂, and thus increased the concentration of photo-induced electrons available for Mn(IV) reduction upon illumination of the mineral by sunlight. Manganite, also known as γ -MnOOH, is the most stable manganese oxyhydroxide (MnOOH) and a favorable precursor for synthesizing other manganese oxides [31, 32]. γ -MnOOH with different morphologies such as rods [33], lines [34], fiber [35], tubes [36], and branched structures [37] could be synthesized by the hydrothermal method with or without templates. Meanwhile, it has attracted attention due to its promising application potential in contaminant adsorption [38], lithium-ion batteries [35], supercapacitors [36], and electrical catalysis [39]. Li et al. [40] reported that γ -MnOOH exhibited better performance toward the activation of persulfate to oxidize phenol compared to those of Mn₃O₄ and α -Mn₂O₃. γ -MnOOH also exhibited the highest catalytic activity for the electrochemical reduction of O₂ among four manganese oxides (Mn₂O₃, Mn₃O₄, Mn₅O₈, and MnOOH) [39]. The γ -MnOOH nanorods with tetragonal prism cross section exhibited catalytic activity toward formaldehyde oxidation and could be completely converted into CO₂ and H₂O at 120 °C under a gas hourly space velocity (GHSV) of 30 L/(g·h) [41]. However, thus far, the catalytic activity of γ -MnOOH for other gaseous pollutants has not been reported. In the present study, a Mn vacancy-rich γ -MnOOH catalyst was synthesized and exhibited high efficiency toward hexanal removal, achieving complete degradation of hexanal at 85 °C under a GHSV of 240 L/(g·h), which is much better than those reported in the literatures. This finding is also essential for the development of efficient catalysts for

the oxidation of VOCs other than hexanal.

2. Experimental

2.1. Synthesis of γ -MnOOH

All the reagents were of analytical grade and were used as received without further purification. Three types of γ -MnOOH catalysts were synthesized via the hydrothermal process. The well-crystallized γ -MnOOH for comparison was synthesized via the oxidation of Mn²⁺ ions by hydrogen peroxide. Mn(CH₃COO)₂·4H₂O (20 mmol) was dissolved in 70 mL of deionized water; subsequently, 4.4 mL of NH₃H₂O (25%) and 8.4 mL of H₂O₂ (30%) were added under continuous stirring, which continued for 30 min. Afterward, the above mixture was transferred to a Teflon-lined stainless-steel autoclave (100 mL). The autoclave was sealed and kept at 120 °C for 30 h and then cooled to room temperature. The products were filtered and washed severally with deionized water, and then dried at 105 °C in an oven for 12 h. The as-obtained sample was denoted as S0.

The Mn vacancy-rich γ -MnOOH samples were obtained via the reaction between KMnO₄ and ethylene glycol. KMnO₄ (20 mmol) and 0.5 mL of ethylene glycol (EG) were first dissolved in 60 and 20 mL of deionized water, respectively; thereafter, the aqueous solution of ethylene glycol was slowly added to the KMnO₄ solution under continuous stirring, which continued for 30 min. Subsequently, the mixture was added with 0 or 1 mL of H₂SO₄ (5 mol/L). Finally, the mixtures were hydrothermally treated, and the products were filtered, washed, and dried using the same procedures mentioned above. The two as-obtained samples were denoted as S1 (without H₂SO₄) and S2 (with H₂SO₄).

2.2. Characterization of catalysts

The X-ray diffraction (XRD) patterns were obtained by X-ray diffractometry (Bruker D8-Advance Germany) with Cu K α radiation, and the scanning rate was 10°/min in a 2 θ range of 5°–90°. SEM images were obtained using a field-emission scanning electron microscope (FESEM, Carl Zeiss, Germany). Transmission electron microscopic (TEM) and high-resolution TEM analyses (HRTEM) were conducted on a JEM-2100 instrument (JEOL, Japan) with an accelerating voltage of 150 kV. The Brunauer-Emmett-Teller (BET) specific surface area measurements were conducted on a Micromeritics ASAP 2020 analyzer (USA) by the multipoint method. Before testing, the samples were degassed at 150 °C for 4 h. Raman spectra were obtained using a confocal Raman spectrophotometer (Renishaw, Britain); the laser has a wavelength of 532 nm with a low power of 0.1 mW due to the sensitivity of manganese oxides to the laser.

X-ray photoelectron spectroscopy (XPS) analyses were carried out on an ESCALAB 250Xi X-ray photoelectron spectrometer (Thermo Fisher, USA). The operated pass energy was 30 eV, and the Al K α radiation (λ =1486.7 eV) was used as an exciting X-ray source. The element compositions of Mn and K were de-

terminated by inductively coupled plasma-optical emission spectroscopy (Vista-Mpx, Varian, USA) after the sample was digested with nitric acid. H₂-TPR and O₂-TPD were performed on an AutoChem-2920 instrument (Micromeritics, USA) equipped with a TCD detector. In these experiments, 50 mg samples were loaded in quartz tubes. Before measurement, the samples were pretreated at 105 °C for 30 min and cooled to 40 °C with helium gas (50 mL/min). For the H₂-TPR experiment, the sample was reduced by 5% H₂/Ar (50 mL/min) from 40 to 800 °C at a ramp rate of 5 °C/min. For the O₂-TPD experiment, after pretreatment, the sample was treated by 5% O₂/Ar (50 mL/min) for 30 min, and then purged by He flow for 30 min to stabilize the baseline and remove physically adsorbed O₂. Next, the sample was heated from 40 to 950 °C at a ramp rate of 5 °C/min in the helium flow (50 mL/min).

In-situ diffuse reflectance Fourier transform infrared spectra (DRIFTS) data were obtained using a Nicolet 6700 FTIR spectrometer (Micromeritics, USA) with a 4 cm⁻¹ resolution and 32 scans accumulation. The instrument was equipped with a temperature controlled *in-situ* cell and an MCT detector. The samples were pretreated with N₂ (50 mL/min) at a set temperature for 30 min; subsequently, IR data were collected at the airflow (80% N₂, 20% O₂), which contained ~15 ppm hexanal. Electron spin resonance (ESR) analyses were performed on a JEOL FA-200 instrument to detect the radicals using 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as a trapping agent in an aqueous or DMSO suspension.

2.3. Evaluation of the activity for hexanal removal

Samples of 50 mg (40-60 mesh) were put in a flow-through quartz reactor with an inner diameter of 6 mm, which was loaded on a piece of temperature-programmed control equipment. The temperature was maintained for 1 h at every set point to achieve a stable removal efficiency. Hexanal gas was generated by flowing synthetic air (N₂/O₂=79/21) over an hexanal-containing glass bottle kept in a temperature-controlled circulator; thereafter, the hexanal air was mixed with the dry air flow and the wet air flow in a buffer glass bottle to achieve an inlet hexanal concentration of 15 ppm and a relative humidity (RH) of 50% (detected at 25 °C). The total flow rate was 200 mL/min with a corresponding GHSV of 240 L/(g·h). The concentrations of hexanal and CO₂ were determined on-line by gas chromatography (GC2014, Shimadzu, Japan) equipped with an FID detector and methanizer. To identify the intermediates of hexanal in the gas phase, the hexanal was first adsorbed with the Tenax TA adsorbent, after which it was analyzed by automatic thermal desorption (ATD)-GC/MS (Turbomatrix 650 ATD, Perkin Elmer; GCMS-QP2010, Shimadzu). The catalytic stability of S2 was tested at 85 °C under the same condition, for 12 h; subsequently, the catalyst was regenerated *in-situ* at 180 °C by a clean airflow (500 mL/min) for 1 h. After regeneration, its activity was further tested under the same condition. The hexanal conversion and corresponding CO₂ conversion were calculated, respectively, as follows:

$$\text{Hexanal conversion} = \frac{[\text{hexanal}]_{\text{in}} - [\text{hexanal}]_{\text{out}}}{[\text{hexanal}]_{\text{in}}} \times 100\%.$$

$$\text{CO}_2 \text{ conversion} = \frac{[\text{CO}_2]_{\text{out}}}{6 \times [\text{hexanal}]_{\text{in}}} \times 100\%.$$

3. Results and discussion

3.1. Crystal structure and morphology

Fig. 1 shows the XRD patterns of the three samples synthesized under different conditions. All three samples exhibited strong crystallinity, and the peaks were coincident with the monoclinic structure of γ -MnOOH (JCPDS 41-1379). However, compared to that of sample S0 synthesized by oxidation of Mn²⁺ by H₂O₂, the samples synthesized by the reaction between KMnO₄ and ethylene glycol exhibited relatively weak crystallinity. Moreover, with the addition of H⁺ in the synthesis solution, sample S2 exhibited weaker crystallinity than that of S1.

The morphologies and structures of the samples were characterized by SEM and TEM. As shown in Fig. 2, all three γ -MnOOH samples had rod-like nanostructures. The S0 nanorods exhibited uniform morphologies with a diameter of ~20 nm and length of ~2–5 μ m. Its lattice fringe of 0.34 nm corresponding to the plane of (-1,1,1) can be clearly identified, which indicates a single-crystal structure of the nanorod. For S1 and S2, the nanorods presented a similar size with diameters ranging from 150–400 nm and lengths ranging from 10–15 μ m. Besides the nanorods, little nanoparticles attached to the nanorods could also be observed. Moreover, as shown in the HRTEM images, although S1 exhibited relatively clear lattice fringes of 0.34 and 0.26 nm corresponding to the planes of (-1,1,1) and (0,0,2), respectively, amorphous regions could be observed as indicated by the dash circles in Fig. 2. With the addition of sulfuric acid to the synthesis solution, the lattice fringe of 0.26 nm in the S2 sample became opaque, and it showed a much more disordered surface with relatively large amorphous regions. The above result, i.e., the addition of H⁺ that led to the distortion of the γ -MnOOH crystal structure and surface defects (amorphous regions), could be ascribed to the disproportionation reaction of Mn³⁺ under an acidic condition [42]:

Fig. 1. XRD patterns of the three samples synthesized under different conditions.

Fig. 2. SEM, TEM, and HRTEM images of the three samples: S0 (a1, a2, a3), S1 (b1, b2, b3), and S2 (c1, c2, c3).

Consequently, some of the Mn^{3+} ions in the lattice structure were dissolved into the solution in the form of Mn^{2+} , and some were oxidized into Mn^{4+} , leading to the increase in the average oxidation state of Mn. Lee et al. [43] also reported that acid treatment would cause the dissolution of Mn^{2+} , leading to the lattice contraction of the $\text{Na}_{0.44}\text{MnO}_2$ nanowire.

3.2. Physical and chemical properties

As shown in Table 1, the samples synthesized with KMnO_4 and ethylene glycol had a much larger BET surface area compared to that of S0. Although the addition of sulfuric acid into the synthesis solution distorted the $\gamma\text{-MnOOH}$ crystal structure and increased the surface amorphous regions, it did not change the general nanorod-like morphology. The specific surface area of the S2 sample ($120.4 \text{ m}^2/\text{g}$) was close to that of the S1 sample ($125.9 \text{ m}^2/\text{g}$).

Fig. 3 shows the Raman spectra of the three samples. Eight peaks could be observed at 146, 219, 258, 357, 386, 529, 557, and 620 cm^{-1} , which match well with other studies [44,45]. Until now, few studies on the identification of chemical bonds corresponding to the Raman shifts of $\gamma\text{-MnOOH}$ have been reported. Smith et al. [45] assigned the peaks at 357 and 388 cm^{-1} to the terminal Mn-O(H) tunnel and surface stretches, respectively. The peaks at 558 and 530 cm^{-1} were assigned to the

Fig. 3. Raman spectra of the three samples.

symmetric stretching vibration of the “long” [Mn-O-Mn] bridges from the two types of longer Mn-O bonds, while the peak at 621 cm^{-1} may be attributed to the symmetric stretch of the “short” [Mn-O-Mn] bridges from the shorter Mn-O bonds. The S0 sample showed the strongest peaks, and sample S2 showed even weaker peaks than those of S1, which was consistent with the XRD results. However, the peak at 621 cm^{-1} , corresponding to the short Mn-O bond, showed similar intensity in all three samples, which implies that the short Mn-O bonds are slightly affected by the changes in the crystallinity and surface defects of $\gamma\text{-MnOOH}$.

XPS measurements were performed to determine the surface elemental constitution and chemical states of the samples. The surface elemental contents determined by XPS are shown in Table 1. The difference in the binding energies (ΔE) between Mn 3s doublet peaks was used to calculate the average oxidation state (AOS) of Mn using the following empirical formula: $\text{AOS} = 8.956 - 1.126 \times \Delta E$ [46]. As shown in Fig. 4(a), ΔE values for the S0, S1, and S2 samples were 5.38, 5.24, and 5.03 eV, respectively; the corresponding AOSs of Mn were 2.90, 3.05, and 3.29, respectively. The increase in the AOS is accompanied with an increase in Mn vacancies and K^+ , as reflected by the increasing ratios of O/Mn and K/Mn in Table 1. These results can be explained as follows: first, in the acidic synthesis condition, some of the Mn^{3+} ions in $\gamma\text{-MnOOH}$ are dissolved in the form of Mn^{2+} and transformed into Mn^{4+} due to the disproportionation reaction. Accordingly, Mn vacancies occur, and the AOS of Mn increases. In addition, K^+ ions are adsorbed to compensate for the charge imbalance due to the loss of Mn^{2+} from $\gamma\text{-MnOOH}$, i.e., the content of K^+ is increased. As reported by Wang et al., the presence of Mn vacancies and a corresponding increase in K^+ concentration significantly increased the activity of $\delta\text{-MnO}_2$ toward HCHO oxidation [28].

The O 1s spectrum was fitted into three peaks [44,47]. As shown in Fig. 4(b), the peaks at the binding energies of 529.5, 530.7, and 532.2 eV are respectively assigned to O^{2-} , OH^- , and the surface adsorbed water or oxygen species. Ideally, $\gamma\text{-MnOOH}$ should have equal quantities of O^{2-} (Mn-O) and OH^- (Mn-OH); however, the state of the redox reaction, acidity-alkalinity of the crystal growth environment, disproportion-

Table 1

BET, XPS, and ICP-OES results of the as-synthesized samples.

Sample	Surface area (m^2/g)	ICP K/Mn	XPS			
			K/Mn	$\text{O}^{2-}/\text{OH}^-$	O/Mn	AOS of Mn
S0	31.8	0.0	0.0	0.98	1.92	2.9
S1	125.9	0.103	0.10	1.36	2.01	3.05
S2	120.4	0.107	0.14	1.97	2.03	3.29

Fig. 4. XPS spectra of the as-prepared samples. (a) Mn 3s; (b) O 1s; (c) Mn 2p_{3/2}.

ation, and surface defects may cause pronounced changes in the formation of surface oxygen. As shown in Table 1, the ratio of O²⁻/OH⁻ in the S0 sample was 0.98 (close to the ideal value), which is consistent with its perfect crystallinity, as reflected by XRD analysis. Conversely, the S1 and S2 samples exhibited much higher O²⁻/OH⁻ ratios (1.36 and 1.97, respectively), which is consistent with their increased AOSs of Mn and the Mn⁴⁺ ratio in Mn2p_{3/2}. The increase in the Mn AOS implies the increase in Mn⁴⁺ content (solely coordinated to O²⁻) and decrease in Mn³⁺ content (coordinated to O²⁻ and OH⁻). Consequently, the O²⁻/OH⁻ ratio significantly increased with an increase in the Mn AOS. Gao et al. reported [44] that the γ -MnOOH sample synthesized via the reaction of KMnO₄ and ethanol also had much higher O²⁻ than OH⁻. They thought that the deficit of hydrogen may be compensated for by the surface complexes with K⁺ ions, which is supported by our results, i.e., S1 and S2 had a relatively high content of K⁺.

H₂-TPR was used to evaluate the reducibility of the catalysts and to distinguish their catalytic activities. A relatively low starting reduction temperature usually means strong mobility of the lattice oxygen or more active adsorbed oxygen species, which, in turn, leads to a relatively high catalytic activity to-

ward the oxidation reaction of the corresponding materials [48]. As shown in Fig. 5(a), among the three samples, S0 had the highest starting reduction temperature; S1 and S2 had similar starting reduction temperatures. Ideally, γ -MnOOH would be gradually reduced via two reduction processes, i.e., being assigned to MnOOH→Mn₃O₄ and subsequently to Mn₃O₄→MnO. S0 presented two well-separated peaks, while the peaks of S1 or S2 partly overlapped; the S2 sample presented three peaks, which further confirmed the presence of Mn⁴⁺ in these two samples.

O₂-TPD was also used to evaluate the mobility of the oxygen species in the catalyst. As shown in Fig. 5(b), the profile can be divided into three regions [49]: low-temperature desorption (LT, <350 °C), medium temperature (MT, 350–650 °C), and high temperature (HT, >650 °C), which were ascribed to the release of surface active oxygen species / chemisorbed oxygen molecules, sub-surface lattice oxygen, and bulk lattice oxygen, respectively [46]. The oxygen species released at the LT are considered active and are responsible for the hexanal oxidation. As shown in Fig 5(b), S2 has a wider and stronger oxygen desorption peak at LT compared to those of the other samples, which should be beneficial to its catalytic activity.

Fig. 5. H₂-TPR (a) and O₂-TPD (b) profiles of the three samples.

Fig. 6. Temperature dependence of hexanal conversion (a) and corresponding CO₂ generation (b) over different samples.

3.3. Performance for hexanal oxidation and mechanism

The catalytic performances of the as-synthesized three samples for hexanal removal and CO₂ conversion are shown in Fig. 6. The S0 sample exhibited the lowest activity toward hexanal removal under a high GHSV of 240 L/(g·h); even at temperatures as high as 160 °C, the hexanal removal rate was less than 60%, and the corresponding CO₂ conversion was only 30%. Conversely, the samples with Mn vacancies showed better performance than S0 did. The S2 sample showed the best activity; even at room temperature (30 °C), it achieved 25% removal of hexanal, and 100% at 85 °C. At 160 °C, hexanal was completely converted into CO₂, which is evidently the best result. The high efficiency of the S2 sample could be ascribed to its abundance of Mn vacancies and surface defects, which act as active sites for hexanal oxidation.

As the catalytic stability is commonly considered, we further examined the stability of the S2 sample at 85 °C under the same test conditions. As shown in Fig. 7, after about 5 h, the hexanal removal ratio started to decrease from 100% to ~62% within

Fig. 7. The stability of S2 at 85 °C and its performance after regeneration at 180 °C for 1 h.

the next 7 h. After the catalyst was regenerated at 180 °C for 1 h, under the clean airflow of 500 mL/min, both the hexanal removal ratio and CO₂ conversion were completely recovered, and no obvious decline was observed during the repeated three cycles.

ESR analysis was used to detect the radicals in the as-synthesized samples, which would help to know what kind of active oxygen species is responsible for the hexanal removal and to further illustrate why the S2 sample exhibited the highest activity. DMPO (5,5-dimethyl-1-pyrroline N-oxide) was used as the trapping agent. In the aqueous suspension of DMPO and different γ -MnOOH samples, no significant signals were observed (not shown). However, as shown in Fig. 8, in the DMSO suspensions, the typical signals for the presence of the DMPO- $O_2^{\cdot -}$ adduct were clearly observed [50,51], which indicates that superoxide anion radicals were generated by the as-synthesized γ -MnOOH samples without irradiation at room temperature. The intensity of the DMPO- $O_2^{\cdot -}$ signal followed the order, S2 > S1 > S0, which is consistent with the order of their activities toward hexanal oxidation. It is well known that the

Fig. 8. ESR spectra of the $\bullet O_2^-$ radicals trapped by DMPO in DMSO solution.

superoxide anion radical is generated when an oxygen molecule accepts one electron [52,53]. The above results indicate that the richness in Mn vacancies and surface defects facilitates the facile activation of oxygen molecules in the S2 sample to generate superoxide anion radicals, which, in turn, leads to a high efficiency toward hexanal oxidation.

Fig. 9 shows the results of gas chromatography (GC) of the inlet gas and outlet gas at 100 and 30 °C, respectively. Obviously, gaseous intermediates were generated when the hexanal was degraded at 30 °C. While when the reaction temperature was increased to 100 °C, no significant intermediates were detected by GC. The gaseous intermediates during hexanal oxidation at 30 °C were collected and concentrated with an adsorbent tube, and subsequently analyzed by ATD-GC/MS. Besides the parent reactant, hexanal, pentanal and butanal were detected; however, no alcohols, ketones, and carboxylic acids were detected in the gas phase. This result, regarding the intermediates, is consistent with the report by Kolar et al. [21].

To further clarify the degradation pathway and intermediates of hexanal, *in-situ* DRIFTS observation of the S2 sample exposed to a 15 ppm hexanal/air flow was conducted (Fig. 10). The broad peak at 3558 cm⁻¹ can be ascribed to the surface -OH or adsorptive water; the peak at 1660 cm⁻¹ belongs to adsorbed water [54], and the peaks at 2343 and 1234 cm⁻¹ can be assigned to adsorbed CO₂ and carbonate, respectively, which further confirm the conversion of hexanal into H₂O and CO₂ during the catalytic reaction. The peak at 1030 cm⁻¹ can be assigned to the ν_s(C-O) of unspecified intermediates, such as dioxymethylene (DOM). The peaks at 1385 and 1420 cm⁻¹ can be assigned to ν(-CHO) and ν_s(-COOH), respectively. The peaks at 1550 and 1595 cm⁻¹ can be assigned to the ν_{as}(COO⁻) of carboxylate [55], which indicates the formation of carboxylic acids during the hexanal oxidation, although no carboxylic acids were detected in the gas phase due to their relatively lower volatility than that of aldehydes. According to the intermediates detected both on the catalyst surface and in the gas phase, we propose that the degradation of hexanal catalyzed by γ-MnOOH occurs in a stepwise manner. First, hexanal is oxidized into hexanoic acid, which is decarboxylated to generate CO₂ and form pentanal. Subsequently, the pentanal is further oxidized

Fig. 9. Gas chromatography of the inlet hexanal and outlet gas at 30 and 100 °C.

Fig. 10. *In-situ* DRIFTS spectra of the S2 sample exposed to a 15 ppm hexanal air flow at 60 °C.

into pentanoic acid, which is also decarboxylated to generate CO₂ and form butanal. The butanal is further oxidized in a similar manner. Finally, the hexanal and intermediates are completely converted into CO₂ and H₂O.

4. Conclusions

Mn vacancy-rich γ-MnOOH samples were synthesized and used for the degradation of hexanal. The γ-MnOOH samples synthesized via the hydrothermal reaction between permanganate and ethylene glycol contained much larger amounts of Mn vacancies than those synthesized via oxidation of Mn²⁺ ions by H₂O₂. In addition, the amount of Mn vacancies could be further increased via acid addition into the synthesis solution. The Mn vacancy-rich γ-MnOOH exhibited considerably high activity, achieving 100% removal of 15 ppm hexanal at 85 °C and complete conversion to CO₂ at 160 °C under the GHSV of 240 L/(g·h). The catalytic activity of Mn vacancy-rich γ-MnOOH can be completely regenerated by *in situ* heat-treatment at 180 °C under the flow of clean air. The high activity of Mn vacancy-rich γ-MnOOH can be ascribed to its large specific surface area and surface defects, which are beneficial for activating adsorbed oxygen to form active oxygen species. ESR analysis indicated that the Mn vacancy-rich sample contained much stronger intensity of superoxide anion radicals. ATD/GC-MS and *in-situ* FTIR observation implied that hexanal degrades in a stepwise manner; pentanal and butanal could be detected in the gas phase when the degradation is conducted at room temperature (30 °C), while carboxylate and carbonate groups could be observed on the catalyst surface.

Acknowledgments

This work was financially supported by National Natural Science Foundation of China (21677083) and Suzhou-Tsinghua Innovation Guiding Program (2016SZ0104).

Graphical Abstract

Chin. J. Catal., 2019, 40: 1525–1533 doi: S1872-2067(19)63415-7

Low-temperature catalytic degradation of the odorous pollutant hexanal by γ -MnOOH: The effect of Mn vacancies

Shanhong Sui, Pengyi Zhang *, Huiyu Zhang, Ranran Cao
Tsinghua university

Mn-vacancy rich γ -MnOOH was synthesized via the hydrothermal reaction between MnO_4^- and ethylene glycol with the addition of H_2SO_4 , which could efficiently degrade a major indoor odorant, hexanal, at a low temperature.

References

- [1] C. Zhou, Y. Zhan, S. Chen, M. Xia, C. Ronda, M. Sun, H. Chen, X. Shen, *Build. Environ.*, **2017**, 121, 26–34.
- [2] T. Salthammer, S. Mentese, R. Marutzky, *Chem. Rev.*, **2010**, 110, 2536–2572.
- [3] W. Liang, C. Yang, X. Yang, *Build. Environ.*, **2014**, 82, 693–701.
- [4] R. Kostianinen, *Atmos. Environ.*, **1995**, 29, 693–702.
- [5] S. Cakmak, R. E. Dales, L. Liu, L. M. Kauri, C. L. Lemieux, C. Hebborn, J. Zhu, *Environ. Pollut.*, **2014**, 194, 145–151.
- [6] K. M. Granström, *Fuel*, **2014**, 126, 219–223.
- [7] K. M. Granström, *For. Prod. J.*, **2010**, 60, 27–32.
- [8] R. Ghadiriasli, M. Wagenstaller, A. Buettner, *Anal. Bioanal. Chem.*, **2018**, 410, 6595–6607.
- [9] C. Jiang, D. Li, P. Zhang, J. Li, J. Wang, J. Yu, *Build. Environ.*, **2017**, 117, 118–126.
- [10] K. Hamaguchi-Hamada, C. Sanbo, S. Hamada, T. Yagi, *Neuroscience Res.*, **2004**, 48, 259–267.
- [11] Y. Cho, M. K. Song, S. C. Jeong, K. Lee, Y. Heo, T. S. Kim, J. C. Ryu, *Environ. Toxicol.*, **2016**, 31, 1909–1921.
- [12] M. Yao, Q. Zhang, D.W. Hand, D.L. Perram, R. Taylor, *J. Air Waste Manage. Assoc.*, **2009**, 59, 882–890.
- [13] D. Britt, D. Tranchemontagne, O. M. Yaghi, *P. Natl. Acad. Sci. U.S.A.*, **2008**, 105, 11623–11627.
- [14] T. Wang, S. Chen, H. Wang, Z. Liu, Z. Wu, *Chin. J. Catal.*, **2017**, 38, 793–804.
- [15] H. Ye, Y. Liu, S. Chen, H. Wang, Z. Liu, Z. Wu, *Chin. J. Catal.*, **2019**, 40, 681–690.
- [16] X. Li, J. Xie, C. Jiang, J. Yu, P. Zhang, *Front. Env. Sci. Eng.*, **2018**, 12, 1–32.
- [17] T. Xu, H. Zheng, P. Zhang, *Build. Environ.*, **2018**, 142, 379–387.
- [18] L. Qi, W. Ho, J. Wang, P. Zhang, J. Yu, *Catal. Sci. Technol.*, **2015**, 5, 2366–2377.
- [19] W. Li, H. Ye, G. Liu, H. Ji, Y. Zhou, K. Han, *Chin. J. Catal.*, **2018**, 39, 946–954.
- [20] X. Yao, Y. Li, Z. Fan, Z. Zhang, M. Chen, W. Shangguan, *Ind. Eng. Chem. Res.*, **2018**, 57, 4214–4224.
- [21] P. Kolar, J.R. Kastner, *Chemosphere*, **2010**, 78, 1110–1115.
- [22] Y. Li, T. T. Zhang, J. Wang, Z. Zhu, B. Jia, J. Yu, *Acta Phys. Chim. Sin.*, **2016**, 32, 2084–2092.
- [23] D. Xiang, G. Zhao, D. Ye, *Sciencepaper Online*, **2010**, 5, 355–359.
- [24] C. Chen, T. Liu, H. Wang, Q. Yu, J. Fan, L. Xiao, X. Zheng, *Chin. J. Catal.*, **2012**, 33, 941–951.
- [25] M. Wang, P. Zhang, J. Li, C. Jiang, *Chin. J. Catal.*, **2014**, 35, 335–341.
- [26] J. Ma, C. Wang, H. He, *Appl. Catal. B*, **2017**, 201, 503–510.
- [27] K. Qi, J. Xie, D. Fang, F. Li, F. He, *Chin. J. Catal.*, **2017**, 38, 845–852.
- [28] J. Wang, J. Li, C. Jiang, P. Zhou, P. Zhang, J. Yu, *Appl. Catal. B*, **2017**, 204, 147–155.
- [29] K. D. Kwon, K. Refson, G. Sposito, *Geochim. Cosmochim. Acta*, **2009**, 73, 4142–4150.
- [30] W. Zhao, H. Cui, F. Liu, W. Tan, X. Feng, *Clays Clay Miner.*, **2009**, 57, 513–520.
- [31] C. Wei, C. Xu, B. Li, D. Nan, J. Ma, F. Kang, *Mater. Res. Bull.*, **2012**, 47, 1740–1746.
- [32] F. Li, J. Wu, Q. Qin, Z. Li, X. Huang, *J. Alloys Compd.*, **2010**, 492, 339–346.
- [33] Y. Cao, Y. Xiao, Y. Gong, C. Wang, F. Li, *Electrochim. Acta*, **2014**, 127, 200–207.
- [34] C. C. Hu, Y. T. Wu, K. H. Chang, *Chem. Mater.*, **2008**, 20, 2890–2894.
- [35] X. B. Chen, C. Wang, F. M. Ye, Q. Zhu, G. Du, Y. Zhong, X. Peng, J. Z. Jiang, *CrystEngComm*, **2012**, 14, 3142–3148.
- [36] H. T. Tan, X. Rui, W. Shi, C. Xu, H. Yu, H. E. Hoster, Q. Yan, *ChemPlusChem*, **2013**, 78, 554–560.
- [37] Y. Li, H. Tan, O. Lebedev, J. Verbeeck, E. Biermans, G. Van Tendeloo, B. L. Su, *Cryst. Growth. Des.*, **2010**, 10, 2969–2976.
- [38] S. Guo, W. Sun, W. Yang, Q. Li, J. K. Shang, *RSC Adv.*, **2015**, 5, 53280–53288.
- [39] L. Mao, T. Sotomura, K. Nakatsu, N. Koshiba, D. Zhang, T. Ohsaka, *J. Electrochem. Soc.*, **2002**, 149, A504.
- [40] Y. Li, L. D. Liu, L. Liu, Y. Liu, H. W. Zhang, X. Han, *J. Mol. Catal. A*, **2016**, 411, 264–271.
- [41] X. F. Tang, J. H. Li, J. H. Chen, R. H. Wang, J. M. Hao, *Chin. J. Inorg. Chem.*, **2008**, 24, 1468–1473.
- [42] M. Ramstedt, S. Sjöberg, *Aquat Geochem*, **2005**, 11, 413–431.
- [43] J. H. Lee, R. Black, G. Popov, E. Pomerantseva, F. Nan, G. A. Botton, L. F. Nazar, *Energy Environ. Sci.*, **2012**, 5, 9558–9565.
- [44] T. Gao, F. Krumeich, R. Nesper, H. Fjellvåg, P. Norby, *Inorg. Chem.*, **2009**, 48, 6242–6250.
- [45] P. F. Smith, B. J. Deibert, S. Kaushik, G. Gardner, S. Hwang, H. Wang, J. F. Al-Sharab, E. Garfunkel, L. Fabris, J. Li, G. C. Dismukes, *ACS Catal.*, **2016**, 6, 2089–2099.
- [46] S. Rong, P. Zhang, F. Liu, Y. Yang, *ACS Catal.*, **2018**, 8, 435–446.
- [47] M. Ramstedt, A.V. Shchukarev, S. Sjöberg, *Surf. Interface. Anal.*, **2002**, 34, 632–636.

- [48] D. Chen, D. He, J. Lu, L. Zhong, F. Liu, J. Liu, J. Yu, G. Wan, S. He, Y. Luo, *Appl. Catal. B*, **2017**, 218, 249–259.
- [49] Y. Yang, J. Huang, S. Wang, S. Deng, B. Wang, G. Yu, *Appl. Catal. B*, **2013**, 142–143, 568–578.
- [50] S. U. Kim, Y. Liu, K. M. Nash, J. L. Zweier, A. Rockenbauer, F. A. Villamena, *J. Am. Chem. Soc.*, **2010**, 132, 17157–17173.
- [51] Y. Takanami, T. Nakayama, *Biosci. Biotechnol. Biochem.*, **2011**, 75, 34–39.
- [52] S. J. Liu, F. T. Li, Y. L. Li, Y. J. Hao, X. J. Wang, B. Li, R. H. Liu, *Appl. Catal. B*, **2017**, 212, 115–128.
- [53] N. Zhang, X. Li, H. Ye, S. Chen, H. Ju, D. Liu, Y. Lin, W. Ye, C. Wang, Q. Xu, J. Zhu, L. Song, J. Jiang, Y. Xiong, *J. Am. Chem. Soc.*, **2016**, 138, 8928–8935.
- [54] H. D. Lutz, *Struct. Bond.*, **1988**, 69, 97–125.
- [55] L. Zhu, J. Wang, S. Rong, H. Wang, P. Zhang, *Appl. Catal. B*, **2017**, 211, 212–221.

γ -MnOOH低温催化降解异味气体正己醛：锰缺陷的影响

随山红^{a,b}, 张彭义^{a,b,*}, 张惠玉^{a,b}, 曹冉冉^{a,b}

^a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

^b室内空气质量评价与控制北京市重点实验室, 北京100084

摘要: 正己醛是室内常见的挥发性有机物, 主要由板材类家具等释放, 由于其嗅味阈值很低、检出率高, 是引起室内异味的主要成分之一, 目前对正己醛的催化去除研究很少。 γ -MnOOH是常见的羟基锰氧化物, 常作为合成其他锰氧化物的前驱体, 在超级电容、离子电池、催化等领域有广泛的应用前景, 但将其作为气相反应催化剂的研究较少, 关于 γ -MnOOH中锰缺陷含量对其催化性能的影响未有报道。 本文通过两种水热反应体系制备了结晶性良好的 γ -MnOOH催化剂, 通过在高锰酸钾-乙二醇制备体系中添加一定量的硫酸制备了高锰缺陷含量的 γ -MnOOH催化材料, 通过正己醛的动态催化氧化反应体系对不同样品的催化性能进行了评价。 结果表明, 高锰缺陷含量的 γ -MnOOH对正己醛具有很高的催化活性, 85 °C下可以将浓度为15ppm、相对湿度50%、质量空速(GHSV)为240 L/(g·h)的正己醛完全去除, 在160 °C下可将正己醛完全转化为CO₂。

通过X射线衍射、扫描电镜、透射和高分辨透射电镜、N₂吸附-脱附, 拉曼光谱(Raman)、X射线光电子能谱(XPS)、氢气程序升温还原(H₂-TPR)、氧气程序升温脱附(O₂-TPD)和电子自旋共振谱(ESR)对材料的结构、形貌及物理化学性质等进行了表征, 并通过热脱附-气相色谱/质谱联用(ATD-GC/MS)和原位红外光谱分别对正己醛催化氧化反应中的气相产物、催化剂表面的中间物种进行了鉴别。 材料结构和形貌表征结果表明, 高锰缺陷含量的 γ -MnOOH结晶性相对较差, 表面晶格条纹畸变及化学键无序性很大, 锰的平均价态较高; H₂-TPR和O₂-TPD的测试结果表明, 添加硫酸制备的催化剂起始还原温度低, 还原过程连续性及晶格氧的迁移转化能力增强, 表面吸附氧物种含量增大; ESR的测试结果也表明, 该材料活化氧气产生超氧自由基(•O₂⁻)的能力更强, 这些都有利于提高催化剂的催化活性。 ATD-GC/MS的表征结果表明, 当正己醛未完全分解时, 正戊醛和正丁醛是最主要的气相产物; 通过原位红外对催化过程中催化剂表面的中间物种进行测定, 检测到醛类和羧酸类的吸收峰, 由此推测正己醛的催化氧化途径为正己醛氧化为己酸, 脱羧并氧化生成正戊醛, 后者再被氧化脱羧, 最终正己醛被逐级完全降解。

关键词: γ -MnOOH; 锰缺陷; 己醛降解; 室内空气; 催化

收稿日期: 2019-04-22. 接受日期: 2019-05-25. 出版日期: 2019-10-05.

*通讯联系人. 电话: (010)62773720; 传真: (010)62796840; 电子邮箱: zpy@tsinghua.edu.cn

基金来源: 国家自然科学基金(21677083); 苏州-清华创新引领行动专项(2016SZ0104).

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>).