available at www.sciencedirect.com

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

Article (Special Issue on Environmental and Energy Catalysis for Sustainable Development)

Structural effect and reaction mechanism of MnO₂ catalysts in the catalytic oxidation of chlorinated aromatics

Xiaole Weng^{a,b}, Yu Long^a, Wanglong Wang^a, Min Shao^{c,d}, Zhongbiao Wu^{a,b,*}^a Key Laboratory of Environment Remediation and Ecological Health, Ministry of Education, College of Environmental and Resource Sciences, Zhejiang University, Hangzhou 310058, Zhejiang, China^b Zhejiang Provincial Engineering Research Center of Industrial Boiler & Furnace Flue Gas Pollution Control, Hangzhou 310058, Zhejiang, China^c State Joint Key Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing 100871, China^d Environmental and climate Research institute, Jinan University, Guangzhou 511443, Guangdong, China

ARTICLE INFO

Article history:

Received 29 December 2018

Accepted 31 January 2019

Published 5 May 2019

Keywords:

MnO₂

Chlorobenzene

Catalytic oxidation

Polychlorinated byproducts

Environmental risk

ABSTRACT

Various MnO₂ structures have been extensively applied in catalysis. In this study, γ -MnO₂, α -MnO₂, and δ -MnO₂ with corresponding rod, tube, and hierarchical architecture morphologies were prepared and applied for the catalytic oxidation of chlorobenzene (CB). The redox ability, H₂O activation behavior, and acidity of MnO₂ were analyzed using a range of techniques, including TPR, H₂O-TPD, XPS, and pyridine-IR. The catalytic activities in CB oxidation were assessed; this revealed that γ -MnO₂ exhibited the highest activity and best stability, owing to its enriched surface oxygen vacancies that functioned to activate O₂ and H₂O, and capture labile chlorine, which reacted with dissociated H₂O to form HCl. All the MnO₂ phases generated toxic polychlorinated by-products, including CHCl₃, CCl₄, C₂HCl₃, and C₂Cl₄, indicating the occurrence of electrophilic chlorination during CB oxidation. In particular, the dichlorobenzene detected in the effluents of α -MnO₂ might generate unintended dioxins via a nucleophilic substitution reaction.

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

Published by Elsevier B.V. All rights reserved.

1. Introduction

Many industrial sources emit chlorinated volatile organic compounds (VOCs), including municipal and medical waste incineration, pharmaceutical production, and organic chemical industries [1–3]. The generation of chlorinated VOCs can cause a series of environmental risks, and threatens the health of humans because of the high toxicity and potential carcinogenicity of these compounds [4]. A number of measures have been taken to eliminate chlorinated VOCs, and catalytic combustion is considered to be an efficient and low-energy-cost option

[5–7]. However, challenges exist for the industrial application of this technique. Particularly, the applied catalysts tend to suffer from chlorine poisoning, leading to catalyst deactivation and the production of more hazardous byproducts [8].

Mn-based catalysts have been extensively applied in catalysis, e.g., in formaldehyde oxidation [9,10], toluene oxidation [11], CO oxidation [12,13], and selective catalytic reduction of NO_x [14,15]. The use of Mn-based catalysts for the catalytic oxidation of chlorinated VOCs has also been studied [16–18], and the textural properties of MnO₂ with different structures have been determined [19,20]. However, the correlation be-

* Corresponding author. Tel/Fax: +86-571-8795308; E-mail: zbwu@zju.edu.cn

This work was supported by the Outstanding Youth Project of Zhejiang Natural Science Foundation (LR19E080004) and the National Natural Science Foundation of China (51478418).

DOI: S1872-2067(19)63322-X | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 40, No. 5, May 2019

tween these structural features and the activity/stability for chlorinated VOCs oxidation has not been investigated.

In this study, γ -MnO₂, α -MnO₂, and δ -MnO₂ with corresponding rod, tube, and hierarchical architecture morphologies were prepared and subsequently applied for the catalytic oxidation of chlorobenzene (CB). The crystal phases and morphologies of MnO₂ were analyzed using powder X-ray diffraction (XRD) and scanning electron microscopy (SEM). The redox ability, H₂O activation behavior, and surficial chemical states were probed using H₂-temperature programmed reduction (H₂-TPR), O₂-temperature programmed desorption (O₂-TPD), H₂O-TPD, and X-ray photoelectron spectroscopy (XPS). The reaction mechanism and byproducts of CB oxidation were investigated to assess the applicability and potential environmental risk of the MnO₂ phases.

2. Experimental

2.1. Catalyst syntheses

All the reagents used in the experiments were of analytical grade and were used without any further treatments. Three different phase structures of MnO₂ were prepared using the following procedures. For α -MnO₂, 1.35 g of KMnO₄ and 3.0 mL of HCl (37 wt%) were added to 120 mL of water. After stirring magnetically for about 30 min, the solution was transferred to a Teflon-lined stainless-steel autoclave (200 mL), sealed, and maintained at 120 °C for 12 h in an electric oven. After cooling to room temperature, the sediment was washed with distilled water and ethanol several times, and then dried at 80 °C for about 12 h. δ -MnO₂ was prepared similarly, except that the amount of HCl added was 1.0 mL and the maintenance temperature was 100 °C. For γ -MnO₂, 6.32 g MnSO₄ mixed with 8.56 g (NH₄)₂S₂O₈ was dissolved in 150 mL of water under magnetic stirring for 30 min, and the solution was then transferred to a Teflon-lined stainless-steel autoclave, sealed, and maintained at 90 °C for 24 h. After cooling to room temperature, the sediment was treated in the same way as α -MnO₂ and δ -MnO₂.

2.2. Catalyst characterizations

Powder XRD was carried out using a powder diffractometer (Model D/MAX RA, Rigaku Co., Japan), with Cu K α radiation. The data were obtained at scattering angles (2θ) ranging from 10° to 80°.

The BET surface areas (S_{BET}) were measured using a static volumetric adsorption analyzer (JW-BK132F, Beijing JWGB Sci. & Tech. Co., Ltd., Beijing, China). All the samples were pretreated at 300 °C for 2 h in vacuum prior to the measurements.

SEM (Ultra 55, Carl Zeiss AG, USA), operated at 10 kV, was used to observe the microstructures and morphologies of the prepared samples. The powders were coated onto a conductive tape.

H₂-TPR experiments were carried out on a TP-5089 (supplied by Tianjin Xianquan Industry and Trade Development Co.). During the TPR measurements, 0.05 g sample (40–60 mesh) was loaded into a quartz fixed-bed micro-reactor and

pretreated under an 5% O₂/He flow of 30 mL/min at 350 °C for 1 h. The sample was then naturally cooled to room temperature, purged with N₂ containing 6% H₂ (30 mL/min), and heated from room temperature to 800 °C with a ramp of 10 °C/min. O₂-TPD experiments were conducted on the same apparatus as that used for H₂-TPR. 0.1 g sample (40–60 mesh) was pretreated under a flow of He containing 5% O₂ at 350 °C for 1 h before the experiment. After cooling to room temperature, the sample was heated from room temperature to 900 °C at a rate of 10 °C/min under a He flow of 20 mL/min. The evolution of oxygen from the sample was monitored with a mass spectrometer (MS, Hidden Analytical, Ltd.).

NH₃-TPD was also carried out in the TP-5089. Before the experiment, 0.1 g samples were pretreated at 350 °C for 2 h under He atmosphere. Then, they were purged with 6% NH₃/N₂ at a flow rate of 30 mL/min and temperature of 80 °C for 1 h. Subsequently, the samples were swept with pure He at a flow rate of 30 mL/min for 2 h at 100 °C and then heated to 800 °C at a rate of 10 °C/min. The desorbed NH₃ signals were recorded using a quadrupole mass spectrometer (Hidden Analytical, Ltd.). H₂O-TPD was conducted under a He stream, from 100 to 650 °C, similar to NH₃-TPD, with pretreatment and rehydration at 100 °C for 1 h.

XPS analysis was performed using a Thermo ESCALAB 250 spectrometer with an Al K α X-Ray ($h\nu = 1486.6$ eV) radiation excitation source. The data were calibrated using the signal of adventitious carbon (a binding energy of 284.8 eV) and fitted using the Shirley background and Gaussian peak shape with 20% Lorentzian character.

Pyridine-IR experiments were conducted using an FT-IR spectrometer (Tensor 27, Bruker, Germany) equipped with a custom-made IR cell that was connected to a vacuum adsorption apparatus. The measurements were carried out in situ and the spectra were recorded at a resolution of 5 cm⁻¹. The catalyst was pretreated at 300 °C for 1 h and then cooled to room temperature. After pretreatment, pyridine vapor was introduced until the adsorption attained saturation. Then, the desorption peaks were recorded at 250 °C.

2.3. Catalytic activity

Activity measurements were performed in a fixed-bed reactor. Prior to the tests, approximately 1 g of catalyst (with a trace amount of quartz sand to keep the mass of the active phase consistent) was loaded into a glass wool packing. All the samples were stabilized at 300 °C for 1 h under the flow of 10 vol% O₂/N₂. After the catalysts were cooled to room temperature, 500 ppm CB was introduced. The inlet flow rate was set to 160 mL/min with a gas hourly space velocity of 10000 h⁻¹. The reaction temperature was measured using a thermocouple with a measuring range of 150–400 °C loaded in the core of the catalyst bed. The catalysts were sieved into 40–60 mesh and each reaction temperature was maintained for 30 min to achieve a steady state of the reaction system. It should be noted that all the MnO₂ structures suffered from deactivation in long-term tests, particularly at temperatures lower than 300 °C. Therefore, the CB conversion and mineralization rates obtained

by 30 min stabilization only revealed an apparent activity of each MnO_2 phase. These data were used solely for evaluating the correlation between the redox ability and catalytic activity of MnO_2 in CB oxidation. The concentrations of CB and the generated CO_2 were measured on-line using a chromatograph (GC, Agilent 6890, USA) equipped with a flame ionization detector, an electron capture detector, and a nickel converting equipment. The error for the CB conversion and mineralization rate measurements was estimated to be approximately 3%.

2.4. By-product analyses

An adsorption tube (Tenax TA, 200 mg) was used to collect the off-gas (containing various gaseous products) at a given temperature for 20 min. A thermal desorption instrument (TDI, PERSEE-TP7, PR China) was used to release the adsorbed compounds into a GC/MS system (Agilent 7890A GC equipped with Agilent 5975C MS) equipped with a J&W GS-GasPro (113-4332) chromatography column (USA). The surficial accumulation compounds on the used catalysts were measured by heating the catalysts at 300 °C in a thermal desorption instrument, and analyzed using a GC/MS system with a J&W DB-624 (123-1334) gas chromatography column (USA).

3. Results and discussion

3.1. XRD and SEM analyses

It is well-known that MnO_2 can form multiple crystalline phases based on the way MnO_6 octahedra are interlinked. The MnO_2 crystal phase comprises various proportions of tunnels or interlayers [21]. There are one-dimensional (1×1) and (2×2) tunnels in the crystal structure of $\alpha\text{-MnO}_2$, constructed by the double chains of edge-sharing MnO_6 octahedra that are stabilized with K^+ or H_3O^+ . $\delta\text{-MnO}_2$ is birnessite-type MnO_2 with a two-dimensional (2D) layer structure containing edge-shared MnO_6 octahedra [22]. $\gamma\text{-MnO}_2$ contains random intergrowth of pyrolusite lamellar (1×1) channels and ramsdellite matrix (2×1) channels. As shown in Fig. 1, the powder XRD patterns of MnO_2 can all be indexed to the corresponding crystal phases,

Fig. 1. XRD patterns of MnO_2 .

Table 1

Specific surface area (S_{BET}), pore volume (V_{pore}), average pore size (D_{pore}), and average crystallite size of MnO_2 .

Catalyst	S_{BET} (m^2/g)	V_{pore} (cm^3/g)	D_{pore} (nm)	Average crystal- line size (nm)
$\alpha\text{-MnO}_2$	23.7	0.0470	7.61	20.7
$\gamma\text{-MnO}_2$	60.9	0.210	12.9	16.5
$\delta\text{-MnO}_2$	40.6	0.0880	8.32	18.2

i.e., $\delta\text{-MnO}_2$ (JCPDS Card No. 80-1098), $\alpha\text{-MnO}_2$ (JCPDS Card No. 44-0141), and $\gamma\text{-MnO}_2$ (JCPDS Card No. 44-0412), indicating that the applied synthetic conditions successfully yield the expected MnO_2 phases. The crystallite sizes of MnO_2 were estimated using the XRD peak half-widths, by applying the Scherrer equation, which revealed that $\gamma\text{-MnO}_2$ had a size of 16.5 nm, smaller than those of $\delta\text{-MnO}_2$ (18.2 nm) and $\alpha\text{-MnO}_2$ (20.7 nm). The BET surface area measurements (Table 1) were in line with the crystallite size calculations; $\gamma\text{-MnO}_2$ exhibited the highest specific surface area, total pore volume, and average pore size amongst the MnO_2 phases.

The morphologies of MnO_2 were analyzed using SEM. As shown in Fig. 2, $\alpha\text{-MnO}_2$ is mainly composed of tubes, typically 1–3 μm in length, with a square open end. $\gamma\text{-MnO}_2$ exhibits flat rod morphology, the lengths of which were approximately 1–2 μm . $\delta\text{-MnO}_2$ displays a hierarchical architecture morphology, consisting of microspherical cores and nanosheet coronas. It has been reported [23] that the morphologies of MnO_2 can profoundly affect its catalytic activities. This is due to the variations in the oxygen vacancy density [24], reducibility, and oxygen mobility [25].

3.2. XPS analyses

The chemical nature and composition of the surface species of MnO_2 were determined via XPS. Fig. 3(a) illustrates the O 1s XPS spectra of MnO_2 . In general, the O 1s XPS spectrum can be deconvoluted into three binding energy (BE) regions. The BE of O_{latt} at 529.8–530.3 eV can be ascribed to lattice oxygen (O_2^{2-}); the BE of O_{ads} at 531.1–531.6 eV belongs to surface-adsorbed oxygen (O_2^{2-} or O^-) and/or OH groups, and the BE at 533 eV is associated with adsorbed molecular water [26]. The molar ratio of $\text{O}_{\text{ads}}/(\text{O}_{\text{latt}}+\text{O}_{\text{ads}})$ in MnO_2 was calculated, and it followed the sequence $\gamma\text{-MnO}_2$ (20.7%) > $\alpha\text{-MnO}_2$ (15.4%) > $\delta\text{-MnO}_2$ (7.7%). Since the O_{ads} mainly originates from the dissociative adsorption of gaseous O_2 on the surface oxygen vacancies [27–29], it can be deduced that $\gamma\text{-MnO}_2$ contains the most surface oxygen vacancies amongst the MnO_2 phases.

The average oxidation state (AOS) of surface Mn was evaluated based on the Mn 3s doublet splitting (ΔE_s) [30]:

$$\text{AOS} = 8.956 - 1.126\Delta E_s$$

Fig. 2. SEM images of $\alpha\text{-MnO}_2$ (a), $\gamma\text{-MnO}_2$ (b), and $\delta\text{-MnO}_2$ (c).

Fig. 3. XPS spectra of O 1s (a), Mn 3s (b), and Mn 2p (c) of MnO₂.

The AOS of MnO₂ was calculated, and it followed the sequence $\delta\text{-MnO}_2$ (3.80) > $\alpha\text{-MnO}_2$ (3.75) > $\gamma\text{-MnO}_2$ (3.74), as shown in Fig. 3(b). This indicates that $\delta\text{-MnO}_2$ is mostly composed of the Mn⁴⁺ chemical state and $\gamma\text{-MnO}_2$ and $\alpha\text{-MnO}_2$ are enriched with Mn³⁺. These results were further supported by Mn 2p_{3/2} analyses, which revealed that the BE of Mn 2p_{3/2} followed the sequence $\delta\text{-MnO}_2$ > $\alpha\text{-MnO}_2$ > $\gamma\text{-MnO}_2$. These results were also consistent with O 1s XPS analyses, which indicated that the enriched Mn³⁺ on the surface of $\gamma\text{-MnO}_2$ and $\alpha\text{-MnO}_2$ were accompanied by the oxygen vacancies created for charge compensation, leading to more O_{ads} in the catalysts [31].

3.3. Temperature-programmed analyses

The redox abilities of MnO₂ were analyzed using H₂-TPR and O₂-TPD. The H₂-TPR profile (Fig. 4a) of $\alpha\text{-MnO}_2$ contains two H₂ consumption peaks centered at 337 and 361 °C. The former peak can be ascribed to the reduction of MnO₂ to Mn₂O₃ or Mn₃O₄ intermediates and the latter is due to the further reduction to MnO [32]. Since the amounts of H₂ consumption for the two peaks are approximately 1:1, the reduction of $\alpha\text{-MnO}_2$ is proposed to follow the MnO₂-Mn₂O₃-MnO sequence [23]. $\gamma\text{-MnO}_2$ exhibits only one H₂ consumption peak centered at approximately 338 °C with a hump at 496 °C. The H₂ consumption amount for the former peak was calculated to be about 2-fold higher than that of the latter. This indicates that the catalyst might undergo an MnO₂-Mn₃O₄-MnO reduction process.

For $\delta\text{-MnO}_2$, a reduction process sequence of MnO₂-Mn₂O₃-MnO was identified. Amongst the various MnO₂ structures, $\delta\text{-MnO}_2$ exhibits the lowest H₂ consumption temperatures, which indicates that this catalyst has the best reducibility, consistent with an earlier report [23].

In the O₂-TPD profile (Fig. 4(b)), the desorbed oxygen species can be categorized into chemisorbed oxygen species ($\alpha\text{-O}$) at 100–300 °C, superficial lattice oxygen ($\alpha'\text{-O}$) at 300–600 °C, and bulk lattice oxygen ($\beta\text{-O}$) above 600 °C [33,34]. For all the MnO₂ structures, the desorption of $\alpha\text{-O}$ was not distinct. Only small humps were observed in the $\gamma\text{-MnO}_2$ and $\alpha\text{-MnO}_2$ profiles after amplifying the data. $\gamma\text{-MnO}_2$ exhibits the most distinct $\alpha'\text{-O}$ desorption peak at approximately 529 °C, followed by $\alpha\text{-MnO}_2$ at approximately 567 °C. $\delta\text{-MnO}_2$ displays a hump at a lower temperature of 490 °C, consistent with the H₂-TPR analysis results. However, the lack of surface oxygen vacancies (as indicated by XPS analyses, see Fig. 3) in $\delta\text{-MnO}_2$ inhibited the mobility of $\alpha'\text{-O}$, leading to the lowest $\alpha'\text{-O}$ desorption among the catalysts.

3.4. NH₃-TPD analyses

NH₃-TPD was applied to identify the acid sites of MnO₂. As shown in Fig. 5(a), $\gamma\text{-MnO}_2$ exhibits three NH₃ desorption peaks at approximately 168, 280, and 440 °C, corresponding to weak, moderate, and strong acid sites, respectively [35,36]. According to pyridine-IR analyses (Fig. 5(b)), both $\gamma\text{-MnO}_2$ and $\delta\text{-MnO}_2$

Fig. 4. H₂-TPR (a) and O₂-TPD (b) profiles of MnO₂.

Fig. 5. NH₃-TPD (a) and pyridine-IR (b) spectra of MnO₂.

contained a majority of Lewis acid sites, as indicated by the appearance of bands at 1445 and 1602 cm⁻¹ [37,38]. This Lewis acidity should have originated from the Mn⁴⁺ and the release of surface oxygen that led to the exposure of unsaturated coordinated Mn³⁺ atom centers [39,40]. For α -MnO₂, the pyridine-IR analysis did not indicate the characteristics of either the Lewis or Brønsted acidities, although the catalyst exhibited certain moderate acid sites in the NH₃-TPD analysis. We repeated the pyridine-IR measurements several times but could not observe any acidity. The reason is unfortunately unknown. As reported [41,42], both Lewis and Brønsted acid sites can act as the chlorinated VOCs adsorption sites; chlorinated VOCs adsorb on the Lewis sites via chlorine abstraction, which can lead to catalyst chlorination, and on the Brønsted acid sites via a hydrogen abstraction, to form HCl.

3.5. Activity and CO₂ selectivity measurements

Fig. 6(a) illustrates the activities of MnO₂ in the catalytic oxidation of CB. γ -MnO₂ and δ -MnO₂ displayed similar activities in CB conversion. Their T_{90} (i.e., the temperature for 90% CB conversion) were measured to be approximately 175 °C. For α -MnO₂, a relatively higher T_{90} was obtained at approximately

205 °C. Based on the CO₂ selectivity measurements (Fig. 6(b)), however, δ -MnO₂ exhibits the worst CO₂ selectivity. Only approximately 35% CO₂ production was achieved. This is unusual because, according to the H₂-TPR and O₂-TPD analyses, δ -MnO₂ shows the best redox ability, and can be expected to exhibit a high CO₂ selectivity in CB oxidation.

CB-temperature-programmed surface reduction (TPSR) measurements were then performed to evaluate the chlorine adsorption and desorption behaviors over the MnO₂ phases. As shown in Fig. 7(a), none of the MnO₂ phases exhibited Cl₂ desorption at temperatures lower than 400 °C. Only after elevating the temperature up to 550 °C was distinct Cl₂ desorption observed (Fig. 7(b)). This indicated that the Deacon reaction did not occur within the investigated temperature range. In contrast, all the MnO₂ phases produced HCl at temperatures of 100–300 °C, and γ -MnO₂ exhibited the highest HCl production. This indicates that the chlorine dissociated from CB was mainly removed in the form of HCl over all the MnO₂ phases.

To evaluate the origin of H for the formation of HCl, H₂O activation was evaluated using H₂O-TPD. In general, the H₂O-TPD profile can be classified into three regions. The first region with temperatures less than 300 °C can be ascribed to the adsorbed H₂O molecules that directly contact the MnO₂ surface (denoted

Fig. 6. CB conversions (a) and mineralization rates (b) of MnO₂ versus temperature.

Fig. 7. (a) CB-TPSR profiles for all the MnO₂ phases; (b) CB-TPSR profile for γ -MnO₂; (c) H₂O-TPD profiles of MnO₂; (d) stability measurements of MnO₂. Reaction conditions: 500 ppm CB, 10 vol% O₂, He balance, WHSV 10000 mL/(g_{cat}·h).

as Type I) [43,44]; the second region with temperatures at approximately 300–450 °C is associated with the dehydration of structural hydroxyl group clusters (denoted as Type II); and the third region with temperatures higher than 450 °C corresponds to the dehydration of strongly bonded hydroxyl groups [45] (via the interaction of migrated vicinal and spaced groups [46], denoted as Type III). As shown in Fig. 7(c), all the MnO₂ phases were capable of dissociating H₂O, which produced M-OH and H protons (i.e. Type II), and γ -MnO₂ exhibited the most Type II H₂O, whereas α -MnO₂ exhibited the lowest. According to Gun'ko et al. [46] and Yin et al. [47], the dissociation of H₂O preferentially occurs on the oxygen vacancies and high-valence Mnⁿ⁺-O, i.e., the acid-base centers [18,46,47]. This explains why α -MnO₂, with the lowest surface area and moderate oxygen vacancies or Mn⁴⁺, exhibits the worst H₂O dissociation ability amongst the MnO₂ phases.

It should be noted that the H₂O-TPD results were in conflict with the CB-TPSR results, which showed that α -MnO₂ generated more HCl than δ -MnO₂ but with worse H₂O dissociation ability. This was probably because the Cl in δ -MnO₂ had difficulty in reacting with dissociated H₂O to form HCl. As indicated by the XPS and H₂-TPR analyses (Fig. 3 and Fig. 4(a)), δ -MnO₂ mostly contained Mn⁴⁺; the dissociation of CB on enriched Mn⁴⁺ was

expected to produce strong Mn-Cl bands (binding energy of 338.5 kJ/mol). This was evidenced by the H₂-TPR analysis results for aged catalysts (supplementary Fig. S1), which revealed that the majority of Mn⁴⁺ in δ -MnO₂ had been converted into Mn³⁺ by the attack of Cl. Only one H₂ consumption peak at approximately 490 °C was observed for the aged δ -MnO₂. For γ -MnO₂ and α -MnO₂, some Mn⁴⁺, with a H₂ consumption peak at approximately 450 °C, was retained. The preferential adsorption of CB on the oxygen vacancies might protect the Mn⁴⁺ sites. The chlorines captured by the oxygen vacancies were reported to be more labile than those bonded with Mn⁴⁺ [48], and tended to react with dissociated H₂O, forming HCl and facilitating Cl desorption. Stability measurements (Fig. 7(d)) confirmed that γ -MnO₂ exhibited a stable CB oxidation at 300 °C, whereas α -MnO₂ was initially deactivated to produce 80% CB conversion and was then stabilized. In comparison, δ -MnO₂ exhibited a continuous deactivation at 300 °C, showing a more severe Cl poisoning in CB oxidation. This also explained why this catalyst exhibited the worst CO₂ selectivity amongst the MnO₂ phases.

3.6. Byproduct measurements

Gaseous by-products in the effluents after 10 h of ageing at

Fig. 8. GC-MS analyses of gaseous by-products (a) and surface-accumulated compounds (b) of MnO_2 after ageing at 300 °C for 10 h.

300 °C were collected using an adsorption column, and were then released for GC/MS analyses. The accumulated organics on the catalyst surface were directly released for analyses. As shown in Fig. 8, significant polychlorinated by-products, including CHCl_3 , CCl_4 , C_2HCl_3 , and C_2Cl_4 were detected for all the MnO_2 phases, indicating that an electrophilic chlorination reaction occurred during the CB oxidation. $\alpha\text{-MnO}_2$ produced the most polychlorinated by-products, owing to its enriched labile chlorine (captured in oxygen vacancies) and a lack of H_2O dissociation ability for efficient chlorine desorption. In particular, $\alpha\text{-MnO}_2$ was found to produce certain amounts of dichlorobenzene. These byproducts tended to form chlorophenols via a nucleophilic substitution reaction, and eventually condensed into dioxin-like compounds [49–51]. The byproduct measurements indicated that all the MnO_2 phases generated polychlorinated byproducts in the catalytic oxidation of CB; this might cause environmental risks in such applications.

4. Conclusions

Three MnO_2 phases with different structures were prepared and applied for the catalytic oxidation of CB. XRD and SEM analyses confirmed the successful formation of the $\alpha\text{-MnO}_2$, $\delta\text{-MnO}_2$, and $\gamma\text{-MnO}_2$ phases. After being subjected to TPR analyses, the redox abilities of the MnO_2 products were found to follow the sequence $\delta\text{-MnO}_2 \geq \gamma\text{-MnO}_2 > \alpha\text{-MnO}_2$, which was in line with their performances in CB conversion but was not consistent with their CO_2 selectivity. The enriched Mn^{4+} in $\delta\text{-MnO}_2$ was found to generate strong Mn-Cl bonds that hindered the subsequent reaction of Cl with dissociated H_2O to form HCl. This resulted in a continuous deactivation of $\delta\text{-MnO}_2$ even at a temperature of 300 °C, leading to the lowest CO_2 selectivity in CB oxidation. All the MnO_2 phases were found to produce toxic polychlorinated by-products, including CHCl_3 , CCl_4 , C_2HCl_3 , and C_2Cl_4 . In particular, the generation of dichlorobenzene by $\alpha\text{-MnO}_2$ might lead to the production of unintended dioxins. This work explores the effect of MnO_2 structures on the catalytic activity for CB oxidation and reveals the potential environmental risks of MnO_2 applied for the combustion of chlorinated aromatics.

References

- [1] J. A. Conesa, L. Rey, S. Egea, M. D. Rey, *Environ. Sci. Technol.*, **2011**, 45, 5878–5884.
- [2] H. B. Duan, J. H. Li, Y. C. Liu, N. Yamazaki, W. Jiang, *Environ. Sci. Technol.*, **2011**, 45, 6322–6328.
- [3] Z. Cheng, J. R. Li, P. Yang, S. F. Zuo, *Chin. J. Catal.*, **2018**, 39, 849–856.
- [4] M. J. Morra, V. Borek, J. Koolpe, *J. Environ. Qual.*, **2000**, 29, 706–715.
- [5] J. Xiang, Q. Wu, X. Mei, J. Liu, Y. Wei, Z. Zhao, D. Wu, J. Li, *ACS Catal.*, **2018**, 8, 7915–7930.
- [6] M. Y. Lin, X. L. Yu, X. Q. Yang, K. Z. Li, M. F. Ge, J. H. Li, *Catal. Sci. Technol.*, **2017**, 7, 1573–1580.
- [7] X. X. Dai, W. Y. Jiang, W. L. Wang, X. L. Weng, Y. Shang, Y. H. Xue, Z. B. Wu, *Chin. J. Catal.*, **2018**, 39, 728–735.
- [8] S. K. Agarwal, J. J. Spivey, J. B. Butt, *Appl. Catal. A*, **1992**, 82, 259–275.
- [9] J. L. Wang, J. E. Li, C. J. Jiang, P. Zhou, P. Y. Zhang, J. G. Yu, *Appl. Catal., B*, **2017**, 204, 147–155.
- [10] L. Zhu, J. L. Wang, S. P. Rong, H. Y. Wang, P. Y. Zhang, *Appl. Catal., B*, **2017**, 211, 212–221.
- [11] X. L. Weng, W. L. Wang, Q. J. Meng, Z. B. Wu, *Catal. Sci. Technol.*, **2018**, 8, 4364–4372.
- [12] X. D. Zhang, H. X. Li, F. L. Hou, Y. Yang, H. Dong, N. Liu, Y. X. Wang, L. F. Cui, *Appl. Surf. Sci.*, **2017**, 411, 27–33.
- [13] X. D. Zhang, H. X. Li, X. T. Lv, J. C. Xu, Y. X. Wang, C. He, N. Liu, Y. Q. Yang, Y. Wang, *Chem. Eur. J.*, **2018**, 24, 8822–8832.
- [14] D. M. Meng, Q. Xu, Y. L. Jiao, Y. Guo, Y. L. Guo, L. Wang, G. Z. Lu, W. C. Zhan, *Appl. Catal. B*, **2018**, 221, 652–663.
- [15] D. M. Meng, W. C. Zhan, Y. Guo, Y. L. Guo, L. Wang, G. Z. Lu, *ACS Catal.*, **2015**, 5, 5973–5983.
- [16] W. L. Wang, Q. J. Meng, Y. H. Xue, X. L. Weng, P. F. Sun, Z. B. Wu, *J. Catal.*, **2018**, 366, 213–222.
- [17] X. L. Weng, P. F. Sun, Y. Long, Q. J. Meng, Z. B. Wu, *Environ. Sci. Technol.*, **2018**, 52, 8986–8986.
- [18] X. L. Weng, Q. J. Meng, J. J. Liu, W. Y. Jiang, S. Pattison, Z. B. Wu, *Environ. Sci. Technol.*, **2019**, 53, 884–893.
- [19] S. Liang, F. Teng, G. Bulgan, R. Zong, Y. Zhu, *J. Phys. Chem. C*, **2008**, 112, 5307–5315.
- [20] F. Wang, H. Dai, J. Deng, G. Bai, K. Ji, Y. Liu, *Environ. Sci. Technol.*, **2012**, 46, 4034–4041.
- [21] E. Saputra, S. Muhammad, H. Q. Sun, H. M. Ang, M. O. Tade, S. B. Wang, *Environ. Sci. Technol.*, **2013**, 47, 5882–5887.
- [22] S. Q. Zhao, T. M. Liu, D. W. Hou, W. Zeng, B. Miao, S. Hussain, X. H. Peng, M. S. Javed, *Appl. Surf. Sci.*, **2015**, 356, 259–265.
- [23] J. H. Zhang, Y. B. Li, L. Wang, C. B. Zhang, H. He, *Catal. Sci. Technol.*, **2015**, 5, 2305–2313.

Graphical Abstract

Chin. J. Catal., 2019, 40: 638–646 doi: S1872-2067(19)63322-X

Structural effect and reaction mechanism of MnO₂ catalysts in the catalytic oxidation of chlorinated aromatics

Xiaole Weng, Yu Long, Wanglong Wang, Min Shao, Zhongbiao Wu *
 Zhejiang University;
 Zhejiang Provincial Engineering Research Center of Industrial Boiler
 & Furnace Flue Gas Pollution Control;
 Peking University;
 Jinan University

Three different crystal structures of MnO₂ were prepared to explore their reaction mechanisms and environmental risks for the catalytic oxidation of chlorinated aromatics.

- [24] F. Wang, H. X. Dai, J. G. Deng, G. M. Bai, K. M. Ji, Y. X. Liu, *Environ. Sci. Technol.*, **2012**, 46, 4034–4041.
- [25] Y. J. Zhang, L. Zhang, J. G. Deng, H. X. Dai, H. He, *Inorg. Chem.*, **2009**, 48, 2181–2192.
- [26] K. Jirátová, J. Mikulová, J. Klempa, T. Grygar, Z. Bastl, F. Kovanda, *Appl. Catal. A*, **2009**, 361, 106–116.
- [27] P. J. Gellings, H. J. M. Bouwmeester, *Catal. Today*, **2000**, 58, 1–53.
- [28] V. V. Pushkarev, V. I. Kovalchuk, J. L. d'Itri, *J. Phys. Chem. B*, **2004**, 108, 5341–5348.
- [29] J. Haber, W. Turek, *J. Catal.*, **2000**, 190, 320–326.
- [30] V. P. Santos, O. S. G. P. Soares, J. J. W. Bakker, M. F. R. Pereira, J. J. M. Orfao, J. Gascon, F. Kapteijn, J. L. Figueiredo, *J. Catal.*, **2012**, 293, 165–174.
- [31] Y. Yang, S. Z. Zhang, S. W. Wang, K. L. Zhang, H. Z. Wang, J. Huang, S. B. Deng, B. Wang, Y. J. Wang, G. Yu, *Environ. Sci. Technol.*, **2015**, 49, 4473–4480.
- [32] V. P. Santos, M. F. R. Pereira, J. J. M. Orfao, J. L. Figueiredo, *Appl. Catal. B*, **2010**, 99, 353–363.
- [33] J. B. Jia, P. Y. Zhang, L. Chen, *Catal. Sci. Technol.*, **2016**, 6, 5841–5847.
- [34] Y. Yang, J. Huang, S. Wang, S. Deng, B. Wang, G. Yu, *Appl. Catal. B*, **2013**, 142, 568–578.
- [35] B. H. Aristizabal, C. Maya, C. M. de Correa, *Appl. Catal. A*, **2008**, 335, 211–219.
- [36] R. Barthos, F. Lonyi, G. Onyestyak, J. Valyon, *J. Phys. Chem. B*, **2000**, 104, 7311–7319.
- [37] V. D. Makwana, Y. C. Son, A. R. Howell, S. L. Suib, *J. Catal.*, **2002**, 210, 46–52.
- [38] T. Zhang, J. Liu, D. X. Wang, Z. Zhao, Y. C. Wei, K. Cheng, G. Y. Jiang, A. J. Duan, *Appl. Catal. B*, **2014**, 148, 520–531.
- [39] A. Auroux, A. Gervasini, *J. Phys. Chem.*, **1990**, 94, 6371–6379.
- [40] G. S. Qi, R. T. Yang, *J. Phys. Chem. B*, **2004**, 108, 15738–15747.
- [41] M. A. Larrubia, G. Busca, *Appl. Catal. B*, **2002**, 39, 343–352.
- [42] S. Albonetti, S. Blasioli, R. Bonelli, J. E. Mengou, S. Scire, F. Trifiro, *Appl. Catal. A*, **2008**, 341, 18–25.
- [43] Q. Dai, L. L. Yin, S. Bai, W. Wang, X. Wang, X. Q. Gong, G. Lu, *Appl. Catal. B*, **2016**, 182, 598–610.
- [44] C. Zhang, C. Wang, W. Zhan, Y. Guo, Y. Guo, G. Lu, A. Baylet, A. Giroir-Fendler, *Appl. Catal. B*, **2013**, 129, 509–516.
- [45] S. Afzal, X. Quan, J. L. Zhang, *Appl. Catal. B*, **2017**, 206, 692–703.
- [46] V. M. Gun'ko, V. I. Zarko, B. A. Chuikov, V. V. Dudnik, Y. G. Ptushinskii, E. F. Voronin, E. M. Pakhlov, A. A. Chuiko, *Int. J. Mass Spectrom. Ion Processes*, **1998**, 172, 161–179.
- [47] H. Yin, S. Zhao, K. Zhao, A. Muqit, H. Tang, L. Chang, H. Zhao, Y. Gao, Z. Tang, *Nat. Commun.*, **2015**, 6, 6430.
- [48] H. A. Miran, M. Altarawneh, Z. T. Jiang, H. Oskierski, M. Altarawneh, B. Z. Dlugogorski, *Catal. Sci. Technol.*, **2017**, 7, 3902–3919.
- [49] C. C. Du, S. Y. Lu, Q. L. Wang, A. G. Buekens, M. J. Ni, D. P. Debecker, *Chem. Eng. J.*, **2018**, 334, 519–544.
- [50] S. L. Alderman, G. R. Farquar, E. D. Poliakoff, B. Dellinger, *Environ. Sci. Technol.*, **2005**, 39, 7396–7401.
- [51] P. F. Sun, W. L. Wang, X. X. Dai, X. L. Weng, Z. B. Wu, *Appl. Catal. B*, **2016**, 198, 389–397.

MnO₂催化剂用于催化氧化含氯芳香烃的形貌效应与反应机制研究

翁小乐^{a,b}, 龙宇^a, 王望龙^a, 邵敏^{c,d}, 吴忠标^{a,b,*}

^a浙江大学环境与资源科学学院, 教育部环境修复与生态健康重点实验室, 浙江杭州310058

^b浙江省工业锅炉炉窑烟气污染控制工程技术研究中心, 浙江杭州310058

^c北京大学环境科学与工程学院, 国家环境模拟与污染控制联合重点实验室, 北京100871

^d暨南大学环境与气候研究所, 广东广州511443

摘要: 含氯挥发性有机物(Chlorinated VOCs)被广泛应用于工业、农业、医药、有机合成等领域, 在使用过程中会通过挥发、泄漏、废气排放等途径进入大气环境中, 造成臭氧层破坏与光化学烟雾, 且很难被生物降解, 对人体具有很强的“三致”效应。

在众多治理方法中,催化燃烧因高效低能耗的特点而被认为是具有应用前景的含氯VOCs处理方式,然而催化剂中毒以及毒副产物生成极大限制了该技术的工业应用. 锰基催化剂由于价格低廉、来源广泛以及价态多变等特点被广泛应用于环境催化领域,包括甲醛、甲苯、CO催化氧化以及选择性催化还原脱硝等. MnO_2 的晶体形貌与其催化性能息息相关,二者的构效关系已有广泛研究,但在含氯VOCs催化氧化中, MnO_2 的形貌特征与催化活性、反应稳定性、副产物等的关系尚不明晰. 因此,本文通过水热法制备了纳米棒状 $\gamma\text{-MnO}_2$,纳米管状 $\alpha\text{-MnO}_2$ 以及具有层状结构的 $\delta\text{-MnO}_2$,系统研究了这三种形貌结构在氯苯催化氧化中的反应特征,利用XRD, XPS, TPR, TPD, 吡啶-IR等手段对催化剂的形貌、表面元素价态、氧化还原性能以及表面酸性等进行了表征,获得了 MnO_2 在含氯VOCs催化氧化应用中的构效关系.

XRD以及SEM分析结果表明,三种形貌的 MnO_2 样品均由水热法成功制得. H_2 -TPR和 O_2 -TPD测试分析显示, MnO_2 催化剂的氧化还原性能按如下顺序递减 $\delta\text{-MnO}_2 \geq \gamma\text{-MnO}_2 > \alpha\text{-MnO}_2$,与这些催化剂活性测试中的氯苯转化率结果一致,但与其 CO_2 选择性的结果不一致. 氧化还原能力最佳的 $\delta\text{-MnO}_2$ 上 CO_2 选择性表现最差,即使提高温度仍无法提升. XPS结果表明,三种催化剂的Mn元素平均价态高低顺序为 $\delta\text{-MnO}_2$ (3.80) $>$ $\alpha\text{-MnO}_2$ (3.75) $\geq$ $\gamma\text{-MnO}_2$ (3.74). $\delta\text{-MnO}_2$ 催化剂表面因具有最丰富的 Mn^{4+} ,反应过程中易生成强的Mn-Cl键,从而抑制了Cl与解离水反应生成HCl,导致催化剂富集氯失活, CO_2 选择性差. 对反应尾气及催化剂表面产物分析后发现,三种 MnO_2 催化剂均生成了具有更高毒性的多氯副产物,其中主要有 CHCl_3 , CCl_4 , C_2HCl_3 , C_2Cl_4 等,尤其在 $\alpha\text{-MnO}_2$ 催化剂表面发现了二氯苯存在,其可能通过进一步的亲核取代生成氯苯酚,并最终聚合成二噁英类物质.

关键词: MnO_2 ; 氯苯; 催化氧化; 多氯副产物; 环境风险

收稿日期: 2018-12-29. 接受日期: 2019-01-31. 出版日期: 2019-05-05.

*通讯联系人. 电话/传真: (0571)8795308; 电子信箱: zbwu@zju.edu.cn

基金来源: 浙江省杰出青年基金(LR19E080004); 国家自然科学基金(51478418).

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>).