



Tungsten doped manganese dioxide for efficient removal of gaseous formaldehyde at ambient temperatures

Fang Liu^a, Ranran Cao^{a,b}, Shaopeng Rong^{a,b}, Pengyi Zhang^{a,b,c,*}

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

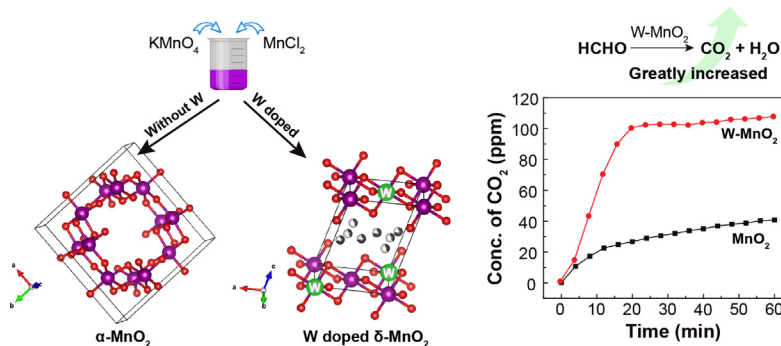
^b Laboratory of Solid Waste Management and Environment Safety (Tsinghua University), Ministry of Education, Tsinghua University, Beijing 100084, China

^c Beijing Key Laboratory for Indoor Air Quality Evaluation and Control, Beijing 100084, China

HIGHLIGHTS

- Tungsten doped MnO₂ was first investigated for HCHO decomposition at ambient temperatures.
- Tungsten modification decreased crystallinity of MnO₂ and increased specific surface area.
- Substitution of W⁶⁺ reduced the chemical valence of Mn and made adsorbed surface oxygen species more active.
- W-MnO₂ catalyst with the W/Mn ratio 0.2 achieved efficient and stable activity for real-level indoor HCHO.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 1 October 2017

Received in revised form 7 March 2018

Accepted 8 April 2018

Available online 11 April 2018

Keywords:

Formaldehyde
Manganese oxides
Tungsten-doped
Indoor air

ABSTRACT

Room-temperature active catalysts are very important to combat against ubiquitous indoor HCHO pollution. Here, tungsten doped MnO₂ (W-MnO₂) was first synthesized and investigated for HCHO decomposition at ambient temperature. With addition of WCl₆ as precursor into the mixture of permanganate and manganese chloride, tungsten-doped δ-MnO₂ with weak crystallinity and large specific surface area (>230 m²/g) was synthesized. Substitution of W⁶⁺ for Mn in MnO₆ groups reduced the chemical valence of Mn and made adsorbed surface oxygen species more active. As a result, the W-MnO₂ catalyst with the nominal W/Mn ratio achieved efficient and stable activity for real-level indoor HCHO (0.3 mg/m³) under the GHSV as high as 600 L/g_{cat}·h, the removal efficiency reaching 90% at 30 °C and 60% at 5 °C, respectively.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

Formaldehyde (HCHO) is a ubiquitous indoor pollutant, which is mainly released from wood-based building materials, furnishing, and various decorative materials [1–3]. Long-term exposure to even low concentration HCHO would increase the risk of human health, such as

irritation of skin, eyes, nose and throat and some types of cancers [4,5]. Thus, removal of HCHO from the indoor environment is very important for public health. Numerous efforts have been devoted to combat HCHO pollution, and catalytic oxidation is one of the most promising and cost-effective technologies due to its lower reaction temperature required and no extra energy demand [6–9]. Noble metal-based catalysts, such as Pt and Au supported on various metal oxides, show high activity for HCHO removal at room temperature [6,10]. However, their application is largely restricted by their high cost and scarce source. In addition, noble metal-catalysts would be easily deactivated by some

* Corresponding author at: State Key Joint Laboratory of Environment Simulation and Pollution Control, School of Environment, Tsinghua University, Beijing 100084, China.
E-mail address: zpy@tsinghua.edu.cn. (P. Zhang).

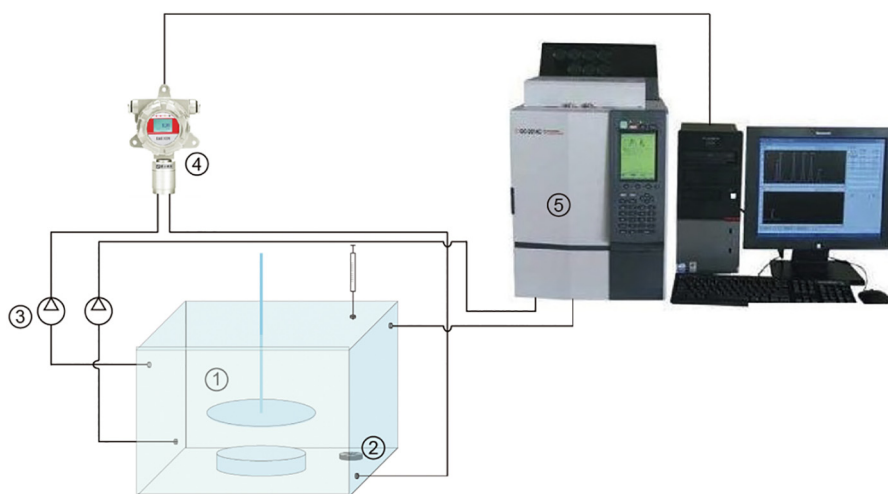


Fig. 1. The static reaction device for evaluating HCHO decomposition. (① organic glass reactor, ② fan, ③ air pump, ④ PN-2000 sensor, ⑤ gas chromatography).

gases such as sulfur containing compounds in the practical application. Thus, it is of great necessary to develop more stable and cost-effective catalysts for indoor HCHO elimination. Among numerous metal oxides, manganese dioxides (MnO_2) show much better activity for HCHO removal [11–13]. Researchers made many efforts to improve their performance to meet the increasing requirement, such as increasing the specific surface area, doping with transition metal, and optimizing crystal structures and morphologies [14–16].

Nowadays, substitutional doping of various transition metal cations into the framework of MnO_2 has been extensively studied [15,17]. Due to the impact of doping transition metal atom, the morphology and crystal structure are often influenced [18]. Generally, doped metal cations may occur in $[\text{MnO}_6]$ octahedral framework and/or in the tunnel, which is largely dependent on the crystal size and the coordination geometry of the cation dopant. Cations with similar size to Mn^{4+} can easily introduced into the octahedral framework, while relatively larger cations tend to be introduced into the tunnel of manganese oxides [15,19]. It has been reported that, doping of transition metal cations, such as Cr^{3+} , V^{5+} , Mo^{6+} , and W^{6+} , into the framework or tunnel of manganese oxides, which may modify the crystal structure, resulting in the increase of the specific surface areas and the number of catalytic active sites. Mizuno et al. [15] prepared Mo^{6+} -doped α - MnO_2 and examined their structure-activity relationships for aerobic oxygenation of thioanisole. They found that manganese vacancies were likely formed by doping of Mo^{6+} , which would prevent the growth of α - MnO_2 crystals along the c -axis direction. As a result, Mo-modified α - MnO_2 possessed larger surface area and more catalytically active sites. Reddy groups [20] introduced Zr, Hf, La, Pr, Fe and Mn into the CeO_2 for CO and soot oxidation. They found that doped ceria exhibited more loosely bound lattice oxygen and higher concentration of surface adsorbed oxygen species than the unmodified CeO_2 , accordingly, the activity for CO oxidation was significantly promoted.

Other element such as Ni^{2+} (0.69 Å), Ce^{3+} (1.02 Å), Cu^{2+} (0.73 Å), V^{5+} (0.54 Å) Cr^{3+} (0.615 Å) and W^{6+} (0.60 Å) may be as a candidate for MnO_2 modification [21–24]. Among them, tungsten ion has comparable ionic radius in six-coordinated $[\text{MnO}_6]$ structure (Mn^{3+} 0.645 Å, Mn^{4+} : 0.53 Å), which provides the high probability to be doped into the MnO_2 structure. Moreover, tungsten has been proven to be a promoter to raise the catalytic activity and stabilize the active phase. Hong's group [25] investigated the influence of tungsten incorporation in Mn/Ce/W/Ti. The activity increased upon addition of an appropriate amount of tungsten. Liu et al. [26] also found the addition of WO_3 significantly enhanced the catalytic performance of Mn-Zr mixed oxide catalyst. The highly dispersed WO_3 enhanced the acidity and redox property of

the catalyst, both of which would promote the adsorption and activation of NH_3 .

Aiming to obtain more efficient MnO_2 -based catalyst, herein, the tungsten doped MnO_2 (W-MnO_2) catalysts with different doping ratio were synthesized for HCHO oxidation. As far as we know, the present investigation first reports the effects of tungsten modification on the activity of MnO_2 for HCHO removal, revealing that the addition of tungsten significantly enhanced the activity of adsorbed surface oxygen species on MnO_2 . Accordingly, W-MnO_2 showed excellent performance for HCHO removal at ambient temperatures.

2. Experimental section

2.1. Materials and catalyst preparation

All the chemical reagents were analytical grade and used without further purification. KMnO_4 , and $\text{MnCl}_2 \cdot \text{H}_2\text{O}$ were purchased from Sinopharm Chemical Reagent Co., Ltd. WCl_6 was purchased from Shanghai Aladdin Chemical Reagent Co., Ltd. Aqueous solution of formaldehyde (37% v/v) was provided by Beijing Chemical Reagent Factory.

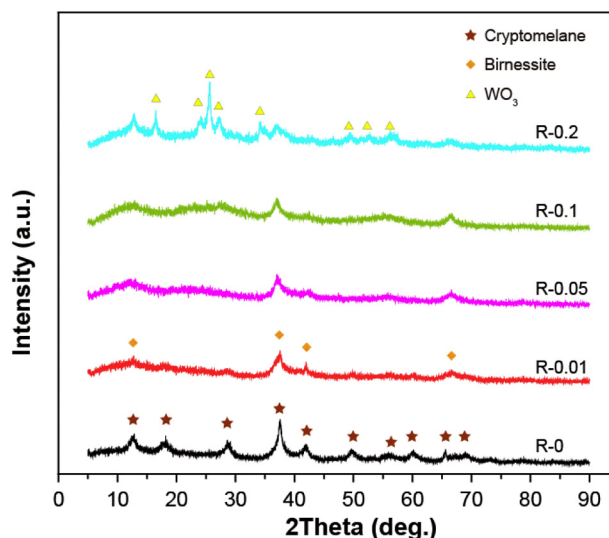


Fig. 2. Powder XRD patterns of MnO_2 doped with different content of tungsten.

Download English Version:

<https://daneshyari.com/en/article/7217080>

Download Persian Version:

<https://daneshyari.com/article/7217080>

[Daneshyari.com](https://daneshyari.com)