Catalytic Decomposition of Formaldehyde on Nanometer Manganese Dioxide

Xiujuan Chu & Hua Zhang (Corresponding author)
Tianjin Municipal Key Lab of Fibres Modification and Functional Fibres Institute of Functional Fibres
Tianjin Polytechnic University
Tianjin 300160, China
Tel: 86-22-2452-8453   E-mail: eva@tjpu.edu.cn

This research was funded by Tianjin nature science Found (No. 07JCYBJC02400).

Abstract
In this paper, nanostructure MnO₂ was synthesized in aqueous solution, without using any templates, catalysts, and organic reagents. The as-prepared nano-MnO₂ was systematically characterized by X-ray diffraction (XRD), and transmission electron microscopy (TEM) Fourier transform infrared (FT-IR) spectroscopy analysis. The catalytic decompositions of HCHO were studied at different conditions using the nano-MnO₂ as catalyst. The resulting nano-MnO₂ particles were found to exhibit remarkable environmental catalytic performance in catalytic decomposition of formaldehyde in aqueous solution.

Keywords: Chemical coprecipitation, Nano-MnO₂, HCHO, Catalytic decomposition

1. Introduction
Manganese oxides (MnO₂) are of considerable interest since these materials can be used in adsorption, catalysis, and other applications. Nano-MnO₂ has a great potentially application in environment protection field as a new generation of environmental friendly catalyst. Cai et al. (2006, p.1971-1976) investigated the removal of a cationic dye, methylene blue, from aqueous solutions by adsorption onto manganese dioxide and found that δ manganese dioxide had the strongest ability for removal among the materials. Gaseous toluene can be oxidated into CO₂ by nano-MnO₂ at ambient temperature (Liu et al. 2005, p.276-283). Formaldehyde (HCHO) is one of the main pollutants in indoor air. Yoshika et al. (2002, p.5543-5547) have found that manganese oxide could react with HCHO and release carbon dioxide even at room temperature.

MnO₂ with different physical and chemical properties, such as crystallinity, amount of combined water, specific surface areas, and electrochemical performance, can be yielded under different synthesis conditions. Up to now, many routes for the preparation of MnO₂ have been developed including thermal oxidation of Mn (II) nitrates, chemical coprecipitation route (Cai et al., 2006, 1971-1976), electrolysis of Mn (II) salts, and sol–gel method. The chemical coprecipitation process was simple and the reaction conditions were easy to control, so it has been widely applied.

In the paper, the chemical coprecipitation process was used to prepare nano-MnO₂ powders. The catalytic decomposition of HCHO was also studied using as-prepared MnO₂ powders as catalyst at different conditions.

2. Experiments
2.1. Chemicals
Potassium permanganate was obtained from Tianjin Standard Science And Technology Co., Ltd. (Tianjin, China). Manganic sulfate was purchased from Tianjin Kermel Chemical Reagent Co., Ltd. Carmellose Sodium was obtained from Tianjin Bodi Chemical Co., Ltd. All other chemicals were of analytical grade and used without further purification.

2.2. Preparation of the MnO₂ samples
A chemical coprecipitation route was used to prepare MnO₂ catalyst. The detailed process was as follows: Manganic sulfate were dissolved in distilled water, potassium permanganate aqueous solution was added slowly with magnetic stirring at a molar ratio of KMnO₄/MnSO₄ = 2/3 at room temperature. The resulting black solution was kept at room temperature in air for 24 h, then filtered and washed with double deionized water for several times to remove any
soluble products. After that, the deposition was dried at 80°C in air for about 12 h.

2.3. Characterization of the as-prepared MnO2 particles

Structures of the MnO2 were characterized using X-ray diffraction (XRD). XRD data were collected using a Rigaku D/MAX 2500 diffractometer with Cu Kα radiation (λ=0.15418nm). The diffractograms were recorded in the range of 10°-80°. Transmission electron microscope (TEM; Hitachi 7650, Japan) was used to observe the morphology of the MnO2. FT-IR analysis was carried out on a Nicolet 510P FT-IR spectrophotometer.

2.4 Decomposition experiments of HCHO

Under atmospheric pressure, MnO2 particles were placed in 100mL of glass vessels. And 50mL of HCHO solution with different concentration was introduced into the vessels and the vessels were closed with rubber stopper. The concentrations of HCHO were measured every 12 h. Formaldehyde was spectrophotometrically determined by the acetylacetone method at 412 nm, following Chinese Standards GB18580-2001.

3. Results and discussions

3.1 Characterization of the as-prepared MnO2 nanoparticles

Fig.1 shows the XRD recorded for the chemical coprecipitation MnO2 nanostructures. It can be seen from the figure that the peak profile is broad and most of the peaks (2θ= 23.5°, 37.14°, 42.48°, 56.30°) are indexable to γ-MnO2 phase with a peak (2θ=66.84°) of δ-MnO2 phase. The broadness of the peaks indicates that the formed compound has predominantly nanophase.

Fig.2 shows the TEM micrograph MnO2 particles. The results show distinctly that a nanorod structure with diameter about 5-10nm can be fabricated with this method. Here, we can observe the highly agglomerated nanorods of MnO2 as shown in the inset of Fig.2.

The FT-IR spectra for MnO2 before and after catalytic decomposition are shown in Fig.3. Broad absorption peaks centered at around 3421cm⁻¹ and 1635cm⁻¹ are caused by the absorbed water molecules and carbon dioxide because the nanocrystalline materials exhibit a high surface-to-volume ratio (Zhang Y.C. et al, 2005, p. 652-657). A peak due to Mn–O vibrations was observed at 578cm⁻¹ in the spectra of MnO2. The band at 1109 cm⁻¹ is absorption peak of the Mn-OH functional group, and band at 1400 cm⁻¹ are associated with the hydration water of MnO2. The FT-IR spectra were no obvious difference between before and after catalytic decomposition.

3.2 Catalytic decomposition of HCHO using nano-MnO2 particles

3.2.1 Effect of initial HCHO concentration

Fig.3 and fig.4 represent the experimental results for the decompositions of HCHO at different initial concentrations using 0.5g nano-MnO2 powers at 30°C. It is clear that the decomposition of HCHO is relatively high in the region of high HCHO concentration, but it is quickly slowed down in the region of low HCHO concentration (fig.3). The amount HCHO decomposed takes a maximum at the initial concentration of 0.44 mg/m³ (fig.4).

3.2.2 Effect of decomposition temperature

Fig.5 represents the effect of temperature on the decomposition of HCHO at an initial concentration of 40mg/m³ using 0.5g nano-MnO2 powers, where the temperature was maintained at 30, 45 and 60 °C. The rate of decomposition of HCHO takes a maximum at 45°C and tends to decrease with the increase or decrease in the temperature, indicating that the catalytic decomposition of HCHO should be carried out at an appropriate temperature.

3.2.3 Effect of amount of nano-MnO2 particles

Fig.6 shows the effect of applied amount of nano-MnO2 particles on the removal efficiencies of HCHO at an initial concentration of 44 mg/m³ at 30°C. The removal efficiencies measured after 12 h increased with the amount of nano-MnO2 particles and reached 87.2% (fig.7) using 0.5 g nano-MnO2 particles.

4. Conclusions

In summary, the nanostructure MnO2 particles have been prepared using chemical coprecipitation route. We investigated the catalytic decompositions of HCHO at different conditions using the nanostructures MnO2. IR spectra indicate that structures of the nano-MnO2 were no obvious difference between before and after catalytic decomposition. The experimental results show that the catalytic decompositions can be influenced by initial concentration of HCHO, catalytic temperature and amount of nano-MnO2.

References


F. Shiraishi et al. (2005). Decomposition of gaseous formaldehyde in a photocatalytic reactor with a parallel array of


![Figure 1. X-ray diffraction patterns of MnO₂ particles](image1)

![Figure 2. TEM micrograph MnO₂ particles](image2)
Figure 3. FT-IR spectra for MnO$_2$

Figure 4. Time courses of concentrations of HCHO at different initial concentration using 0.5g nano-MnO$_2$ particles at 30°C

Figure 5. The amount HCHO decomposed at different initial concentration of HCHO using 0.5g nano-MnO$_2$ particles at 30°C after 12h
Figure 6. Time courses of concentrations of HCHO at different temperature using 0.5g nano-MnO2 particles at an initial concentration of 44mg/m³

Figure 7. Time courses of concentrations of HCHO at an initial concentration of 44mg/m³ at 30°C using different amount of nano-MnO2 particles

Figure 8. Decomposition rate of HCHO at an initial concentration of 44mg/m³ at 30°C using different amount of nano-MnO2 particles after 12h