Facile In-Situ Synthesis of Manganese Dioxide Nanosheets on Cellulose Fibers and their Application in Oxidative Decomposition of Formaldehyde

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ABSTRACT: In situ synthesis of manganese dioxide was carried out under ambient conditions on porous cellulose fibers as support. MnO2/cellulose composites with different MnO2 loadings were obtained by tuning the concentration of aqueous KMnO4. Physical and chemical properties of the MnO2/cellulose composites were characterized by SEM, TEM, and XRD. When the concentration of aqueous KMnO4 falls in the range of 6.33−12.6 mM, the obtained MnO2 shows a nanosheet morphology and is uniformly coated on the cellulose fiber. The catalytic activities of MnO2/cellulose composites were investigated for the oxidative decomposition of HCHO. The nanostructured MnO2/cellulose composites show excellent catalytic performance for the oxidative decomposition of HCHO. Among them, 8.86 wt % MnO2/cellulose has the highest catalytic activity. The HCHO conversion per milligram of MnO2 of 8.86 wt % MnO2/cellulose is about 9−17 times as high as that of birnessite MnO2 powder prepared by a hydrothermal method. The catalytic activity was found to be dependent not only on the content of MnO2 but also on the adsorption of HCHO on cellulose fibers as well. These two factors are supposed to give rise to the highest catalytic activity for 8.86 wt % MnO2/cellulose. The high efficiency combined with the easy applicability makes the MnO2/cellulose composites more promising for practical applications as compared to MnO2 powders.

1. INTRODUCTION

Formaldehyde is an important chemical for the global economy and is widely used in construction, wood processing, furniture, textiles, carpeting, and the chemical industry.1−7 Formaldehyde pollution is everywhere, as it were. It is well-known that long exposure to indoor air with concentrations of formaldehyde that exceed safe limits is greatly harmful to human health.4,5 It has been classified as a human carcinogen that causes nasopharyngeal cancer and probably leukemia. Thus, it is of great urgency to remove indoor HCHO.

To remove low concentration HCHO from indoor air, there are generally two methods from the practical and economic points of view: one is conventional physical adsorption and/or chemical reactions; the other is catalytic oxidation. Conventional physical adsorption and/or chemical reactions prove efficient for HCHO elimination in field experiments, but these absorptions are effective only for a short period of time due to their limited removal capacities.6−8 Catalytic oxidation has great potential to degrade HCHO, which yields CO2 and H2O as final products.9,10

So far, a variety of metal oxides have been tested for the oxidative decomposition of formaldehyde. Sekine found that manganese dioxide (MnO2) was most effective for the removal of formaldehyde and that harmful byproducts were not released through the catalytic reaction.11 Manganese oxides have been extensively studied as a well-known transition-metal oxide because of their outstanding structural multiformity combined with novel chemical and physical properties and wide applications in catalysis.12−15

As far as field applications are concerned, using any metal oxides including manganese oxide in powder form, especially in nanosize, has several engineering limitations as follows: difficulty in the operation process, giving rise to dust contamination, and the leaching of nanoparticles along with the treated exhaust gas.16−18 Various methods have been developed to synthesize manganese oxides with different physical and chemical properties.19−21 Direct synthesis of nanostructures on solid matrices is attracting increasing interest in terms of engineering applications and synthetic challenges.22−24 Natural cellulose fibers have a porous structure and are composed of microfibrils of 10−30 nm width that are three-dimensionally connected with...
each other. They are abundantly available, economical, renewable, and environment friendly, and are gaining increasing interest as a support.

In this article, we report on facile in situ synthesis of manganese oxide nanosheets on porous cellulose fibers as a unique nanoreactor and template, as well as support. The catalytic activity of resulting MnO2/cellulose composites has been investigated. These composites can not only avoid the disadvantages of power catalysts encountered in oxidative decomposition of formaldehyde but also improve the catalysts performance, providing promising potentials in a variety of practical applications.

2. MATERIALS AND METHODS

2.1. Chemicals. All chemicals used were of analytic grade and were used as received without further purification. Ultrapure water used in experiments had a resistivity of 18.2 MΩ·cm and was obtained from a Millipore Milli-Q system. Lens paper (10 × 15 cm, 100% cellulose, Hangzhou, China) was used as the source of cellulose fibers. Potassium permanganate (K MnO4) and oleic acid (OA) were purchased from Beijing Chemical Reagent Company.

2.2. Synthesis of Catalysts. Manganese dioxides were in situ grown onto cellulose fibers by impregnating potassium permanganate (K MnO4) solution into a cellulose fiber matrix for 30 min. KMnO4 impregnated cellulose fibers were subsequently reduced by oleic acid added dropwise under fleetly stirring. The emulsion was maintained at room temperature for a certain period of time. The product was then washed several times with distilled water and alcohol to remove any possible residual reactants. Finally, the product was dried in an oven at 60 °C for 10 h.

2.3. Material Characterization. X-ray diffraction (XRD) patterns of as-prepared products were recorded on a Bruker D8 Focus X-ray diffractometer (Germany) using Cu Kα radiation (λ = 0.1542 nm) operated at 40 kV and 40 mA, and were used to identify their phase constitutions and crystalite sizes. Scanning electron microscopy (SEM) observations were carried out on a Hitachi S-4300 field emission scanning electron microscope operated at 10 kV. All samples were sputtered with gold before observation. Transmission electron microscopy (TEM) images were recorded on a JEOL JEM-200CX transmission electron microscope at an acceleration voltage of 150 kV. The samples were dispersed in ethanol and transferred onto a carbon-coated copper grid. TEM observations were performed after drying under atmosphere overnight. Fourier-transform infrared (FT-IR) spectra were recorded in the range of 650−4000 cm−1 at a resolution of 2 cm−1 on a Varian Excalibur 3100 spectrometer.

2.4. Formaldehyde Decomposition Studies. Catalytic activities of as-prepared manganese oxides for the oxidation of HCHO were studied with a fixed-bed quartz flow reactor (length = 300 mm, diameter = 4 mm) by passing a gas mixture of 100 ppm HCHO, 20 vol % O2, and the balance gas (He) at a total flow rate of 50 mL/min in a space velocity of GHSV = 50 000 h−1. Gaseous HCHO was generated by passing a purified air flow over the HCHO solution in an incubator kept at 0 °C. A total of 5 mg of catalysts were loaded in the quartz tube reactor. HCHO was analyzed online using an infrared spectrum. The HCHO conversion was determined by the following equation:

$$\text{HCHO conversion (\%)} = \frac{[\text{HCHO}]_b - [\text{HCHO}]}{[\text{HCHO}]_b} \times 100$$

where $[\text{HCHO}]_b$ (ppm) is the HCHO concentration without passing over the catalyst, and $[\text{HCHO}]$ (ppm) is the HCHO concentration after passing over the catalyst.

3. RESULTS AND DISCUSSION

3.1. Material Synthesis and Characterization. Lens papers were first used as the source of cellulose fibers. Figure 1 illustrates the texture of the lens paper and the surface morphology of the cellulose fibers. Clearly, the cellulose fibers are belt-like in shape with a width of 20−50 μm (Figure 1a). The surface of the cellulose fiber has a wrinkled structure (Figure 1b).

The effect of the concentration of the precursor on MnO2 loading was studied. The structure and morphology of the obtained MnO2/cellulose composites were revealed by SEM. Figure 2 shows the SEM of the MnO2/cellulose composites obtained using KMnO4 solutions of varied concentrations. At a low KMnO4 concentration (Figure 2a−b), MnO2 nanostructures could be observed on the cellulose fiber surface, but the cellulose fiber surface was not completely covered. When the concentration of aqueous KMnO4 increases to 12.6 mM (Figure 2c−d), MnO2 nanoparticles are well dispersed on the cellulose fiber surface. This has also been confirmed by TEM images as shown in Figure 3. From these images, it can be clearly seen that manganese oxide nanosheets are arranged roughly perpendicular to the surface of the cellulose fiber. With further increase of the concentration of aqueous KMnO4, the MnO2 nanosheets agglomerated together, and even the nanosheets eventually self-assembled to form larger particles as shown in Figure 2e−h.

Figure 4 shows the digital photographs of MnO2/cellulose fiber composites prepared from aqueous KMnO4 of varied concentrations. The color of cellulose fibers changes from light brown to brownish black with increasing KMnO4 concentration, suggesting the formation of MnO2 on cellulose fibers and indicating that the amount of loaded MnO2 on the cellulose fiber is varied by changing the molar concentration of KMnO4 from 6.33 to 25.3 mM under identical KMnO4/OA molar ratios. The result is in good agreement with the above SEM images.

The contents of MnO2 in MnO2/cellulose composites prepared from aqueous KMnO4 of varied concentrations could be estimated by TG-DSC. Figure 5 shows the TG-DSC curves (in air atmosphere from ambient to 900 °C) of MnO2/cellulose fiber composites prepared from aqueous KMnO4 of varied concentrations. All TG curves can be divided into three stages. In the low temperature range (up to 200 °C), the mass slowly decreased by 4−8% and should be attributed to the removal of surface-adsorbed water and some physisorbed oxygen, as well as...
as part of the adsorbed oleic acid. A large weight loss was observed in the range of 200–400 °C, which is believed to correspond mainly to the decomposition of cellulose fibers, the release of water from manganese oxide crystallites, and the complete removal of adsorbed oleic acid. The weight loss of about 2.8–4.6% in the 400–900 °C region is probably attributed solely to lattice oxygen. The amount of MnO2 in the MnO2/cellulose fiber composites was estimated to be 3.17%, 8.86%, 7.81%, and 13.98%, when the concentration of KMnO4 was 6.33 mM, 12.6 mM, 19 mM, and 25.3 mM, respectively.

The XRD pattern of the cellulose fibers is shown in Figure 6a. There is a strong peak at 2θ = 22.7°, which can be ascribed to the high intensity (120) plane of cellulose. Two weak peaks at 2θ of 4.8° and 16.6° are also observed and are characteristic of cellulose I crystal structure. No visible diffraction peaks corresponding to manganese oxide were observed even when the manganese loading reached 13.98%, which may be attributed to the strong diffraction peak of cellulose fibers and the weak diffraction peaks of MnO2. In order to determine the crystalline structure of MnO2 on cellulose, XRD specimens were prepared by the following procedure: the manganese oxide nanosheets coated on cellulose fibers were stripped off and calcined at 200 and 400 °C (Figure 6b–d). The intense diffraction peaks at 2θ of 12.27°, 24.64°, 36.50°, and 65.50° should be assigned to the characteristic peaks of birnessite MnO2, and even if calcined at 400 °C, the crystalline pattern of MnO2 hardly changed. The results indicate that there occurred no phase transformation in the range from room temperature to 400 °C.

In addition to XRD, FTIR was also employed to investigate the crystallinity of the samples. Figure 7 shows the FT-IR spectra of cellulose fibers and MnO2/cellulose fibers. The infrared spectra in the region of 850–1500 cm⁻¹ had been used to characterize the polymorphs of highly crystalline cellulose. The absorption band at 1427 cm⁻¹ and 895 cm⁻¹ can be assigned to the CH2 scissoring motion and C−O−C stretching at the β-(1→4)-glycosidic linkage. The spectrum shown in Figure 7a indicates that the cellulose possesses a cellulose I crystal type, which is also suggested by the XRD patterns. The absence of change in the IR bands at 1427 cm⁻¹ and 895 cm⁻¹ also suggests that the MnO2/cellulose fiber did not modify the initial structure of cellulose.
The result indicates that no chemical modification has happened to MnO₂ in cellulose. Although the current IR spectra do not show the range of 650–500 cm⁻¹ due to the equipment limitation, the IR spectra of MnO₂ in our previous works showed bands at 519 and 613 cm⁻¹, which arose from the stretching vibrations of the Mn–O and Mn–O–Mn bonds.³¹–³³

3.2. Catalytic Activity. The catalytic activity of MnO₂/cellulose for formaldehyde decomposition was examined as a function of temperature (Figure 8). The effects of MnO₂ loading were investigated on the MnO₂/cellulose activity for HCHO oxidation. Clearly, the catalytic activity of MnO₂/cellulose first increases and then decreases with an increase of the percentage of MnO₂. At low temperature (< 150 °C), the order of activity of different MnO₂/cellulose loadings is 8.86% MnO₂/cellulose > 7.81% MnO₂/cellulose > 3.17% MnO₂/cellulose > 13.98% MnO₂/cellulose. The optimal MnO₂ loading is 8.86%. At this loading, the HCHO conversion over the MnO₂/cellulose composite reaches 16.7% at 60 °C, and HCHO can be completely oxidized at 140 °C.

The catalytic oxidation of HCHO on a catalyst is an adsorption–degradation–desorption process. Thus, the MnO₂ content and formaldehyde adsorption may both play a very important role in the formaldehyde oxidation process. MnO₂ provides catalytically active sites, while cellulose fibres are porous carriers, which are in favor of the adsorption of formaldehyde. The catalytic activity gradually increases with an increase of the MnO₂ content within a certain range. As already known from the TEM images (Figure 3), MnO₂ nanosheets are arranged roughly perpendicular to the surface of the cellulose fibre. With further increase of the MnO₂ content, the MnO₂ nanosheets might agglomerate together (Figure 2e–h). The nanopores of cellulose fibres were thus blocked by excessive MnO₂ nanoparticles, which would hinder the adsorption of formaldehyde. Therefore, 13.98% MnO₂/cellulose has the lowest catalytic activity for HCHO oxidation. However, under identical conditions, when the temperature is above 120 °C, 3.17% MnO₂/cellulose still has the lowest catalytic activity. This may be because 3.17% MnO₂/cellulose not only has the lowest MnO₂ content, but also the adsorption of HCHO molecules on cellulose fibres were weakened as well over 120 °C.

The catalytic activity of MnO₂/cellulose prepared from aqueous KMnO₄ of 12.6 mM (Figure 9) is also compared with birnessite MnO₂ powder prepared by a hydrothermal method. The latter has a flower-like nanosphere morphology. The MnO₂/cellulose (60 mg, including 5.3 mg of MnO₂) showed higher...
The catalytic activity than the birnessite MnO₂ powder for the decomposition of HCHO, and at 60 °C, the HCHO conversion reached 16.7% (shown in Table 1). The birnessite MnO₂ powder (50 mg) achieved a HCHO conversion of 9.4% at the same temperature. The HCHO conversion by MnO₂/cellulose increased to 99.1% when the temperature was raised to 140 °C.

In order to better compare their activities, the HCHO conversion per milligram of MnO₂ was calculated, and the results are shown in Figure 7. The HCHO conversion per milligram of MnO₂ in situ grown on porous cellulose fibers is about 17 times as high as that of the birnessite MnO₂ powder at 60 °C and is about 9 times as high as that of the birnessite MnO₂ powder at 140 °C. The birnessite MnO₂ powder gave a HCHO conversion per milligram of less than 2 at 140 °C. Thus, the catalytic activities per milligram of catalyst for HCHO oxidation fall in the order of MnO₂/cellulose, the birnessite MnO₂ powder.

Perhaps it is because MnO₂/cellulose not only facilitated the adsorption of HCHO, but also increased the interface between MnO₂ and HCHO molecules. Therefore, the catalytic activity of MnO₂/cellulose had been greatly enhanced.

4. CONCLUSIONS

 Novel MnO₂/cellulose composites were fabricated in situ by impregnating cellulose fibers with aqueous KMnO₄ followed by a reduction by oleic acid. The content of MnO₂ in the MnO₂/cellulose composites could be tuned by adjusting the concentration of aqueous KMnO₄. When the concentration of aqueous KMnO₄ falls in the range of 6.33—12.6 mM, the obtained MnO₂ shows a nanosheet morphology, and is uniformly coated on the cellulose fiber. The catalytic activities of MnO₂/cellulose composites were investigated for the oxidative decomposition of HCHO. The nanostructured MnO₂/cellulose composites show excellent catalytic performance for oxidative decomposition of HCHO. Among them, 8.86 wt % MnO₂/cellulose has the highest catalytic activity. The HCHO conversion per milligram of MnO₂ of 8.86 wt % MnO₂/cellulose is about 9—17 times as high as that of the birnessite MnO₂ powder prepared by a hydrothermal method. The high efficiency combined with the easy applicability makes...
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