Manganese oxide nanorods as a robust Fenton-like catalyst at neutral pH: Crystal phase-dependent behavior

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ABSTRACT

Manganese oxide nanorods with different crystal phases (α-, β-, γ-, and δ-MnO_2) were prepared *via* a mild hydrothermal method, and examined as heterogeneous catalysts for the decomposition of H_2O_2 into active radicals and concomitant degradation of methylene blue (MB) dye at neutral pH. The catalytic activity of MnO_2 nanorods was highly dependent upon their crystal structures, following the order of γ-MnO_2 > β-MnO_2 > α-MnO_2 > δ-MnO_2. Complete degradation of MB was achieved with γ-MnO_2 in a short duration of 20 min. Furthermore, γ-MnO_2 exhibited much higher activity compared to iron-containing nanoparticles (Fe° and Fe_3O_4) and several reported catalysts in the literature. The observed trend in catalyst performance was discussed in terms of surface area, degree of crystallinity, and exposed facets. It was found that γ-MnO_2 showed considerable activity over a broad range of pH and temperature as well as desired reusability for four consecutive cycles. Quenching studies indicated that hydroxyl radicals ($^\bullet$OH) played a major role in the degradation of MB. These results provide important insight into the design of more efficient manganese oxide catalysts for wastewater treatment.

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1. Introduction

The advanced oxidation processes (AOPs), including chemical, photocatalytic, and electrocatalytic methods with hydrogen peroxide, and/or metal salts, ozone, and UV radiation have been successfully applied in wastewater treatment over the past decades [1–5]. The most classic example of AOPs is the Fenton reaction ($Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^\bullet OH$), being effective for the oxidative mineralization of various organic pollutants [6]. However, the application of homogeneous Fenton procedure at a large scale is hindered by the narrow working pH range (2–3) and difficult recovery. To alleviate these problems, later studies have focused on the use of iron-containing solids (ferrihydrite, magnetite, zerovalent iron, etc.) instead of Fe^{2+} due to possible advantages, such as a lower sensitivity to pH and ease of separation and recycling [7–13]. Unfortunately, most reported iron-based systems still suffer from slow and insufficient rates of H_2O_2 decomposition at higher pH values.

Thus, the search for the ideal heterogeneous catalysts that have high activity for H_2O_2 activation and good stability under a wide range of pH is of long-standing interest.

Among various non-noble transition metal oxides, nanostructured manganese oxides (MnO_x) have received much attention as technologically important materials since they show earth abundance, low toxicity, structural flexibility, and multivalent nature (3+ and 4+) [14–17]. Despite plenty of reports on the use of MnO_x in catalysis, information regarding their capacity to catalyze Fenton-like reactions is relatively lacking. Several literatures describe that MnO_x reacts with H_2O_2 or peroxymonosulfate (PMS) and generates different types of active radicals as intermediates, such as $^\bullet$OH in MnO_2/H_2O_2 [18,19], graphene/MnO_2/H_2O_2 [20], and carbon nanotube/γ-MnO_2/H_2O_2 systems [21], $O_2^{\bullet-}$ and $HO_2^\bullet$ in pyrolusite/H_2O_2 system [22], and $SO_4^{\bullet-}$ in MnO_2/PMS system [23,24]. It has been shown that the crystalline phases intrinsically influence the catalytic activity of MnO_2. In this respect, such an understanding of the structure-activity relationship in MnO_2 materials can contribute to the future development of more efficient and rational catalysts. However, controversial results exist on this issue because they often ignore the morphological variation that is another important influential factor. Each MnO_2 polymorph exhibits a range of morphologies, which relies heavily on the syn-
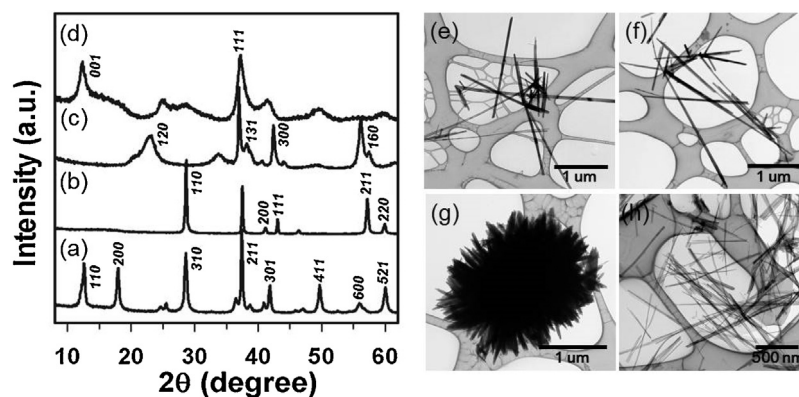
Fig. 1. XRD patterns and TEM images of MnO_2 nanorods: (a, e) α-MnO_2 (2×2 tunnel), (b, f) β-MnO_2 (1×1 tunnel), (c, g) γ-MnO_2 (1×2 and 1×1 tunnel), and (d, h) δ-MnO_2 (layered).

thesis procedures. Therefore, to demonstrate the actual role of crystal structure in the activity of MnO_2, the particle shapes should be identically tailored.

The present study aims at investigating how the crystal structure of MnO_2 affects its catalytic activity for wet hydrogen peroxide oxidation of methylene blue (MB), a typical organic pollutant in dyeing wastewater, at neutral pH ($\sim$6.5). To this end, four different MnO_2 polymorphs with rod shapes are prepared via a hydrothermal method: α-, β-, and γ-MnO_2 (tunneled) and δ-MnO_2 (layered), and tested their performance in degrading MB. Furthermore, we have examined the kinetics of MB degradation under various reaction conditions with γ-MnO_2 that is most reactive, in order to ensure the applicability and relevance of this system. The durability of γ-MnO_2 catalyst is confirmed through the reuse tests and manganese leaching. Specific quenching studies are also carried out to identify the main radical species involved in the degradation process.

2. Experimental

2.1. Materials

All chemicals used in the experiments were of analytical grade, and solutions were prepared with deionized (DI) water (>18 MΩ-cm). Single-crystal α-, β-, γ-, and δ-MnO_2 nanorods were prepared by the hydrothermal method in the literature [25]. Briefly, the different phases of MnO_2 were successfully synthesized by simply controlling the reaction temperature, time, and precursor concentration. The as-obtained products were washed with DI water and ethanol several times and dried in vacuum at 60 °C for 12 h. Fe_3O_4 (50–100 nm particle size, 97% purity) and commercial Fe° nanoparticles (reactive nanoscale iron particles; RNIP) were supplied from Sigma-Aldrich and Toda Kogyo Corp, respectively.

2.2. Characterization

The morphology and structure of particles were characterized by field emission scanning electron microscopy (FESEM, JEOL-J840), transmission electron microscopy (TEM, Hitachi H-7600), and X-ray diffraction (XRD, PANalytical X'Pert diffractometer). The Brunauer−Emmett−Teller (BET) surface area, pore volume, and pore diameter were measured at 77 K by nitrogen adsorption-desorption using a Micromeritics ASAP 2010 analyzer. Magnetic moments were obtained from a magnetic property measurement system (MPMS, Quantum Design MPMS-XL 7) between 2 and 300 K in an applied field of 100 Oe.

2.3. Catalytic experiments

The catalytic reaction was performed at room temperature ($T = 25 \pm 1$ °C) in a 50 mL glass beaker, which contained 30 mL of a methylene blue (MB) solution ($C_0 = 0.16$ mM, $pH_i = 6.5 \pm 0.1$), catalysts, and H_2O_2 (30 wt%) under continuous stirring. All experiments were done in triplicate. Along the reaction, the solution pH only slightly increased in a range of 6.5–7.5 (Fig. S1), so unbuffered solutions were used. At certain time intervals, samples (0.5 mL) were diluted with DI water to 10 mL, and the diluted solution was immediately centrifuged at 4000 rpm for 1 min. Then, the MB concentration in the supernatant was analyzed using a UV–vis spectrophotometer (Varian Cary 50) at 664 nm.

To test the recyclability of γ-MnO_2, the used catalyst was collected by centrifugation in 4000 rpm for 2 min and washed with DI water several times to be reused.

2.4. Analytical methods

Total organic carbon (TOC) was quantified using a TOC analyzer (Shimadzu TOC-VCSH). The amount of Mn leached during recycling test was measured through an inductively coupled plasma-atomic emission spectrometry (ICP-AES, Thermo IRIS-AP). For H_2O_2 determination, the titanium oxysulfate method was used [26]. The $^\bullet$OH generation was detected by the fluorescence method using coumarin as a chemical trap of $^\bullet$OH (see Eq. (1)) [27]. The fluorescence emission intensity of 7-hydroxycoumarin was measured at 460 nm under the excitation of 332 nm with a spectrofluorometer (Shimadzu RF-5301).
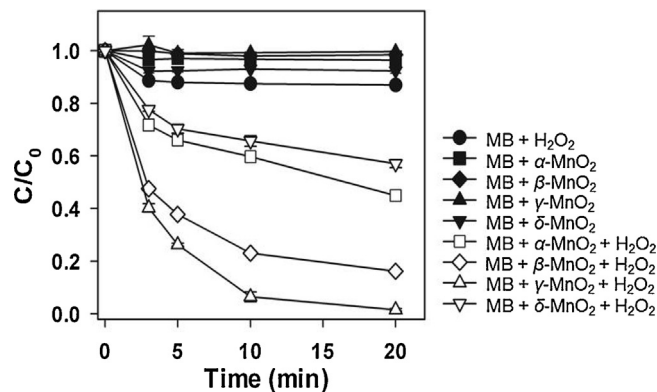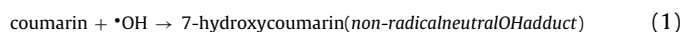
$$\text{coumarin} + {}^\bullet OH \rightarrow \text{7-hydroxycoumarin}(non\text{-}radical\,neutral\,OH\,adduct) \qquad (1)$$

Fig. 2. Time profiles of MB degradation with different MnO_2 nanorods ([MB]$_0$ = 0.16 mM, [catalyst] = 0.1 g/L, [H_2O_2] = 1.45 M).