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Nano-sized Mn_3O_4 and β-MnOOH from the decomposition of β-cyclodextrin-Mn: 2. The water-oxidizing activities

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ABSTRACT

Nano-sized Mn oxides contain Mn_3O_4, β-MnOOH and Mn_2O_3 have been prepared by a previously reported method using thermal decomposition of β-cyclodextrin-Mn complexes. In the next step, the water-oxidizing activities of these Mn oxides using cerium(IV) ammonium nitrate as a chemical oxidant are studied. The turnover frequencies for β-MnO(OH) and Mn_3O_4 are 0.24 and 0.01–0.17 (mmol O_2/mol Mn s), respectively. Subsequently, water-oxidizing activities of these compounds are compared to the other previously reported Mn oxides. Important factors affecting water oxidation by these Mn oxides are also discussed.

1. Introduction

Mn oxides are among abundant, low-cost, stable and environmentally friendly compounds [1–4] and many groups reported on catalytic activities of these compounds as bulk, supported, nano-sized, colloidal forms and with high surface area in different reactions [1–4]. Many redox active centers in the structure of these oxides could favor the occurrence of multi-electron and multi-step reactions [1–4].

In contrast to Mn complexes [5,6], in Mn oxides no easily oxidizable ligands are present that make the compounds stable under different conditions [1–4,7]. Mn oxides are promising as water-oxidizing catalysts in artificial photosynthetic systems and they are the true catalysts in many water-oxidation reactions catalyzed by Mn-based compounds [8–12].

For the first time, Mn oxides were reported as water-oxidizing catalysts by the Russian scientists. Glikman and Shcheglova introduced MnO_2 as a water-oxidizing catalyst in the presence of cerium(IV) ammonium nitrate (Ce(IV)) in 1968 [13]. Electrochemical water oxidation catalyzed by MnO_2 was reported by Morita's group in 1977 [14]. The group showed that the platinum-supported Mn dioxide electrode shows low overvoltage for water oxidation. Morita proposed Mn(III) as active sites for water oxidation [14]. Shilov extended the studies of water oxidation catalyzed by Mn oxides in the presence of Ce(IV) and $Ru(bpy)_3^{3+}$ [15]. Harriman's group in 1988 extensively studied many metal oxides and introduced Mn(III) oxide among water-oxidizing catalysts in the presence of chemical oxidants [16]. Frei and Jiao placed Mn_2O_3 clusters on mesoporous silica and synthesized efficient water oxidizing catalysts in the presence of $Ru(bpy)_3^{3+}$ [17]. The silica support is providing high surface area for Mn oxides, protecting the Mn ions from deactivation by surface restructuring and assistance in proton transfer [17]. Layered Mn–Ca oxide and other Mn–A oxides (A: inert-redox ions) without long-range order were reported as efficient catalysts for water oxidation [18–23]. Gold particles on Mn oxides were shown to improve the catalytic activity of Mn oxides toward water oxidation both chemically and electrochemically [24,25].

Interestingly, Najafpour's group showed that different Mn oxides in the presence of Ce(IV) or in electrochemical processes convert to a layered Mn oxide without long-range order after a few hours [26,27]. Spiccia's group showed that water oxidation in the layered Mn oxides is related to the differences in the degree of disorder [28].

Thus, cheap methods to synthesize different Mn oxides with different morphologies are important in artificial photosynthesis. Herein, we report on the synthesis of nano-sized Mn oxides containing Mn_3O_4, β-MnOOH and Mn_2O_3 with different morphologies using a previously reported method comprising thermal decomposition of β-cyclodextrin-Mn [29], and studies of their water-oxidizing activities.

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2. Material and methods

The reagents were purchased from Merck, Sigma–Aldrich and Daejung companies and were used without further purification. SEM images were taken with a Philips LEO 1430VP device. For HRTEM and TEM studies, samples were placed on copper grids covered with carbon film and examined with a 300 keV transmission electron microscope JEM-3010 UHR (Jeol Ltd., Japan), equipped with a retractable high-resolution slow scan CCD-Camera (Gatan Inc., USA) with GOS phosphorous scintillator and lanthanum hexaboride cathode as the electron source. The X-ray powder patterns were recorded with a D8 ADVANCE (Bruker, Germany) diffractometer (CuK_α radiation). Mn atomic absorption spectroscopy (AAS) was performed on an Atomic Absorption Spectrometer Varian Spectr AA 110. Prior to analysis, the oxide (1.0–10.0) was added to 1 mL of concentrated nitric acid and H_2O_2. The sample was left at room temperature for at least 1 h to ensure that the oxides were completely dissolved. The solutions were then diluted, and analyzed by AAS.

2.1. Water oxidation

Oxygen evolution from aqueous solutions in the presence of Ce(IV) was measured using an HQ40d portable dissolved oxygen meter connected to an oxygen monitor with digital readout. The reactor was maintained at 25.0 °C in a water bath. In a typical run, the instrument readout was calibrated against air-saturated distilled water stirred continually with a magnetic stirrer in the air-tight reactor. After ensuring a constant baseline reading, the water in the reactor was replaced with Ce(IV) solution without any additional buffer or acid. Without a catalyst, Ce(IV) was stable under these conditions and oxygen evolution was not observed. After deaeration of the Ce(IV) solution with nitrogen or argon, Mn oxides were added as several small particles, and oxygen evolution was recorded with the oxygen meter under stirring (Fig. S1). The formation of oxygen was followed, and oxygen formation rates per Mn site were determined from linear fits of the data.

2.2. Synthesis

2.2.1. Synthesis of β-cyclodextrin (β-CD)-Mn complexes

The compounds were synthesized by a method previously reported by Dismukes [31]. Briefly, β-CD (0.56 g, 0.5 mM, 30 mL of Ar-flushed DMF) and Mn(II) acetate (Mn:β-CD, 2:1, 1:1, 0.5:1, 0.25:1 and 0.125:1) were added at molar ratio, and the reaction mixture was stirred under Ar for 1 h. An alcoholic solution of NaOH (10 mL, 0.2 M) was added, and the resulting solution was exposed to bubbling air. After the color of the solution remained unchanged, an excess of ethanol was added to precipitate the compound. It was filtered, washed with ethanol, and air-dried.

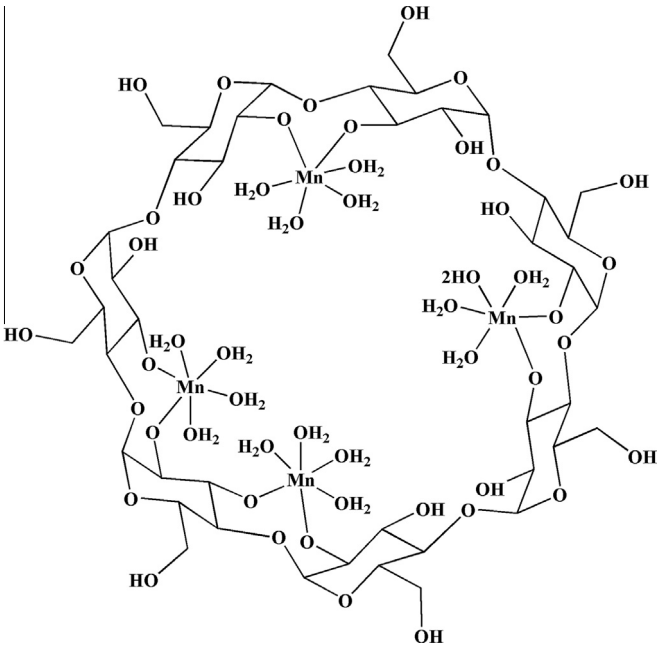
2.2.2. Synthesis of Mn oxide nanoparticles

The compounds were synthesized by a previously reported method [29]. For the synthesis of Mn oxides, the obtained β-CD-Mn complexes were heated at different temperatures (270, 370, 450 and 650 °C) for 10 h in air to yield black or brown powders.

3. Results and discussion

We synthesized different Mn oxides by decomposition of β-CD-Mn complexes at high temperatures. The proposed structure of the β-CD-Mn complex is shown in Scheme 1.

As we reported before [29], two factors affect the phases and morphologies of the Mn oxides: calcination temperatures and the ratio of Mn:β-CD.



Scheme 1. The proposed structure of β-CD-Mn with a ratio of 1:4 for β-CD to Mn, based on Ref. [31].

Using this method, we could simply obtain different morphologies and phases of Mn oxides. For example, SEM images show that for the sample calcinated at 270 °C in the reagents ratio of 0.125:1, Mn:β-CD displays a cauliflower-like morphology, and layers are observed in the resulting structure. At the ratio of 0.5:1 or 1:1 for Mn:β-CD, a cave-like structure is formed. At the ratio of 2:1 again a cauliflower-like morphology is obtained [29]. At 370 °C, in the ratio of 0.25:1, 0.5:1 and 1:1 for Mn:β-CD sword-like, cauliflower-like and sword-like structures are obtained, respectively. At 450 °C, at the ratio of 0.125:1, 0.25:1, 0.5:1, 1:1 and 2:1 (Fig. 1a–e) for Mn:β-CD the sample morphology is rubble-stone, sword form, in addition to undefined shape, rubble-stone, rubble-stone and rod-like, respectively [29].

IR spectrum of Mn_2O_3 shows bands at ~3200–3500, 1630 and 500–600 cm^{-1} related to antisymmetric and symmetric O–H stretchings, H–O–H and Mn–O modes. In addition to this, heating of this compound at 650 °C leads to a powder confirmed by XRD to be Mn_2O_3 (Figs. 1c–e and 2).

In the next step, we studied water-oxidizing activities of these compounds in the presence of Ce(IV). Ce(IV) is a non-oxo transfer agent, soluble in water and a stable oxidant, thus usually used in water-oxidation reactions [10,32]. Table 1 shows the turnover frequencies (TOFs) for the water oxidation catalyzed by these compounds (see Fig. 3).

From these results, we found that water oxidation catalyzed by Mn oxides depends on two factors: sort of oxide phases and their calcination temperatures. Compared with layered Mn oxides, Mn_3O_4, β-MnO(OH) and Mn_2O_3 show lower activities toward water oxidation. Although β-MnO(OH) shows a good activity, it is less efficient than nanolayered Mn oxide phase toward water oxidation. On the other hand, the results indicate that compounds obtained at low ratio of Mn:β-CD show better activities than when higher ratios are used [18–20]. This means that low amounts of dispersed Mn oxides in high amounts of support (β-CD in this case) form a promising catalyst toward water oxidation. Although β-CD is removed in our procedure at high temperatures, different morphologies for Mn oxides are observed at different ratios of Mn:β-CD. Crystalline forms show lower activities toward water oxidation. Correspondingly, the sword-like structures with a higher extent of crystallinity show little activity.