Dalton Transactions

Cite this: Dalton Trans., 2012, 41, 11026



A very simple method to synthesize nano-sized manganese oxide: an efficient catalyst for water oxidation and epoxidation of olefins[†]

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Received 8th March 2012, Accepted 4th July 2012 DOI: 10.1039/c2dt30553d

Nano-sized particles of manganese oxides have been prepared by a very simple and cheap process using a decomposing aqueous solution of manganese nitrate at 100 °C. Scanning electron microscopy, transmission electron microscopy and X-ray diffraction spectrometry have been used to characterize the phase and the morphology of the manganese oxide. The nano-sized manganese oxide shows efficient catalytic activity toward water oxidation and the epoxidation of olefins in the presence of cerium(IV) ammonium nitrate and hydrogen peroxide, respectively.

1. Introduction

Manganese oxides are not only earth abundant and low cost but also environmentally friendly. Thus, they are particularly attractive for use as catalyst materials.¹ Manganese oxides were reported to be useful, versatile, and environmentally friendly catalysts for important reactions and have been used extensively for the oxidation of a variety of molecules, especially for water oxidation,² the deep oxidation of ethylene³ and methane,⁴ the decomposition of nitrogen oxides,⁵ ethylbenzene⁶ and carbon monoxide⁷ and the epoxidation of olefins.⁸

A nanoscale compound is defined as a particle with a size in the range of 1 to 100 nm (10^2 to 10^7 atoms) from zero (0 D) to three dimensions (3 D), which could exhibit unique physiochemical properties as compared with the bulk compound. Interestingly, it was reported that the nanophase transition metal oxides show large thermodynamically driven shifts in oxidation– reduction equilibria.⁹ The size effect could change the redox potential of nano-sized transition metal oxides and may result in the improved catalytic activity of these compounds as compared to bulk manganese oxides. For example, Navrotsky *et al.* reported that cobalt(Π) oxide nanoparticles smaller than 8 nm, when dropped into water, evolved hydrogen.⁹ Such spontaneous oxidation of cobalt(Π) and reduction of water is not seen for larger particles.⁹ In this regard, the synthesis of manganese oxide-nanomaterials has attracted considerable attention.¹⁰ Currently, there are many methods for the synthesis of manganese oxide nanoparticles. Among them, solvothermal,^{11,12} polymeric-precursor¹³ and surfactant-mediated routes^{14–16} are quite popular.

Metal oxide decomposition is also an interesting and feasible way to prepare small metal oxide particles. Decomposition of manganese nitrate depends on some factors such as heating rate, moisture content of the atmosphere or manganese nitrate and different decomposition temperatures, mechanisms, and intermediates are reported for the reaction.¹⁷ In air or oxygen manganese nitrate decomposes up to 200-220 °C.¹⁷ In a moist atmosphere the decomposition of the nitrates can occur at lower temperatures and more interestingly, hydrated manganese nitrate has been reported to decompose at lower temperatures than the dehydrated one.¹⁷ These materials show good catalytic activity toward the oxidation of different compounds.¹⁷ Here, we report the synthesis of nano-sized particles of manganese oxide by a very simple and cheap process, using the decomposition of an aqueous solution of manganese nitrate at 100 °C. The compound shows efficient catalytic activity toward water oxidation and the epoxidation of olefins in the presence of cerium(IV) ammonium nitrate and hydrogen peroxide, respectively.

2. Experimental

2.1 Materials

All reagents and solvents were purchased from commercial sources and were used without further purification.

2.2 Water oxidation

Oxygen evolution from aqueous solutions in the presence of $(NH_4)_2Ce(NO_3)_6$ (Ce(IV)) was measured using an HQ40d portable dissolved oxygen meter connected to an oxygen monitor

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[†]Electronic supplementary information (ESI) available. See DOI: 10.1039/c2dt30553d

with a 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, or 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 catalyst, Ce(IV) was stable in this condition and oxygen evolution was not observed. After deaeration of the Ce(IV) solution with argon, manganese oxides as several small particles were added, and oxygen evolution was recorded with the oxygen meter under stirring (Fig. S1†). The formation of oxygen was followed, and oxygen formation rates per manganese site were obtained from linear fits of the data.

2.3 Synthesis of compounds

We used a new, very easy and cheap method to obtain nanoparticles of manganese oxide, which is based on decomposition of manganese nitrate in moderate temperature.

Hot water (5.0 mL, 95 °C) was added to manganese nitrate $(Mn(NO_3)_2 \cdot 4H_2O)$ (39.8 mmol, 10.0 g). After 10 min of magnetic stirring at room temperature, the solution was heated to 100 °C for 24 h in an oven to obtain a viscous liquid. The black particles were obtained by adding water (10 mL) to the black viscous liquid and centrifugation of the resulting solution. The black particles were washed with water (10 mL, two times) and dried at 100 °C.

2.4 Characterization

MIR spectra of KBr pellets of compounds were recorded on a Bruker vector 22 in the range between 400 and 4000 cm^{-1} . TEM and SEM were carried out with Philips CM120 and LEO 1430VP, respectively. The X-ray powder patterns were recorded with a Bruker, D8 ADVANCE (Germany) diffractometer (Cu-Ka radiation). Manganese atomic absorption spectroscopy (AAS) was performed on an Atomic Absorbtion Spectrometer Varian Spectr AA 110. Prior to analysis, the oxide (2.0 mg oxide) were added to 1 mL of concentrated nitric acid and H₂O₂, which was left at room temperature for at least 1 h to ensure that the oxides were completely dissolved. The solutions were then diluted to 25.0 mL and analyzed by AAS. The products of the oxidation of olefins were determined and analyzed by using a HP Agilent 6890 gas chromatograph equipped with a HP-5 capillary column (phenyl methyl siloxane 30 m \times 320 lm \times 0.25 lm) and a flameionization detector.

3. Results and discussion

3.1 Characterization

The X-ray diffraction (XRD) pattern of the as-prepared manganese oxide was of poor resolution (Fig. 1). However, the peaks observed at $2\theta = 23^{\circ}$, 33° , 38° , 45° , 49° , 54° , and 65° could be indexed to a cubic cell (JCPDS 41-1442), belonging to the α -Mn₂O₃ (Fig. 1 and Fig. S2†). A small amount of ε -MnO₂ could also be detected (Fig. 2S†). Thus, the compound contains Mn₂O₃, some ε -MnO₂ and amorphous manganese oxide.



Fig. 1 XRD patterns of the obtained sample. Blue stars show the peaks for α -Mn₂O₃ (JCPDS 41-1442).

In the IR spectra of the compound, a broad band at \sim 3200–3500 cm⁻¹, related to antisymmetric and symmetric O–H stretchings, and at \sim 1630 cm⁻¹, related to H–O–H bending, are observed (Fig. S3†).¹⁰ The intensities of these peaks reduced in higher temperature. The absorption bands characteristic for a MnO₆ core in the region 400–500 cm⁻¹, assigned to the stretching vibrations of Mn–O bonds in manganese oxide, was also observed in the FTIR spectra of these compounds.¹⁰

Scanning Electron Microscopy (SEM) images allowed us to determine that the compound consists of particles from <100 nm in size (Fig. 2 and Fig. S4†). Transmission Electron Microscopy (TEM) pictures allowed us to determine that the compound consists of amorphous and also crystals of manganese oxide (Fig. 2 and Fig. S5†). The BET test showed that the surface of this compound is 33.49 m² g⁻¹ (Fig. S6 and S7†).

3.2 Water oxidation

Photosystem II, located in the thylakoid membrane of plants, algae, and cyanobacteria, is an enzyme that oxidizes water to oxygen. The generated protons drive ATP synthase and the electrons provide the reducing equivalents that ultimately lead to carbon dioxide fixation.^{18,19} The site of water oxidation to O_2 is known as the water oxidizing complex (WOC) and is a Mn_4O_5Ca cluster.^{19,20}

In this structure, metal ions, one calcium and four manganese ions, are bridged by five oxygen atoms. Four water molecules were found also in this structure and two of them are suggested as the substrates for water oxidation.²⁰ To design an efficient water oxidizing complex for artificial photosynthesis, to evolve hydrogen efficiently in a sustainable manner, we may learn and use wisely the knowledge about water oxidation and the water oxidizing complex in the natural system.²¹ To synthesize a water oxidizing catalyst, manganese compounds have been considered not only because manganese has been used by nature to oxidize water but also because manganese is cheap and environmentally friendly. Manganese oxides have been reported as heterogeneous catalysts for water oxidation by some groups.²

The water oxidation experiment by the prepared compound in the presence of cerium(IV) ammonium nitrate (Ce(IV)), a non-oxo







(c)

Fig. 2 SEM images of manganese nitrate solution after 2 h (a) and 24 h heating at 100 °C (b). TEM image of the nano-sized manganese oxide prepared by decomposition of manganese nitrate solution at 100 °C for 24 h.

transfer and a strong one-electron oxidant, was performed and the formation of oxygen was followed. The oxygen formation rates per manganese site were obtained from linear fits of the data.



Fig. 3 The relation between the rate of water oxidation and T^{-1} over the range of 10–35 °C.



Fig. 4 Water oxidation of an aqueous solution of 0.045-0.91 M Ce(IV) (40 mL) at 25.0 °C in the presence of nano-sized manganese oxides (1.25 mg) prepared at 100 °C.

Membrane-inlet mass spectrometry (MIMS) showed the oxygen evolution of the reactions of Ce(IV) is a "real water oxidation" and both oxygen atoms of the O₂ originate from the water.²² In the temperature range of 15–35 °C, the values for k_0 (oxygen evolution) increased progressively (Fig. 3).

A plot of $-\ln k_0$ (oxygen evolution) versus T^{-1} was linear and gave $\Delta H = +96.8 \ (\pm 0.10) \text{ kJ mol}^{-1}$ and $\Delta S = +292.8$ (± 0.1) J mol⁻¹ as apparent activation parameters for the water oxidation reaction of the nano-sized manganese oxide. The ΔH for water oxidation is higher than the related parameter for layered manganese oxides.²³ It may show that an open structure or other ions $(Ca(II),^{22} Zn(II)^{23} and Al(III)^{23})$ in layered manganese oxides could reduce the activation energy for water oxidation. To study the effect of concentration of Ce(IV), reactions were done with different concentrations of Ce(IV), keeping all other factors constant as shown in Fig. 4. The rate of oxygen evolution increases with an increase in the concentration of Ce(IV). This increase of the rate of oxygen evolution in a low concentration of Ce(IV) is linear in the range of 0.01–0.1 M of Ce(IV). However, in a high concentration of Ce(IV), the slope of the increase of the rate of oxygen evolution becomes shallower



Fig. 5 The relation between calcined temperature and water oxidizing activity of the oxide nano-sized manganese oxides prepared at 100-600 °C.

(Fig. 4). The increase in the rate of oxygen evolution with the increase of oxide concentration is also linear. In other words, under high concentrations of Ce(IV) (>0.1), the derived rate law is first order for the catalyst and zero order for Ce(IV).

Nano-sized manganese oxides prepared at 100-600 °C showed efficient water oxidizing activity in the presence of Ce(IV) (Fig. 5). In contrast to the layered manganese oxides,²³ the temperature in the range of 100-600 °C is not an important factor for the water oxidizing activity of this compound (Fig. 5). Interestingly, after adding the catalyst the reduction of Ce(IV) and MnO₄⁻ formation in solution were also detected by UV-vis (Fig. S8[†]). More interestingly, after ~72 h, a decrease in the concentration of the MnO₄⁻ was observed (Fig. S8[†]) that could be related to self-repair of the catalyst. As we reported before,²³ a small amount of Mn(II) (detected by EPR) dissolved under this condition; these Mn(II) ions could react with MnO_4^{-} and produce manganese oxide again. The reaction could be related to a reduction of the concentration of MnO₄⁻ after 72 h. MnO₄⁻ formation from nano-manganese oxides, and not bulk, in the presence of Ce(IV) could be related to the thermodynamically driven shifts in oxidation-reduction equilibria for metal oxides.⁹

3.3 Epoxidation of olefins

Because of the epoxides' versatility in preparing many chemical intermediates, the epoxidation of olefins is an important catalytic reaction in the industry.^{8,24} Usually, epoxides are produced by the oxidation of olefins with a stoichiometric amount of peracid as oxidant.²⁵ Many manganese complexes were reported for the epoxidation of olefins using peracids and hydroperoxides as oxidants.²⁴ A few manganese oxides, as low-cost, easily synthesized and environmentally friendly compounds, have been used as a catalyst for the epoxidation of olefins.⁸ The nano-sized manganese oxide shows efficient catalytic activity toward the epoxidation of olefins in the presence of hydrogen peroxide as an environmentally friendly and low-cost oxidant. Hydrogen peroxide in the bicarbonate solutions was shown to be a good oxidant for the epoxidation of olefins.^{25,26}

3.3.1. General procedures for the epoxidation of olefins. To a solution of olefins (0.5 mmol), NaHCO₃ (0.1 mmol) and

Entry	Substrate	Product	Conversion ^b (%)	Selectivity ^c (%)
1	$\mathbf{O}^{\mathbf{A}}$	C v	91	93
2	\mathcal{O}^{L}	O_{\uparrow}	78	95
3	$\langle \mathfrak{O} \rangle$		100	100
4	\bigcirc	\bigcirc •	47	100
5	0	\bigcirc	43	100
6	С, сн'	CH ²	33	100
7	$\sim\sim$	~~~~\$	17	100
8	$\sim \sim \sim$	~~~~\$	11	100

^{*a*} Reaction conditions: catalyst (0.05 mmol), CH₃CN (1 mL), alkene (0.5 mmol), NaHCO₃ (0.1 mmol), H₂O₂ (2 mmol), time = 4 h, at room temperature. ^{*b*} The GC conversion (%) are measured relative to the starting olefin. ^{*c*} Selectivity to epoxide = (epoxide%/(epoxide% + aldehyde%)) × 100.

catalyst (0.005 mmol) in CH₃CN (1.0 mL) was added H₂O₂ (2.0 mmol) as oxidant. After stirring at room temperature for 4 h, for the products analysis, the solution was subjected to ether extraction (3 × 10 mL), and the extract was also concentrated down to 0.5 mL by distillation in a rotary evaporator at room temperature. Then, a sample (2 μ L) was taken from the solution and analyzed by GC. The retention times of the peaks were compared with those of commercial standards, and chlorobenzene was used as an internal standard for GC yield calculation.

3.3.2. Catalytic epoxidation of various olefins with H_2O_2 over the nano-sized manganese oxide. In order to choose a suitable solvent, the oxidation of styrene was carried out in dichloromethane, chloroform, acetonitrile, acetone, methanol and a (1:1) mixture of CH₃OH–CH₂Cl₂. Our findings showed that CH₃CN was a much more efficient solvent for the epoxidation of styrene.

The nano-sized manganese oxide not only shows high activity in the epoxidation of aromatic olefins²⁵ but also mild activity in the epoxidation of some non-aromatic olefins (Table 1).

We thus used the manganese oxide catalyst for epoxidation of several linear and cyclic olefins (Table 1). The aromatic substrates (styrene, α -methylstyrene and indene) were oxidized to give the corresponding epoxides with 78–100% conversion (entries 1–3). Linear and cyclic olefins were less reactive in comparison to aromatic olefins (entries 4–8).

Also, the reusability of the catalyst was tested at room temperature for 4 h and the results have been shown in Fig. 6.

In each reaction, the catalyst from the reaction was filtered off, washed several times with water and diethyl ether repeatedly, dried at 50 °C and reused for the next run under the same conditions as the first reaction. Catalyst recycling studies show that the conversion of styrene slowly decreased in the range of 86-ca. 91% after the sixth cycle and the selectivity of the epoxide was kept partly constant around 91% during recycling (Fig. 6). Nano-iron oxides,²⁷ NiO, CoO, MoO₃ and CuO were



Fig. 6 Recycling studies of the nano-sized manganese oxide in the reaction of epoxidation of styrene.



Scheme 1 Proposed mechanism for the epoxidation of olefins by manganese oxide in the presence of H_2O_2 and HCO_3^- .

shown to be highly active for the selective epoxidation of styrene to styrene oxide by *tert*-butyl hydroperoxide or H_2O_2 but mild activity or high peroxide decomposition is an associated problem with these catalytic systems.²⁸ Based on the previous reports,^{25,26} a proposal for the mechanism is shown in Scheme 1. HCO_4^- (eqn (1)), an important active oxidant that is more nucleophilic than H_2O_2 , has been detected by ¹³C MAS NMR in this reaction.

$$H_2O_2 + HCO_3^- \rightleftharpoons H_2O + HCO_4^-$$
(1)

4. Conclusion

Nano-sized manganese oxide, as a low-cost, easily synthesized and environmentally friendly compound, was synthesized by a very simple method in moderate temperature and without using any organic compounds. It was characterized by SEM, XRD, FTIR, AAS and TEM. These compounds act as efficient catalysts for water oxidation in the presence of Ce(IV). The nanosized manganese oxide showed high activity in the epoxidation of aromatic olefins and mild activity in the epoxidation of some non-aromatic olefins in the presence of H_2O_2 and bicarbonate ions.

Acknowledgements

These authors are grateful to Institute for Advanced Studies in Basic Sciences, University of Maragheh, and Sharif University of Technology for financial support.

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