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Synthesis of manganese oxide microparticles using supercritical water

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ABSTRACT

Manganese compounds of different oxidation states such as MnO_2, $MnCO_3$ Mn_2O_3, and a mixture of $MnO + Mn_3O_4$ were synthesized using supercritical water (SCW) and calcination process. The X-ray Diffraction (XRD) patterns confirmed that the use of glycerol as a reducing agent in SCW process was successful in preventing oxidation of manganese products. Scanning electron microscopy (SEM) images of the manganese products showed micro-sized particles with different morphology depending on the product. The simple two step synthesis procedure described in this paper allows easy control of manganese oxidation states with direct applicability in large scale production on an industrial level.

1. Introduction

Manganese oxide is a commonly used transition metal oxide that has a broad range of applications in catalysis, fertilizers, paints, ceramics, capacitors, sensors, and lithium ion batteries. Manganese oxides exist in different oxidations states such as MnO, MnO_2, Mn_2O_3, and Mn_3O_4, all of which are used in different applications [1–4]. Manganese oxides can be synthesized by sol-gel [5], hydrothermal route [6], wet chemical method [7], and solid state method [8,9]. Among the various methods of synthesis, use of supercritical water (SCW) is part of the hydrothermal route which is an environmentally friendly option [10]. Inorganic materials crystallization using SCW began in the early 1990s where SCW was used as a solvent for the synthesis of 6 different metal oxides [11]. Materials synthesis using SCW technology has many advantages; the process can be easily scaled up using a plug flow system, uses cheap and clean solvents, and the process is rapid where residence time can be in the order of seconds.

Manganese oxide synthesis using SCW has been attempted by Lee and Ham and Nugroho and Kim [12,13]. Lee and Ham synthesized MnO_2, Mn_2O_3 and $LiMn_2O_4$ continuously using SCW at varying temperatures where hydrogen peroxide (H_2O_2) and/or potassium hydroxide (KOH) were added to assist oxidation. Nugroho and Kim synthesized MnO_2 and Mn_3O_4 continuously using SCW at 400 °C where KOH was used as a reducing agent. Jankovsky et al. synthesized MnO, Mn_2O_3 and Mn_3O_4 by thermal decomposition of manganese glycerolate at different temperatures and atmospheres [14]. They prepared manganese glycerolate by reacting manganese precursor with glycerol under reflux followed by a subsequent calcination. Manganese has a low reduction potential [15] and therefore is easily oxidized upon hydrothermal reaction. In this work, however, manganese oxides of different oxidation states were synthesized in SCW where glycerol was utilized as a reducing agent to either reduce manganese oxides or prevent oxidation. The objective was to develop an energy efficient two step production process of controlling oxidation states of manganese oxides using SCW and calcination process stepwise. Calcination temperature was fixed at 500 °C to minimize the use of energy.

2. Materials and methods

2.1. Materials

Manganese (II) nitrate hexahydrate [$Mn(NO_3)_2{\cdot}6H_2O$] was purchased from Junsei. Glycerol (99.0%) was obtained from Samchun Chemicals. Deionized water (DIW) was filtered using Milli-Q Ultra-

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Table 1
Hydrothermal conditions summarized.

Temp (°C)	Pressure (bar)	[a]Glycerol/$Mn(NO_3)_2{\cdot}6H_2O$	Particle Size (μm)	Product
250	300	0	N/A	N/A
300	300	0	0.5–15	MnO_2
350	300	0	0.1–10	MnO_2
400	300	0	0.5–10	MnO_2
250	300	5	N/A	N/A
300	300	5	10–50	$MnCO_3$
350	300	5	1–30	$MnCO_3$
400	300	5	1–10	$MnCO_3$

N/A: not applicable.
[a] Mole ratio of glycerol and $Mn(NO_3)_2{\cdot}6H_2O$.

pure Water Purification System with a 0.22 μm filter (Millipore). Nitrogen gas was supplied by Shinyang Sanso Company.

2.2. Experimental methods

Hydrothermal synthesis of manganese oxides was carried out using a stainless steel (SUS316) reactor with 30 ml inner volume. A salt bath (consisting of KNO_3, $NaNO_3$ and $Ca(NO_3)_2$) furnace controlled by a thermostat was used to heat up the reactor to the desired temperature. Manganese nitrate hexahydrate reagent is in solid form at room temperature which required warming up in an oven at 50 °C to obtain liquid form. This liquid form $Mn(NO_3)_2{\cdot}6H_2O$ was used to make 1 M precursor solution in DIW. When glycerol was used, the mole ratio of glycerol to manganese nitrate was 5. A certain amount of the precursor solution was placed in the reactor so that it can reach 300 bar at the experimental temperature. The precursor solution input was calculated using the fluid's density provided in NIST Chemistry Webbook [16]. The tightly sealed reactor was inserted into the molten salt bath with constant shaking for 12 min which includes 2 min of heat-up time. After 12 min, the reaction was terminated by quenching the reactor in a water bath at room temperature. The obtained powders were collected and washed three times with DIW before drying in an oven at 80 °C for overnight.

Calcination was conducted in a custom made furnace installed with a PID temperature controller and a gas flow system. When nitrogen gas was used, the flowrate was 200 cc/min. Heating rate was 5 °C/min and calcination was performed at 500 °C for 60 min. $MnCO_3$ microparticles for calcination were hydrothermally synthesized at 400 °C with glycerol.

2.3. Physical characterization

X-ray diffraction (XRD) patterns were obtained using Bruker AXS Diffraktometer D8 with Cu Kα radiation. FEI Inspect F was used to collect field emission scanning electron microscopy (SEM) images for visual inspection of particle size and morphology.

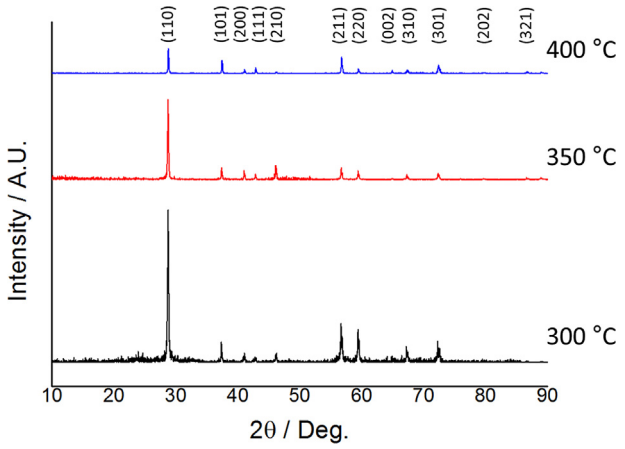

Fig. 1. XRD patterns of MnO_2 synthesized in pure water at 300–400 °C.

3. Results and discussion

3.1. Synthesis of various manganese oxides using sub and supercritical water

Initially, manganese oxides were synthesized using water only and the results are summarized in Table 1. A temperature range of 250–400 °C was tested and the obtained particles were studied using XRD. Fig. 1 shows the XRD patterns of manganese oxides hydrothermally synthesized at 300 °C, 350 °C, and 400 °C. The XRD pattern for 250 °C reaction couldn't be obtained because very few particles were synthesized at 250 °C, indicating insufficient activation energy for crystallization. Crystalline manganese (IV) oxides were synthesized at 300–400 °C where the XRD patterns matched MnO_2 JCPDS card No. 24–0735. Fig. 1 shows the decrease of (110) peak intensity along with the increase in reaction temperature. This decrease in (110) peak intensity is due to the different metal oxide solubility of water in near-critical conditions. In the subcritical water region of 300–350 °C, water is in liquid state with high solubility of metal compounds [17] which allows steady crystal growth. In contrast, supercritical water has negligible metal compound solubility causing rapid crystallization which consequently retards crystal growth. The change in (110) peak intensity was also observed in the SEM images of MnO_2 microparticles. Fig. 2(a) and (b) shows the SEM images of MnO_2 microparticles synthesized at

Table 2
A summary of calcination conditions and results.

Temp (°C)	Manganese precursor	Calcination time (min)	Calcination atmosphere	Particle size (μm)	Product
500	$Mn(NO_3)_2{\cdot}6H_2O$	60	In air (no gas flow)	1–30	MnO_2
500	*$MnCO_3$	60	In air (no gas flow)	1–10	Mn_2O_3
500	*$MnCO_3$	60	N_2 flowing 200 cc/min	1–10	$MnO + Mn_3O_4$

* Synthesized in SCW at 400 °C with glycerol.