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Effect of KOH on the continuous synthesis of cobalt oxide and manganese oxide nanoparticles in supercritical water

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ABSTRACT

The effects of KOH on the supercritical hydrothermal synthesis of cobalt oxide and manganese oxide particles are investigated using a continuous-flow reactor. Significant changes in morphology, particle size, and oxidation state are observed by adding KOH. The spinel Co_3O_4 phase is transformed to a rocksalt CoO phase and the pyrolusite MnO_2 phase is transformed to a hausmannite Mn_3O_4 phase in the presence of 0.5 M KOH. The average particle size of the metal oxides decreased with an addition of KOH. The OH^- ions of KOH may act as a reducing agent as well as a supersaturation enhancing agent under supercritical water conditions.

1. Introduction

Transition metal oxides such as cobalt oxide and manganese oxide are an important group of materials owing to their several interesting properties and applications in catalysis [1–3], sensors [4,5], and so on; further, due to much higher specific discharge capacities (500–1000 mAh g^{-1}) when compared to commercial graphite materials with a theoretical capacity of 372 mAh g^{-1}, transition metal oxides are potential anode active materials for use large-scale lithium-ion battery application such as plug-in hybrid electric vehicles (PHEVs) and energy storage systems (ESS) [4,6–8]. The control of particle size and crystalline structure are crucial to determine the physicochemical properties of the metal oxides. For example, catalytic activities, sensing abilities, and electrochemical properties toward lithium are highly dependent on properties such as particle size, crystalline structure, and oxidation state [2,6,9,10]. Therefore, the development of simpler, reliable and effective techniques to control the properties of metal oxides is a key factor for their use in a variety of applications.

In recent years, supercritical hydrothermal synthesis (SHS) has widely been utilized to produce fine metal oxide nanoparticles formed by hydrolysis of metal salts and subsequent dehydration reactions [11–15]. The unique physical properties of supercritical water (scH_2O, $T_c = 374\,^{\circ}C$ and $P_c = 22.1$ MPa), including low viscosity, fast diffusion, and high supersaturation of reaction intermediates, can yield nanosized metal oxide particles having high crystallinity. In addition, the fast nanoparticle formation rate and the use of continuous flow reactor system enable mass production of the nanosized metal oxide particles [15]. The unique properties of scH_2O has been used to produce various types of metal oxide nanoparticles including CuO, CeO_2, Fe_2O_3, ZnO, AlOOH, NiO, TiO_2, Co_3O_4, ZrO_2, La_2CuO_4, $LiFePO_4$, $LiCoO_2$, and $Li_4Ti_5O_{12}$ [11,15–22]. High OH^- ion concentrations under the water at its supercritical state enhance hydrolysis reactions. Addition of potassium hydroxide (KOH) during SHS is known to decrease the particle size by further increasing supersaturation [23,24]. However, control of the oxidation state is still challenging in the synthesis of metal oxide particles [25]. In this paper, we report the effects of KOH on the oxidation state and the particle size of metal oxides (cobalt oxide and manganese oxide) during continuous SHS. The sections that follow discuss the size, morphology, and surface area of the particles synthesized at different KOH concentrations.

2. Materials and methods

Cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$, purity of 99%) was purchased from Sigma–Aldrich Co. (USA). Manganese nitrate hexahydrate ($Mn(NO_3)_2{\cdot}6H_2O$) was purchased from Kanto Co., Ltd.

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Table 1
The synthesis condition of cobalt oxide and manganese oxide using continuous supercritical hydrothermal synthesis.

Sample code	Produced particles	Pressure (MPa)	Temp. (°C)	$M(NO_3)_x$ conc. (M)	KOH conc. (M)	Flow rates (g/min)			Residence time (s)	BET surface area (m^2/g)
						Raw mater. $M(NO_3)_2$	H_2O	KOH		
Co-1	Co_3O_4	30	400	0.025	0	3	12	–	21	6.7
Co-2	Co_3O_4	30	400	0.025	0.05	1.5	12	1.5	21	15.5
Co-3	Co_3O_4 + CoO	30	400	0.025	0.1	1.5	12	1.5	21	26.9
Co-4	CoO	30	400	0.025	0.5	1.5	12	1.5	21	26.5
MnO_2	MnO_2	30	400	0.05	0	2	6	–	38	1.7
Mn_3O_4	Mn_3O_4	30	400	0.05	0.5	1	6	1	38	12.9

(Japan). Potassium hydroxide (KOH) was obtained from Daejung Chemicals and Metals, Co. (Korea). Distilled and deionized (DDI) water was prepared using a Milli-Q, ultrapure water purification system. The nanoparticles were synthesized in scH_2O using a custom-built, continuous-flow reactor apparatus. The detailed description of the apparatus and the synthetic procedure was given in the previous paper [26]. Details of the synthetic conditions are listed in Table 1. The synthesized nanoparticles were characterized using X-ray diffraction (XRD, D/Max-2500 V/PC Rigaku X-ray diffractometer, Japan), field emission scanning electron microscopy (FE-SEM, Hitachi S-4100 field emission scanning electron microscope, Japan), and Brunauer–Emmett–Teller (BET) surface-area (model Belsorp mini II, BEL Inc., Japan) analysis.

3. Results and discussion

Fig. 1 shows the effect of KOH concentration on the crystalline structure of cobalt oxide particles synthesized in scH_2O. The particles synthesized in the absence of KOH (Co-1) or with a small concentration of KOH (0.05 M, Co-2) retained the spinel Co_3O_4 phase (Fig. 1a and b, JCPDS card no. 43-1003). On increasing the KOH concentration to 0.1 M, additional peaks associated with the rocksalt CoO phase occurred and the peaks associated with Co_3O_4 still persisted (Fig. 1c). In the presence of large KOH concentrations (0.5 M, Co-4), the synthesized particles retained only the CoO crystalline structure (JCPDS card no. 43-1004). This indicates that the oxidation state of cobalt changed from $Co^{2+/3+}$ to Co^{2+} at high concentrations of KOH. The color of the particles changed from black to gray when 0.5 M KOH was used (see Fig. S1 in the Supplementary Material). This result indicates that KOH can act as a reducing agent in the supercritical hydrothermal synthesis of cobalt oxide particles.

As shown in Fig. 2, significant changes in morphology and particle size were observed by adding KOH. In the absence of KOH, well faceted particles with diameters of 100–400 nm were produced; in contrast, upon the addition of KOH up to a concentration of 0.5 M, irregularly shaped particles with diameters of 20–200 nm were produced. As listed in Table 1, the BET surface area decreased with an increase in KOH concentration. The BET surface area of the Co-4 sample was 26.5 m^2/g, which is much

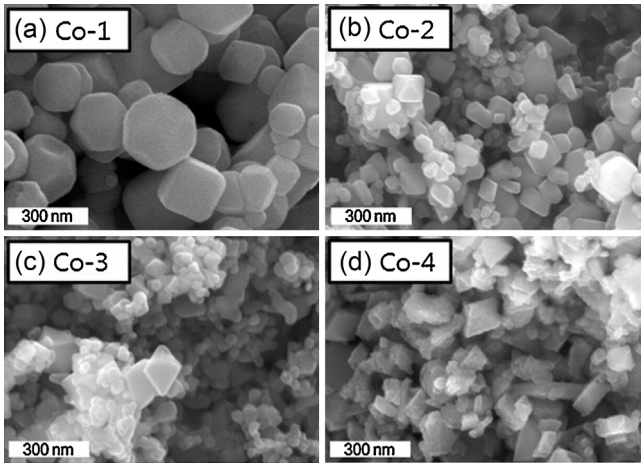

Fig. 2. SEM images of cobalt oxide particles synthesized (a) without KOH (Co-1), (b) at 0.05 M KOH (Co-2), (c) at 0.1 M KOH (Co-3), and (d) at 0.5 M KOH (Co-4).

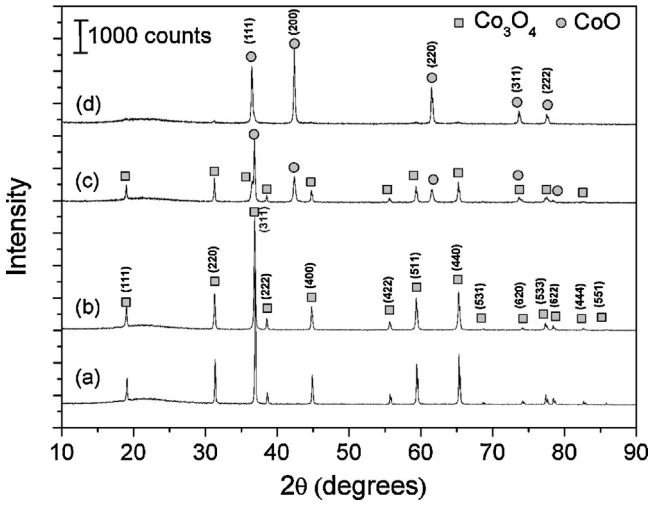

Fig. 1. XRD patterns of cobalt oxide particles synthesized (a) without KOH (Co-1), (b) at 0.05 M KOH (Co-2), (c) at 0.1 M KOH (Co-3), and (d) at 0.5 M KOH (Co-4).

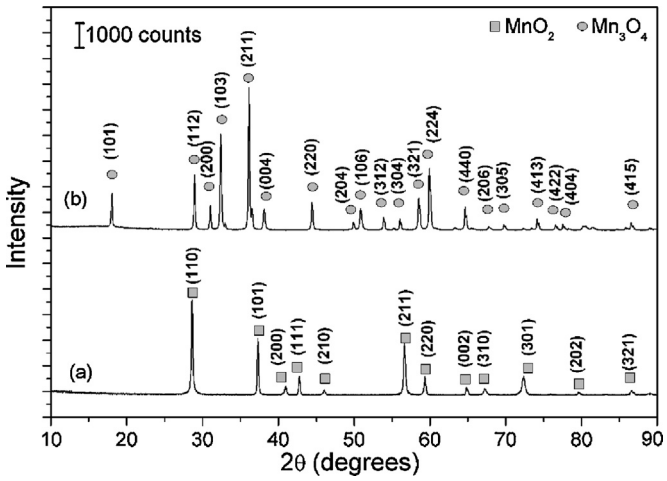

Fig. 3. XRD patterns of manganese oxide particles synthesized (a) without KOH (MnO_2) and (b) at 0.5 M KOH (Mn_3O_4).