CONTINUOUS HYDROTHERMAL SYNTHESIS OF ZINC OXIDE NANOPARTICLES

Kiwamu Sue, Kazuhito Kimura, Kenji Murata, and Kunio Arai
Graduate School of Environmental Studies, Tohoku University
Sendai, 980-8579, Japan
E-mail:sue@arai.che.tohoku.ac.jp, Fax:+81-22-217-7246

Hydrothermal synthesis of zinc oxide (ZnO) nanoparticles and nanorods from zinc nitrate ($Zn(NO_3)_2$) and potassium hydroxide (KOH) solutions was carried out with a flow-through apparatus for continuous production and rapid heating of the starting solution to supercritical states. Effect of $Zn(NO_3)_2$ and KOH concentrations and flow rates on the particle size and morphology was examined at 673 K and 30 MPa. Nanoparticles having an average particle diameter of 22 nm was produced from 1.0×10^{-3} $Zn(NO_3)_2$ and 4.0×10^{-3} KOH aqueous solution at a total flow rate of 22.5 g/min. Increasing the flow rate to 1.5 times larger value, nanorods having an average rod width of ca. 40 nm was produced.

INTRODUCTION

Zinc oxide (ZnO) particles, which attracts much attention for its several applications, have been produced by several techniques such as precipitation, spray pyrolysis, thermal decomposition, and hydrothermal synthesis [1]. In particular, hydrothermal synthesis is well known as an environmentally safe and simple process, since it does not require any organic solvents and additional processing such as comminution or calcination. Typically, hydrothermal synthesis has been conducted with a batch type apparatus. An aqueous solution is heated up slowly to 373 - 573 K and then aged for several hours or days. During the heating up time, hydrothermal reaction takes place to produce nuclei and then crystals grow. As ZnO is more soluble in water compared with the other metal oxides such as TiO_2, hydrothermal synthesis of nanoparticles and nanorods is an especially difficult problem without any surfactants and organics [2].

Over the past ten years, a rapid and continuous hydrothermal synthesis method has been established for forming micro or sub nano size metal oxide fine particles in supercritical water [3]. Generally, near critical pressure (P_C=22.1 MPa) and above the critical temperature (T_C=647 K), the reaction rate of hydrothermal synthesis, which is the dehydration reaction from hydroxide to oxide, is a few orders of magnitude higher than that under T_C. In contrast, the metal oxide solubility above T_C is a few orders of magnitude lower than that under T_C. These features are strongly related to the decreasing of water density and dielectric constant of water. Thus, this method provides high controllability of particle size and morphology by the changing reaction rate and metal oxide solubility by varying the water density with reaction temperature and pressure.

In this work, we conduct the hydrothermal synthesis of ZnO with a flow-through experimental apparatus and examine effect of KOH and $Zn(NO_3)_2$ concentrations in starting solutions, flow rate and heating up procedure of starting solution on particle size and morphology.

I - MATERIALS AND METHODS

The solution was prepared by dissolving precise amounts of $Zn(NO_3)_2 \cdot 6H_2O$ (Wako Pure Chemicals, Osaka, Japan) and potassium hydroxide (KOH, Wako Pure Chemicals, Osaka,

Japan) crystals in distilled water. The concentrations of $Zn(NO_3)_2$ and KOH are summarized in Table 1.

A schematic diagram of experimental flow apparatus is shown in Figure 1. $Zn(NO_3)_2$ and KOH aqueous solutions were fed with two pumps. Two types of mixing procedure were examined. One is that a preheated water is firstly mixed with KOH solution at mixing point 1 (MP1) and then the solution is mixed with $Zn(NO_3)_2$ solution at mixing point 2 (MP2), (Type I). Another is that the preheated water is mixed with each starting solution in reverse order, (Type II). 316 stainless steel tubing (o.d. 1.58 mm, i.d. 0.5 mm) was used for the reactor and tubing at high temperature sections. The reactor has a volume of 0.04 cm^3. Tee (i.d. 1.3 mm) made of 316 stainless steel was used for the mixing sections. Reaction temperature was defined as the temperature (T2) at MP2 and maintained to 673 ± 1 K by an electric furnace. At the exit of the reactor the fluid was quenched with an external water jacket. The temperature was measured with a K-type thermocouple. The system pressure was maintained to 30 ± 0.1 MPa by using a back pressure regulator that was placed after the cooler. Particles were removed by using an in-line filter to minimize plugging at the back pressure regulator. When the system achieved to steady state, as judged by the temperature, products were collected by diverting the flow to a parallel in-line filter with a three-way valve.
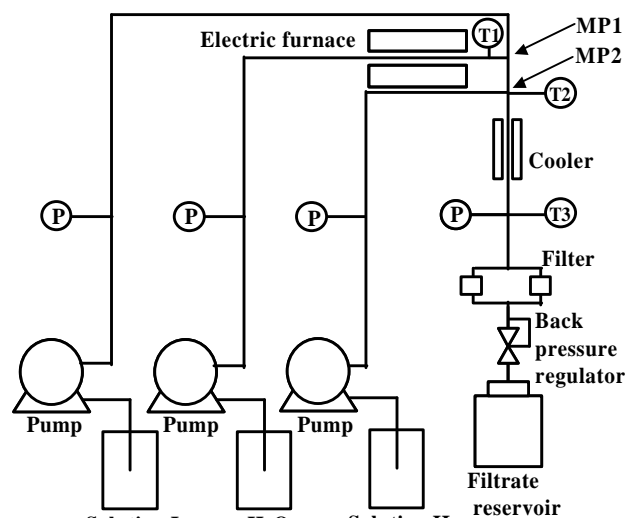

Figure 1. A flow-through experimental apparatus

The crystal structures of the products were analyzed by powder X-ray diffractometry (XRD) (RINT-2200, Rigaku), using CuKa radiation. Observation of these products was performed by transmission electron microscopy (TEM) (LEO-912-OMEGA, Karl Zeiss).

II – RESULTS AND DISCUSSIONS

The products obtained in this work were a single phase of ZnO. Average of particles diameter and width of rods with its standard deviation were summarized in Table 1. Aspect ratios of particles were evaluated as the ratio, long axis / short axis. Particles having a large aspect ratio > 3 were defined as rods. Typical TEM observation of nanorods (Run 6) are shown in Figure 2.

Firstly, with increasing KOH concentration from 2 x 10^{-3} mol/kg (Run 1) to 4 x 10^{-3} mol/kg (Run 2), particle size decreased from 29 nm (s.d. 14 nm) to 22 nm (s.d. 9 nm). This decrease of particle size probably relates to the decrease of ZnO solubility which is brough from the increase of mixing efficiency between KOH and $Zn(NO_3)_2$. With further increasing KOH concentration to 8 x 10^{-3} mol/kg (Run 3), no significant difference of particle size was observed. Secondary, changing mixing procedure from type I (Run 1) to type II (Run 4) at constant concentration and flow rate, particle size decreased to 17 nm (s.d. 2 nm) and content of rods in products increased. This increase probably relates to the change of formation mechanism. At type I, ZnO particles are produced at MP 2. In contrast, at type II, small numbers of ZnO particles (or nuclei) are firstly produced at MP 1 and then selected surfaces are grown in the presence of KOH at MP 2. Thirdly, with increasing KOH and $Zn(NO_3)_2$

Table 1. Experimental results

Run No.	Zn(NO$_3$)$_2$ [mol/kg]	KOH [mol/kg]	Flow rate [g/min]			Mixing procedure	Morphorogy of main products	Average size [nm]	Standard deviation [nm]
			Zn(NO$_3$)$_2$	KOH	Water				
1	10^{-3}	2×10^{-3}	1.5	3	18	Type I	particle	29	14
2	10^{-3}	4×10^{-3}	1.5	3	18	Type I	particle	22	9
3	10^{-3}	8×10^{-3}	1.5	3	18	Type I	particle	23	8
4	10^{-3}	2×10^{-3}	1.5	3	18	Type II	particle _rod_	17 _42_[*]	2 _7_[*]
5	10^{-2}	2×10^{-2}	1.5	3	18	Type II	_rod_	_95_[*]	_5_[*]
6	10^{-2}	2×10^{-2}	2.25	4.5	27	Type II	_rod_	_38_[*]	_2_[*]
7	10^{-2}	4×10^{-2}	2.25	4.5	27	Type II	_rod_	_40_[*]	_2_[*]

* Value was estimated from width of rods

concentrations from 10^{-3} and 2×10^{-3} mol/kg (Run 4) to 10^{-2} and 2×10^{-2} mol/kg (Run 5), respectively, rods in products became main product and the width increased from 42 nm to 95 nm. This trend probably relates to the increase of ionic strength. Fourthly, with increasing flow rate to 1.5 times larger value (Runs 6 and 7), the width of rods decreased to 38 nm. This decrease relates to the decrease of heating up time at MP 1, which gives the formation of smaller ZnO nuclei and then selected surface of the nuclei are grown in the presence of KOH at MP 2. In conclusion, continuous hydrothermal synthesis of not only ZnO nanoparticles but also ZnO nanorods via a flow-through apparatus could be established at supercritical conditions.
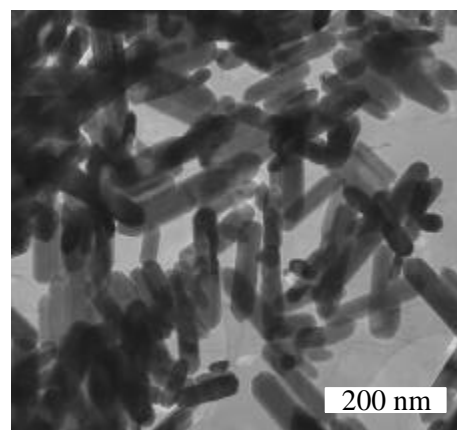

Figure 2. TEM observation (Run 6)

REFERENCES :
[1] PEARTON, S. J., NORTON, D. P., Ip, K., HEO, Y. W., STEINER, T., Superlatt. Microstr., _in press_
[2] VISWANATHAN, R., LILLY, G. D., Gale, W. F., Gupta, R. B., Ind. Eng. Chem. Res., Vol. 42, **2003**, p. 5535.
[3] a) SUE, K., KIMURA, K., MURATA, K., ARAI, K., J. Supercrit. Fluids, _in press_, b) SUE, K., MURATA, K., KIMURA, K., ARAI, K., Green Chem., Vol. 5, **2003**, p. 659., c) HAKUTA, Y., HAGANUMA, T., SUE, K., ADSCHIRI, T., ARAI, K., Mater. Res. Bull., Vol. 38, **2003**, p. 1257., d) ADSCHIRI, T. HAKUTA, Y., SUE, K., ARAI, K., J. Nanopart. Res., Vol. 3, **2001**, p. 227.