Effect of pH on Hydrothermal Synthesis of γ-Al_2O_3 Nanoparticles at 673 K

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Hydrothemal synthesis of γ-Al_2O_3 nanoparticles obtained from aqueous $Al(NO_3)_3$ solutions was carried out at 673 K and under pressures ranging from 30 to 40 MPa for 2 s using a flow apparatus. Effect of pressure and molality of HNO_3 and KOH on crystal phase was examined. All products were a mixture of γ-Al_2O_3 and AlOOH having crystallite sizes less than 18 nm. Weight ratio of γ-Al_2O_3 to AlOOH in the products evaluated from TG showed a good correlation with pH at 673 K and increased from 0.17 to 1.16 with decreasing pH.

Al_2O_3 nanoparticles have been widely known as one of the high-function materials having broad technical applications. Among several fabrication techniques of metal oxide nanoparticles, hydrothermal synthesis promises green chemistry process. However, Al_2O_3 nanoparticles were not obtained by hydrothermal method up to 673 K in previous studies[1–5] owing to the phase stability of AlOOH at 673 K. Recently, Sue et al.[6] reported hydrothermal synthesis of nanoparticles as a mixture of Al_2O_3 and AlOOH at 673 K and 30 MPa for 1 s with a flow apparatus without any additives, but detail formation mechanism of Al_2O_3 was not clarified. In this study, we focus on the clarification of effect of pressure and molality of HNO_3 and KOH on crystal phase of the products synthesized hydrothermally at 673 K from aqueous $Al(NO_3)_3$ solutions.

Raw materials, $Al(NO_3)_3 \cdot 9H_2O$, KOH, and HNO_3, were produced by Wako Pure Chemical Industries. Molality of $Al(NO_3)_3$ was 0.01 mol/kg in a reactor. Molalities of KOH and HNO_3 in the reactor changed from 0 to 0.03 mol/kg and from 0 to 0.01 mol/kg, respectively.

The synthesis was performed with a flow apparatus as described in our previous work.[6] Aqueous $Al(NO_3)_3$ solution was fed with a pump (10 g/min) and was mixed with aqueous HNO_3 or KOH solution (10 g/min). After that, the solution was mixed in a union tee (0.3 mm i.d.) with preheated water (80 g/min), and it was rapidly heated to 673 K within 1 s. A reactor was made of a SUS316 tube (1.74 mm i.d.). At the exit of the reactor, the solution was quenched by mixing cooling water (80 g/min) and by an external water jacket. Residence time was 2 s. System pressure was maintained at 30, 35, and 40 MPa by using a back pressure regulator. Particles were recovered as a slurry solution, collected using a membrane filter, washed with ultrapure water, and dried at 333 K for 24 h. A part of the dried products was calcined at 673, 683, and 693 K for 3 h in order to analyze phase stability of products.

Crystal structures of the products were characterized by powder X-ray diffractometry (XRD, Rigaku, RAD-B system with monochrometer), using Cu Kα radiation. Crystallite size was calculated from the Scherrer equation. Particle size distributions of the products were measured by dynamic light scattering (DLS, BECKMAN COULTER, N5). Observation of these products was performed by a transmission electron microscope (TEM, HITACHI, FE2000). Average particles size, and standard deviation (S.D.) were calculated on the basis of the diameter of about 100 particles measured by TEM. Weight change of the products at temperatures ranging from 298 to 873 K was measured by thermal gravimetric analysis (TG, BRUKER AXS, TG-DTA2020SA). Molality of the remaining Al^{3+} in the recovered solutions was measured by an atomic absorption spectrophotometer (AA, SHIMADZU, AA-6300). Conversion of Al^{3+} to solid was defined as $(1 - m/m_0) \times 100$, where m and m_0 are Al^{3+} molalities in the recovered and starting solutions, respectively, and it was more than 92.6%. Experimental conditions and results are summarized in Table 1.

Typical XRD patterns of the products are shown in Figure 1. All peaks of as-prepared products were assigned to γ-Al_2O_3 and

Table 1. Experimental conditions and results

Run	Molality of starting solution/mol·kg^{-1}			Pressure /MPa	Conv./%	Products	Crystallite size (S.D.)/nm	$I_{Al_2O_3}/I_{AlOOH}$	$W_{Al_2O_3}/W_{AlOOH}$
	$Al(NO_3)_3$	KOH	HNO_3		Al				
1	0.01	—	—	30	94.8	AlOOH	10.6 (7.4)	0.62 ± 0.01	0.98 ± 0.02
						Al_2O_3	2.8 (0.5)		
2	0.01	—	0.01	30	96.3	AlOOH	8.2 (2.3)	0.94 ± 0.01	1.16 ± 0.02
						Al_2O_3	4.7 (2.0)		
3	0.01	0.01	—	30	96.2	AlOOH	6.8 (2.8)	0.18 ± 0.01	0.69 ± 0.02
						Al_2O_3	7.1 (2.2)		
4	0.01	0.02	—	30	97.0	AlOOH	7.9 (3.8)	0.09 ± 0.01	0.28 ± 0.02
						Al_2O_3	7.8 (2.6)		
5	0.01	0.03	—	30	97.0	AlOOH	16.8 (4.4)	0.10 ± 0.01	0.19 ± 0.02
						Al_2O_3	18.0 (5.3)		
6	0.01	—	—	35	97.4	AlOOH	8.4 (1.2)	0.29 ± 0.01	—
						Al_2O_3	6.5 (1.2)		
7	0.01	—	—	40	94.8	AlOOH	7.9 (1.6)	0.26 ± 0.01	0.63 ± 0.02
						Al_2O_3	8.0 (1.1)		
8	0.01	0.03	—	35	92.6	AlOOH	8.4 (1.2)	0.11 ± 0.01	0.17 ± 0.02
						Al_2O_3	7.1 (0.8)		
9	0.01	0.03	—	40	95.8	AlOOH	11.1 (1.4)	0.09 ± 0.01	0.23 ± 0.02
						Al_2O_3	9.8 (1.2)		

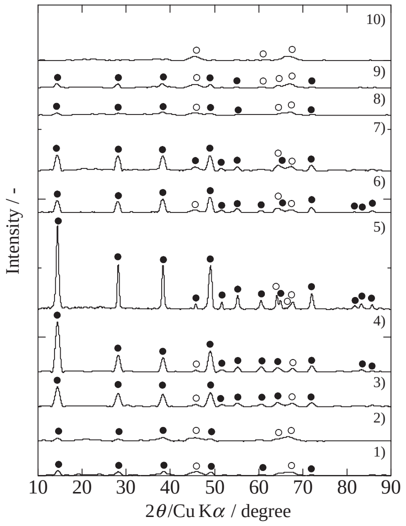

Figure 1. XRD patterns of as-prepared products at 1) 30 MPa (Run 1), 2) 30 MPa with 0.01 mol/kg HNO_3 (Run 2), 3) 30 MPa with 0.01 mol/kg KOH (Run 3), 4) 30 MPa with 0.02 mol/kg KOH (Run 4), 5) 30 MPa with 0.03 mol/kg KOH (Run 5), 6) 35 MPa (Run 6), and 7) 40 MPa (Run 7), and calcined product of Run 1 at 8) 673 K, 9) 683 K, and 10) 693 K (○: γ-Al_2O_3, ●: AlOOH).

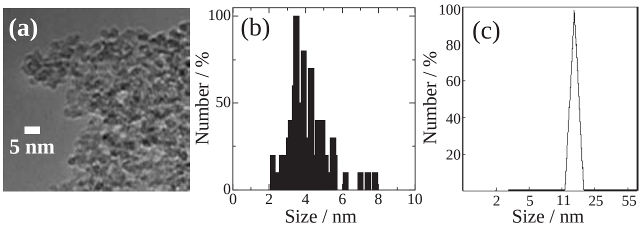

Figure 2. (a) TEM photograph, (b) size distribution from TEM results, and (c) size distribution from DLS results of the products obtained from 0.01 mol/kg $Al(NO_3)_3$ at 673 K and 30 MPa for 2 s.

AlOOH as shown in Figure 1. The crystal structure of all products was stable after the calcinations at 683 K and transformed into a single phase of γ-Al_2O_3 at 693 K.

Typical TEM photograph of the product (Run 1) and the size distribution measured by TEM and DLS are shown in Figure 2. An average particle size (S.D.) from TEM was 4.1 (1.0) nm, which showed agreement with the crystallite size from XRD (10.6 nm for AlOOH and 2.8 nm for γ-Al_2O_3). DLS result showed a unimodal distribution having an average particle size of 15 nm, which was slightly larger owing to the aggregation than those from TEM and XRD results. Crystallite size of all products was less than 18 nm, and no significant differences were observed.

To analyze the ratio of γ-Al_2O_3 to AlOOH in the products, we evaluated peak intensity ratio of (406) plane for γ-Al_2O_3 to (020) plane for AlOOH, $I_{Al_2O_3}/I_{AlOOH}$, measured up from XRD results. In addition, we analyzed the weight ratio of γ-Al_2O_3 to AlOOH, $W_{Al_2O_3}/W_{AlOOH}$, on the basis of weight loss through dehydration reaction of AlOOH to γ-Al_2O_3 ($2AlOOH \rightarrow \gamma\text{-}Al_2O_3 + H_2O$) from TG results. The values are shown in Table 1. HNO_3 addition and decreasing in KOH molality and decreasing pressure without KOH led to increased $I_{Al_2O_3}/I_{AlOOH}$ and $W_{Al_2O_3}/W_{AlOOH}$.

In the following section, effect of pressure and molalities of HNO_3 and KOH on the formation of γ-Al_2O_3 is discussed. We consider that structures of precursor complexes such as $Al(OH)_m{}^{3-m}$ ($m = 0$–4) and $Al(NO_3)_n{}^{3-n}$ ($n = 1, 2$) have probably a strong effect to form different types of crystal structures,[7] but detailed structures of these complexes around 673 K are not clarified. Therefore, we focus on pH at 673 K because the value is a key factor for controlling molality distributions of metal complexes in typical aqueous chemistry.[8] A pH at given conditions was estimated by solving the system of nonlinear equations of dissociation constants[9] of HNO_3, KOH, KNO_3, and H_2O, mass balance relations for K and NO_3, charge balance relation, and formulation for the activity coefficient of ions. Peak intensity ratio, $I_{Al_2O_3}/I_{AlOOH}$, and weight ratio, $W_{Al_2O_3}/W_{AlOOH}$, as a function of estimated pH at 673 K are shown in Figures 3a and 3b, respectively. At given pressures, each ratio increased sharply with decreasing pH at 673 K. In addition, slight pressure dependence of the relation was observed and the ratio decreased with increasing pressure at constant pH. Difference of mixing behavior in a union tee for rapid heating at given pressures is probably one of the possible reasons, and further studies on mixing are necessary for more detailed discussion.

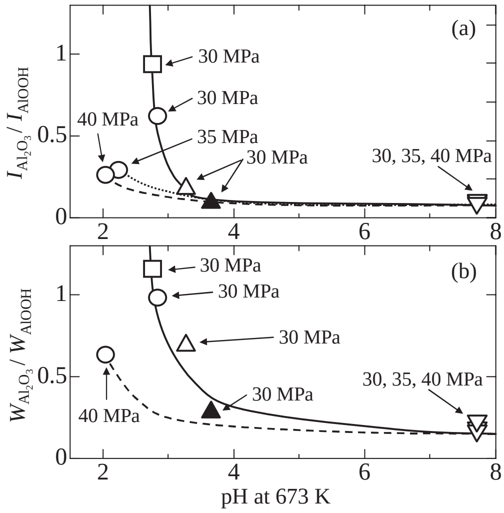

Figure 3. (a) Peak intensity ratio, $I_{Al_2O_3}/I_{AlOOH}$, and (b) weight ratio, $W_{Al_2O_3}/W_{AlOOH}$, as a function of pH at 673 K (○: $Al(NO_3)_3$, △: $Al(NO_3)_3$ + KOH 0.01 mol/kg, ▲: $Al(NO_3)_3$ + KOH 0.02 mol/kg, ▽: $Al(NO_3)_3$ + KOH 0.03 mol/kg, □: $Al(NO_3)_3$ + HNO_3 0.01 mol/kg).

In conclusion, a pH at given conditions was a key factor for controlling weight ratio of γ-Al_2O_3 to AlOOH in hydrothermal synthesis of γ-Al_2O_3/AlOOH nanoparticles with a flow apparatus at 673 K and the ratio increased with decreasing pH at given conditions.

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