JOURNAL OF Materials CHEMISTRY

Crystallinity of boehmite and its effect on the phase transition temperature of alumina

Takayuki Tsukada,[*a] **Hideo Segawa,**[a] **Atsuo Yasumori**[b] **and Kiyoshi Okada**[b]

[a] *Petroleum Refining Research and Technology Center, Japan Energy Corporation, Niizo-minami, Toda, Saitama, 335-8502, Japan. E-mail: ttsuk@j-energy.co.jp*
[b] *Department of Inorganic Materials, Tokyo Institute of Technology, O-okayama, Meguro, Tokyo 152-8552, Japan*

Received 27th August 1998, Accepted 29th October 1998

The effect of the crystallinity of boehmite powders on the temperatures of γ-Al_2O_3 formation and the θ- to α-Al_2O_3 transformation was investigated using boehmite powders of varying crystallite size prepared under various hydrothermal conditions. With increasing crystallite size of the boehmite powders, the specific surface area decreased and the expanded (020) *d*-spacing approached the reported value. Thermogravimetric (TG) profiles of more poorly crystalline boehmite indicated the presence of excess water molecules of different binding energy located on the surface or in the interlayer. The crystallite size of boehmite also showed a strong correlation with the formation temperature of γ-Al_2O_3 and the phase transition temperature of θ- to α-Al_2O_3. Since both these temperatures are increased with increasing the crystallite size of boehmite, this is an important factor in determining the conditions for obtaining γ-, θ- and α-Al_2O_3 from boehmite. By relating the TG weight loss to the water and OH contents in boehmite and γ-Al_2O_3, respectively, the crystallite size of boehmite can be related to the water content. This indicates that the γ-Al_2O_3 transformed from boehmite of smaller crystallite size contains larger amounts of OH groups, implying more poorly crystalline γ-Al_2O_3. The reported topotactic transformation of boehmite *via* γ- to θ-Al_2O_3 indicates a relationship between the crystallite size of the boehmite and that of the resulting transition alumina, which could explain the change of the phase transition temperature from θ- to α-Al_2O_3.

Introduction

Boehmite, aluminium oxyhydroxide (γ-AlOOH), is an important precursor material for γ-Al_2O_3, which is used as a catalyst support and as a membrane due to its high surface area and mesoporous properties. It is also used for monolithic α-Al_2O_3 from sol–gel processing, which finds wide application as an abrasive, a milling material, as a substrate for electronic circuits and as a high temperature refractory material exploiting its good mechanical, electrical, thermal and optical properties.[1–6] The crystallinity of boehmite strongly depends on its preparation conditions and exhibits a continuous gradation in crystallite size and *d*-spacing.[7] Poorly crystalline boehmite is generally termed pseudoboehmite, and has a very small particle size.

In the manufacture of alumina catalyst supports, pseudoboehmite powder is mixed with water, formed, dried, and fired to produce γ-Al_2O_3.[3] The sol–gel process involves complex procedures such as peptization or sol formation by the addition of acid to boehmite and heating to evaporate the water from the sol and form a gel.[8] Little attention has been previously paid to the importance of the boehmite crystallinity in controlling the various properties of the γ-Al_2O_3 and α-Al_2O_3 product.

Boehmite transforms on heating through a series of metastable transition alumina phases including γ-, δ-, θ-Al_2O_3, finally forming thermodynamically stable α-Al_2O_3 (corundum). Dehydration of boehmite on heating causes its transformation to γ-Al_2O_3 at around 500 °C. Since the transformation from γ- through δ- to θ-Al_2O_3 proceeds topotactically,[6,9,10] it involves only a small energy difference. The transformation from θ- to α-Al_2O_3, however, requires a reconstruction of the structure, involving a change in the oxygen sublattice from cubic to hexagonal and occurs with a larger energy difference reflected by a DTA exotherm. Although it has been pointed out that the thermal reaction sequence and kinetics depend on the properties of the boehmite,[6] little quantitative work has been performed to clarify the relation between the boehmite crystallinity and its transformation temperature. The crystallinity is generally defined in terms of the order of the crystal structure.

Here we prepared boehmite powders with various degrees of crystallinity, by hydrothermal treatment of pseudoboehmite in acidic and alkaline solutions at temperatures below 200 °C. The crystallinity of boehmite is evaluated by primary particle size such as apparent crystallite size and specific surface area, lattice constants such as *d*-spacing, and the water and OH content. These were used to examine the quantitative relationship between the crystallinity of the precursor boehmite and its thermal transformation temperature to alumina.

Materials and experimental methods

Materials

Commercially available pseudoboehmite powder (Condea Chemie GmbH, Hamburg, Germany) produced by hydrolysis of aluminium alkoxide was used as the starting material for all experiments.[3] The pseudoboehmite powder contained 94 ppm Fe, 40 ppm Si and 10 ppm Ti. The powder was dried at 300 °C for 4 h to eliminate residual organic species on the particle surfaces, 10 g aliquots were accurately weighed and suspended in 150 ml of solution.

Acidic and alkaline conditions were chosen to promote crystal growth under hydrothermal conditions below 200 °C, because of the relatively high solubility of aluminium in both acidic and alkaline solutions.[11] Tetraethylammonium hydroxide (TEAOH) and nitric acid were selected to avoid metal cation contamination. TEAOH solution (MERCK-Schuchardt, Munchen, Germany) was diluted with ultrapure water to 10% concentration (approximately 0.68 mol l^{-1}). The pH of this TEAOH solution was 14. Nitric acid solution (0.1 M) (KANTO Chemical, Tokyo, Japan) was used for the acidic solution.

Experimental setup and method

Teflon beakers were used in all experiments to avoid contamination from the reaction vessel. The suspensions were sealed in the beakers inside a hydrothermal bomb and were held at temperatures $\leqslant 200$ °C for 20 h without stirring. After hydrothermal treatment, the bomb was immediately cooled down to room temperature by immersing in flowing water. Transparent or translucent gels were deposited in the beaker after hydrothermal treatment in all experiments and were collected by centrifugation. The gels were dried at 130 °C in an oven for 24 h and pulverized in an agate mortar and pestle prior to characterization.

Powder evaluation

The phases present, their crystallinity, specific surface area, porosity, weight loss behavior and transformation temperature on heating were investigated by X-ray diffraction (XRD), N_2 gas adsorption, and thermogravimetric and differential thermal analysis (TG–DTA). XRD was performed using Cu-Kα radiation (Phillips, Almelo, Holland) to confirm that the crystalline phase was boehmite. A step scanning method with a step interval of 0.01 or 0.02 degrees and step time of 3–5 s was used to measure the *d*-spacing of the 020 reflection and to calculate the apparent crystallite size by Scherrer's equation using the 020 reflection. The internal standard used was corundum, which was prepared by calcining the pseudoboehmite at 1600 °C for 36 h. The specific surface areas of the powders were measured by the three point BET method using high purity N_2 gas with an ASAP 2400 (Micromeritics, USA) after drying in vacuum (<0.1 Torr) at 200 °C. TG–DTA measurements were performed at a heating rate of 10 °C min^{-1} in static air using alumina crucibles and α-Al_2O_3 reference from room temperature to 1400 °C using a TAS 200 system (RIGAKU, Japan). The adsorbed water and structural water content of the boehmite were calculated from the TG–DTA data. The formation temperature of γ-Al_2O_3 and the temperature of the θ- to α-Al_2O_3 transition were obtained from the DTA peak maximum. The transformation temperatures of boehmite to γ-Al_2O_3 and θ- to α-Al_2O_3 were determined from the endothermic peak at *ca.* 500 °C and the exothermic peak at *ca.* 1200 °C, respectively.

Results

Property changes in boehmite caused by drying and hydrothermal treatment

The powders treated in 0.1 M HNO_3 and 10% TEAOH solutions at various temperatures for 20 h are confirmed by XRD to contain only crystalline boehmite. The intensity of all diffraction peaks increased with temperature. The XRD crystallite size, *d*-spacings and the other properties of the powders are summarized in Tables 1 and 2. The powder dried at 300 °C showed lower specific surface area, larger crystallite size and narrower *d*-spacing than those of the as-received powder. This may correspond to an improvement in crystallinity due to the local hydrothermal environment related to evaporation of water on drying, similar to the dehydration process of gibbsite[6] or the elimination of random strain by drying. The effect of drying will be discussed in detail elsewhere.[12] At higher hydrothermal temperatures, the crystallite size of boehmite increases, its specific surface area and *d*-spacing decrease, and its endothermic peak position around 500 °C and exothermic peak at around 1200 °C both shift to higher temperatures in the DTA excursions.

Correlation of powder properties

The relationships between crystallite size and specific surface area, and the crystallite size and *d*-spacing are presented in Fig. 1(a) and (b). Upon increasing the crystallite size of the boehmite, the specific surface area decreases from *ca.* 300 to 50 m^2 g^{-1}. This implies that the particle size of boehmite increases corresponding to the increased crystallite size calculated from the 020 reflection. On the other hand, the 020 *d*-spacing of boehmite becomes rapidly smaller in the crystallite size range <5 nm and gradually approaches the value of 0.611 nm corresponding to well crystallized boehmite as the crystallite size increases. The results show the crystallite size and *d*-spacing change continuously depending on the hydrothermal conditions. This is consistent with the results obtained for various boehmites by Tottenhorst and Hofmann.[7]

Fig. 2 shows the TG profiles of three samples of different crystallite size. They exhibit significant weight loss at *ca.* 100 and 500 °C, corresponding to the desorption of water from the particle surfaces and dehydration of OH groups in the phase transition from boehmite to γ-Al_2O_3. The sample with largest crystallite size exhibits only a small weight change between 100 and 300 °C but a steep weight loss around 500 °C, while the sample of smallest crystallite size exhibits a gradual weight loss from 100 to 500 °C. This indicates that boehmite of lower crystallinity contains a variety of excess water molecules of different binding energy on the surface or in the interlayer of the boehmite.

Based on the results discussed above and focusing on the crystallite size as a representative factor defining the crystallinity, it is found that the formation temperature of γ-Al_2O_3 from boehmite and the phase transition temperature from θ- to α-Al_2O_3 increases with increasing crystallite size of boehmite as shown in Fig. 3. The changes in phase transition temperatures as a function of crystallinity are discussed later in this paper.

Discussion

Effect of acidic and alkaline conditions on crystallite size

Because of the amphoteric behavior of boehmite, its solubility is higher in acidic and alkaline solutions than in neutral solution.[13] Therefore, the significant crystallite growth observed under both conditions may reasonably occur by a dissolution–reprecipitation mechanism. However, there are some differences between the samples treated under acidic and alkaline conditions. In alkaline solution, much larger crystallite sizes were attained compared to those of acidic conditions at the same temperature. This may be understood in terms of the solubility of boehmite as a function of pH and temperature. The solubility decreases in acidic solution and increases in alkaline solution as a function of temperature.[13] Higher solu-

Table 1 Various properties of the pseudoboehmite powders after drying

	N_2 adsorption			XRD	
Treatment	Specific surface area/ m^2 g^{-1}	Pore volume/ ml g^{-1}	Mode pore diameter/nm	*d*-spacing/ nm	Crystallite size/ nm
As-received	291	0.42	5	0.636	3.4
Dried at 130 °C	—	—	—	0.633	3.7
Dried at 300 °C	217	0.42	6	0.630	4.0

Table 2 Various properties of the boehmite powders after hydrothermal treatment for 20 h in each solution

Hydrothermal condition		N_2 adsorption			XRD		DTA Phase transition temperature/°C	
Solution	T/°C	Specific surface area/ $m^2\ g^{-1}$	Pore volume/ ml g^{-1}	Mode pore diameter/nm	d-spacing/ nm	Crystallite size/ nm	γ	α
10% TEAOH	80	223	0.36	5	0.6223	5.1	459	1206
10% TEAOH	110	164	0.34	7	0.6161	8.0	463	1222
10% TEAOH	130	135	0.36	11	0.6146	10.1	472	1246
10% TEAOH	150	108	0.38	15	0.6136	13.1	480	1252
10% TEAOH	175	62	0.20	19	0.6130	20.2	497	1275
10% TEAOH	200	50	0.31	43	0.6130	21.6	503	1273
0.1 M HNO_3	80	234	0.40	5	0.6250	4.3	456	1209
0.1 M HNO_3	110	263	0.31	4	0.6227	4.6	452	1200
0.1 M HNO_3	130	253	0.30	4	0.6207	5.0	450	1206
0.1 M HNO_3	150	226	0.30	4	0.6179	5.6	452	1205
0.1 M HNO_3	175	164	0.31	7	0.6151	8.2	464	1234
0.1 M HNO_3	200	108	0.30	11	0.6134	12.1	485	1245

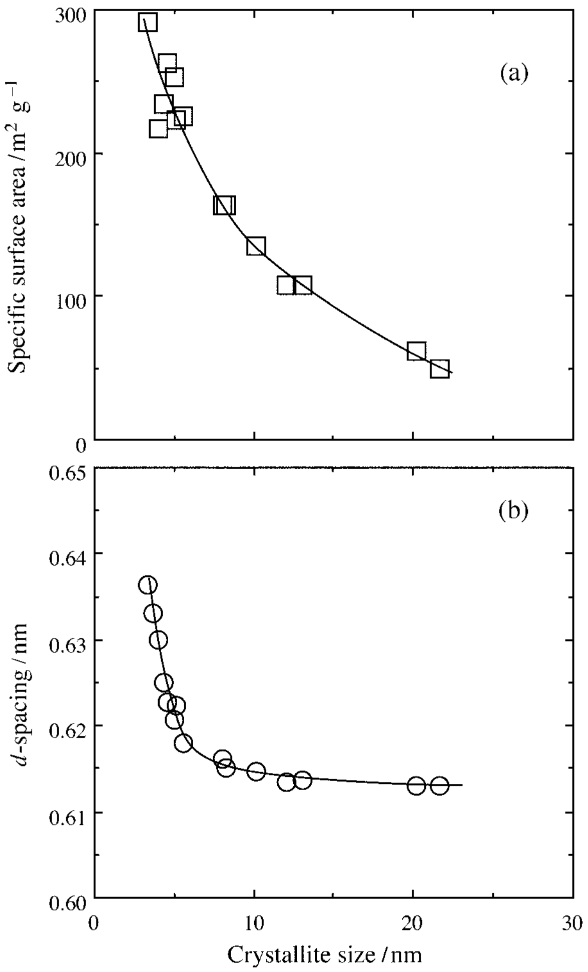

Fig. 1 Relationships between specific surface area and crystallite size (a), and d-spacing and crystallite size (b).

bility in alkaline solution at higher temperature could promote crystallite growth by a dissolution–reprecipitation mechanism by comparison with the lower solubility in acidic solution at higher temperatures.

Excess water in boehmite and γ-Al_2O_3

Two models have been reported to explain the excess water in boehmite; surface water adsorbed on the particles and interlayer water in the crystal structure of boehmite.[6] Several reports have mentioned the presence of water or OH groups in the crystal structure of transition aluminas.[14–16] Soled[17]

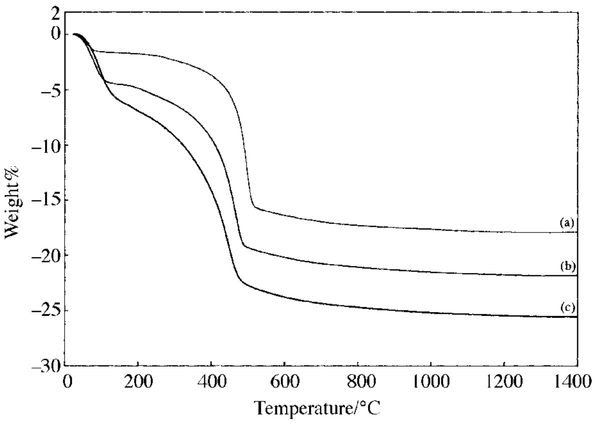

Fig. 2 TG profiles for several boehmite samples with crystallite size of 21.6 (a), 10.1 (b), and 4.6 nm (c).

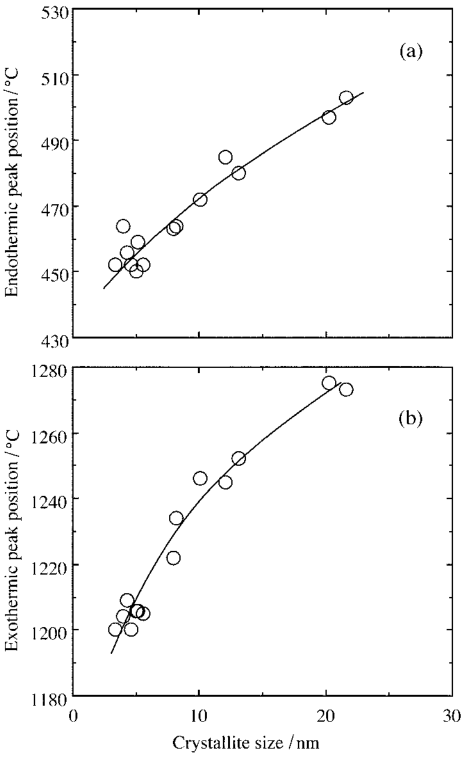

Fig. 3 Relationships between phase transition temperature to γ-Al_2O_3 and crystallite size (a), and phase transition temperature to α-Al_2O_3 and crystallite size (b).

postulated that transition alumina contains OH groups which compensate the cation vacancy in the spinel structure: $Al_{2.5}\square_{0.5}O_{3.5}(OH)_{0.5}$ or $Al_2\square_{0.4}O_{2.8}(OH)_{0.4}$ where, □ represents a vacancy. Burtin *et al.* later extended the formula as follows:[18] $[Al_2\square][O_{3-v/2}(OH)_v\square_{1-v/2}]$.

When $v=0$, the formula contains no OH and this corresponds to α-Al_2O_3. When $v=2$, there are no oxygen defects, and the formula corresponds to boehmite.

We now modify the formula so as to relate the weight loss on heating derived from the TG profile to the content of adsorbed water and hydroxy groups of heated boehmite as follows:

$Al_2O_2(OH)_2\cdot(m+n)H_2O$ $(v=2)$

↓ *ca.* 100 °C corresponding to desorption of adsorbed water

$Al_2O_2(OH)_2\cdot mH_2O+nH_2O$ $(v=2)$

↓ 100–350 °C corresponding to dehydration of

interlayer or surface water

$Al_2O_2(OH)_2+mH_2O$ $(v=2)$

↓ *ca.* 500 °C corresponding to formation of γ-Al_2O_3

$Al_2O_{3-v/2}(OH)_v+(2-v)/2\ H_2O$ $(0<v<2)$

↓ *ca.* 500–1200 °C corresponding to dehydration

of γ-Al_2O_3 and transformation *via* θ- to α-Al_2O_3

$Al_2O_3+v/2\ H_2O$

Here v is the number of hydroxy groups contained in γ-alumina, m is the number of interlayer or surface water molecules of boehmite, and n is the number of adsorbed water molecules on the boehmite particles. In the present work, we assume that boehmite contains adsorbed water, interlayer or surface water, and two types of hydroxy groups, one of which dehydrates during the conversion of boehmite to γ-Al_2O_3 at around 500 °C, and one of which remains in γ-Al_2O_3, being gradually lost on heating. The adsorbed water can be defined as being easily desorbed around 100 °C, and the interlayer or surface water dehydrates before conversion to γ-Al_2O_3 on heating. The TG and DTA profiles are shown in Fig. 4. The adsorbed water content, n, is calculated from the weight loss between room temperature and the temperature of the end point of the endothermic reaction at around 100 °C in the TG and DTA profile (region A). Similarly the content of interlayer or surface water of boehmite, m, is calculated from the weight loss between the temperature of the end point of the endothermic reaction at around 100 °C and the temperature of the end point of the endothermic reaction at around 500 °C (region B), assuming the molar ratio of Al/OH in boehmite is one. Finally the hydroxy content in γ-Al_2O_3, v, is calculated from the weight loss between the temperature of the end point of the endothermic reaction around 500 °C and the temperature just before the starting point of the exothermic reaction at around 1200 °C (region C). All the values of v, m and n tend to decrease with higher hydrothermal temperature, as shown in Fig. 5. From these data, the excess water in boehmite and the residual OH content in the γ-Al_2O_3 can be related to the crystallinity of the precursor boehmite.

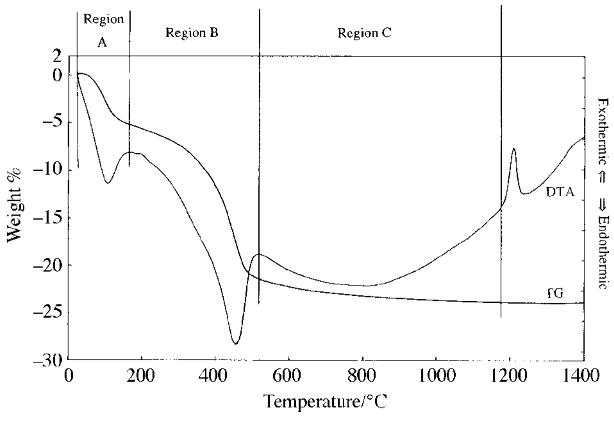

Fig. 4 TG–DTA revealing the presence of several types of water and OH groups.

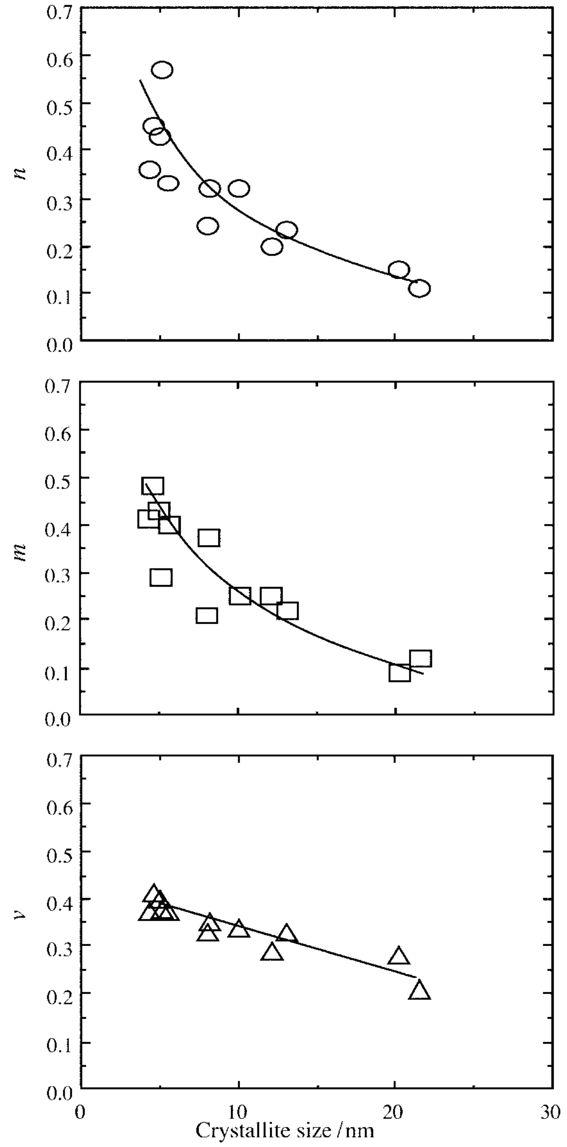

Fig. 5 Water and OH group content of boehmite and γ-Al_2O_3: n and m, numbers of weakly adsorbed water on boehmite and interlayer or surface water of boehmite, respectively, for $Al_2O_2(OH)_2\cdot(m+n)H_2O$: v; number of OH groups in γ-Al_2O_3 for $Al_2O_{(3-v/2)}(OH)_v$.

Thermal stability of boehmite and γ-Al_2O_3

The formation temperature of γ-Al_2O_3 from boehmite increases with increasing crystallite size as shown in Fig. 3. This result is in good agreement with several reports.[6,7,18,19] According to the kinetic study of γ-Al_2O_3 formation by Tsuchida *et al.* the mechanism depends on the crystallite size of the boehmite, being nucleation controlled in large crystallites, phase-boundary controlled in medium-sized crystallites, and diffusion controlled in small crystallites.[19] The conversion from boehmite to γ-Al_2O_3 includes dehydration. The crystal structure of boehmite consists of Al–O octahedral double layers, which are connected by hydrogen bonds.[6,10] The dehydration path inside the boehmite structure is therefore believed to be along the *ac* plane. In large crystallites of boehmite, this path becomes longer and the interlayer spacing is narrow. Dehydration occurs slowly and suppresses the conversion of boehmite to γ-Al_2O_3, elevating the formation temperature of γ-Al_2O_3

As shown in Fig. 3, the phase transition temperature from θ- to α-Al_2O_3 increases with increasing crystallite size of the precursor boehmite. Many studies indicate the transition of θ- to α-Al_2O_3 occurs by a nucleation and growth mechanism.[20] The content of residual OH groups in γ-Al_2O_3 is believed to increase as the crystallinity of boehmite decreases, according to the TG results. This is compatible with the fact that boehmite converts topotactically to γ-Al_2O_3. The transition of γ- to θ-Al_2O_3 does not require a reconstructive recrystallization process because of the similar cubic close-packed oxygen sublattice.[10] The order of the structure increases by alignment and merging of the lamellae and the stacking faults in the [111] direction; and by diffusion of the surface Al ions to more ordered sites.[16] Combining these ideas, the crystallinity of the boehmite can be related to the crystallinity of the resulting γ- and of θ-Al_2O_3. Thus, the reconstruction of the cubic close-packed to a hexagonal oxygen sublattice during the transition from θ- to α-Al_2O_3 should be easier and occur at a lower temperature in a transition alumina of lower crystallinity.

The results obtained in the present work on the thermal stability of γ-Al_2O_3 are in good agreement with Burtin *et al.* but are different from those of Tsuchida *et al.* (1980)[18,19] Burtin *et al.* reported that the conversion rate to α-Al_2O_3 at 1373 K is related to the surface area of the transition aluminas. Tsuchida *et al.* reported that higher hydrothermal temperatures lead to a lower exothermic peak temperature for the α-phase transition. It is known that many factors influence the transformation from γ- to α-Al_2O_3, including impurities,[21–23] seeding material,[24–28] and microstructure.[29] Since the precursor boehmite used in the present work was of high purity, the effect of impurities should be minimal. Since the pore volumes were almost the same and pore size changes are proportional to the crystallite size, packing and agglomeration of the boehmite grains is believed to remain similar after crystal growth. Tsuchida *et al.* prepared boehmite powder from bayerite under various hydrothermal conditions at a temperature of 150–300 °C, and their specific surface areas range from 17 to 110 $m^2\,g^{-1}$. Therefore, their different result is suggested to be due to the difference in impurity levels and microstructure of the boehmite powders prepared from different precursors.

Conclusions

The crystallinity of boehmite can be changed by changing the hydrothermal treatment conditions of pseudoboehmite. There are clear correlations between the crystallite size, *d*-spacing and specific surface areas of these samples. The crystallite size of the boehmite could be related to its water content and to the OH content in the resulting γ-alumina. A clear relationship of increasing γ- to α-Al_2O_3 transition temperature with higher boehmite crystallinity was also found. The TG analysis showed larger amounts of weakly and strongly bounded water in boehmite of lower crystallinity. Larger amounts of residual OH groups were observed in γ-Al_2O_3 of lower crystallinity derived from less-crystalline boehmite. These results indicate that less-crystalline boehmite produces less-crystalline γ-Al_2O_3 which transforms to θ-Al_2O_3 also of lower crystallinity. The reconstruction of the cubic to hexagonal close-packed oxygen sublattice during the transition from θ- to α-Al_2O_3 is likely to be easier at a lower temperature for transition aluminas of lower crystallinity.

Acknowledgment

The authors are grateful to Dr K. J. D. Mackenzie of New Zealand Institute for Industrial Research and Development for proof reading this manuscript.

References

1 J. H. DeBoer and B. C. Lippens, *J. Catal.*, 1964, **3**, 38.
2 H. Knozinger and P. Ratnasamy, *Catal. Rev.-Sci. Eng.*, 1978, **17**, 31.
3 A. B. Stiles, *Catalyst Supports and Supported Catalysts*, Butterworths, London, 1987.
4 F. W. Dynys and J. W. Halloran, in *Ultrastructure Processing of Ceramics, Glasses, and Composites*, ed. L. L. Hench and D. R. Ulrich, John Wiley and Sons, New York, 1984, p. 142.
5 D. L. Clark and J. J. Lannutti, in *Ultrastructure Processing of Ceramics, Glasses, and Composites*, ed. L. L. Hench and D. R. Ulrich, John Wiley and Sons, New York, 1984, p. 126.
6 K. Wefers and C. Misra, *Oxide and Hydroxide of Aluminum*, Alcoa Technical Paper No.19, Alcoa Laboratories, Pittsburgh, PA, 1987.
7 R. D. Tottenhorst and D. A. Hofmann, *Clays Clay Miner.*, 1980, **28**, 373.
8 B. E. Yoldas, *J. Am. Ceram. Soc.*, 1982, **65**, 387.
9 S. J. Wilson, *J. Br. Ceram. Soc.*, 1979, **28**, 281.
10 B. C. Lippens and J. H. D. Boer, *Acta. Crystallogr.*, 1964, **17**, 1312.
11 C. F. J. Baes and R. E. Mesmer, *The Hydrolysis of Cations*, John Wiley and Sons, New York, London, Sydney, Toronto, 1976.
12 T. Tsukada, T. Saito, H. Segawa, A. Yasumori and K. Okada, *J. Ceram. Soc. Jpn.*, submitted.
13 S. Castet, J. Dandurand, J. Schotte and R. Gout, *Geochim. Cosmochim. Acta*, 1993, **57**, 4869.
14 H. Yanagida and G. Yamaguchi, *Bull. Chem. Soc. Jpn.*, 1964, **37**, 1229.
15 H. Yanagida, G. Yamaguchi and J. Kubota, *Bull. Chem. Soc. Jpn.*, 1965, **38**, 2194.
16 R. Zhou and R. L. Snyder, *Acta Crystallogr.*, *Sect. B*, 1991, **47**, 617.
17 S. Soled, *J. Catal.*, 1983, **81**, 252.
18 P. Burtin, J. P. Brunelle, M. Pijolat and M. Soustelle, *Appl. Catal.*, 1987, **34**, 239.
19 T. Tsuchida, R. Furuich and T. Ishii, *Thermochim. Acta*, 1980, **39**, 103.
20 H. Schaper and L. L. Van Reijen, *Thermochim. Acta*, 1984, **77**, 383.
21 B. E. Yoldas, *J. Mater. Sci.*, 1976, **11**, 465.
22 M. Pijolat, M. Dauzat and M. Soustelle, *Thermochim. Acta*, 1987, **122**, 71.
23 Y. Saito, T. Takei, S. Hayashi, A. Yasumori and K. Okada, *J. Am. Ceram. Soc.*, 1998, **81**, 2197.
24 M. Kumagai and G. L. Messing, *J. Am. Ceram. Soc.*, 1984, **67**, C230.
25 J. L. McArdle and G. L. Messing, *Adv. Ceram. Mater.*, 1988, **3**, 387.
26 R. A. Shellmann and G. L. Messing, *J. Am. Ceram. Soc.*, 1988, **71**, 317.
27 J. L. McArdle and G. L. Messing, *J. Am. Ceram. Soc.*, 1989, **72**, 864.
28 S. Jagota and R. Raj, *J. Mater. Sci.*, 1992, **27**, 2251.
29 T. Horiuchi, T. Osaki, T. Sugiyama, H. Masuda, M. Horio, K. Suzuki, T. Mori and T. Sago, *J. Chem. Soc.*, *Faraday Trans.*, 1994, **90**, 2573.

Paper 8/06728G