

Relation among the Aggregation of Boehmite Particles in Sols, Microstructure of Gels, and Crystallization of Corundum

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Aggregation of boehmite particles in sols was studied by dynamic light scattering and corresponding gels were examined by DTA, XRD, BET, SEM, and TEM. Commercial Condea boehmite particles of the size 3–5 nm aggregated in sols into fibres. An aggregation and deaggregation was a reversible process. Fibres were disintegrated during drying, but the repulsive forces between particles oriented them into characteristic microstructures. These microstructures were less dependent on the composition of sols. Similarly, nucleation density of α -Al₂O₃ increased slightly (from $N = 6.1 \times 10^8$ to 3.1×10^9 cm⁻³) with the content of boehmite in sols from 10.0 and 14.7 mass %, respectively.

Boehmite, contrary to other oxide compounds of aluminium, is easily available in the form of nanometer-sized particles. Usually it is prepared from Al alkoxides [1, 2] and for large scale application it comes from the synthesis of higher alcohols (e.g. Condea or Capatal) as a by-product. Boehmite, however, is not generally suitable for the production of bulk α -alumina ceramics. Strong aggregates of boehmite particles are a main obstacle for shaping by dry pressing. For colloidal processing, the disadvantage is the large volume changes during drying and sintering [3] and the difficult nucleation of the α -Al₂O₃ phase [4].

Boehmite, on the other hand, is the most important precursor for γ -Al₂O₃ phase for the applications such as catalysts supports [5] or functional layers of ceramic membranes [6].

The above-mentioned large volume changes of boehmite gels during the heat treatment are linked to the properties of boehmite particles in water, which limits the content of boehmite in peptized sol to 18–20 mass % [7, 8]. So the formed gel microstructure has then specific relationship to the difficult nucleation of α -Al₂O₃ [8, 9]. Due to low nucleation density of α -Al₂O₃ ($\approx 10^8$ cm⁻³), sintering leads to the vermicular microstructure with high porosity (≈ 25 vol. %) and low strength [10]. This problem was effectively solved by seeding of gels

by α -Al₂O₃, α -Fe₂O₃ or Fe(NO₃)₃, [7–12] allowing thus the transformation of transition alumina phases to α -Al₂O₃ to occur at a reasonable rate at lower temperatures. Sol-gel technology of α -Al₂O₃ abrasive grains production is based on this principle [13].

Nucleation density of α -Al₂O₃ in unseeded boehmite gel $\approx 10^8$ cm⁻³ is enhanced by seeding to the level from 10^{12} to 10^{14} cm⁻³ [7–12]. Nucleation density of unseeded gels is given by number of nucleation sites [7–14]. The stability of the microstructure, from the viewpoint of nucleation, is demonstrated by the fact that the same nucleation density $\approx 10^8$ cm⁻³ is reported by several authors (Kumagai and Messing [15], Dynys and Halloran [16]) and it cannot be influenced by heat treatment.

Microstructure of gels is a result of mechanism of particles aggregation and formation of particle network in gel and of its drying process. Aggregation of particles in water depends on the shape and size of particles and the pH, which determines attractive and repulsive forces. Aggregation of boehmite particles at hydrothermal condition as reported by Buining *et al.* [17, 18] leads to the formation of relatively long (25–400 nm) polycrystalline fibres with aspect ratio 2.7–14.5. Elongated hexagonal boehmite plates are connected by the edge planes of crystals.

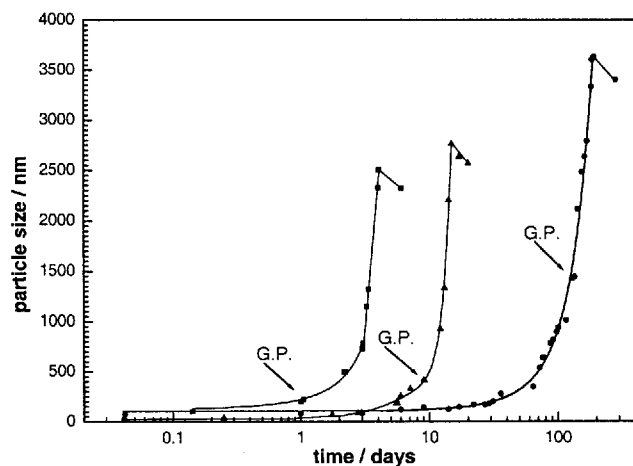


Fig. 1. Change in particle size with aging time for various content of boehmite in sols (10.0 (•), 13.0 (▲), and 14.7 (■) mass %), G. P. – gel point.

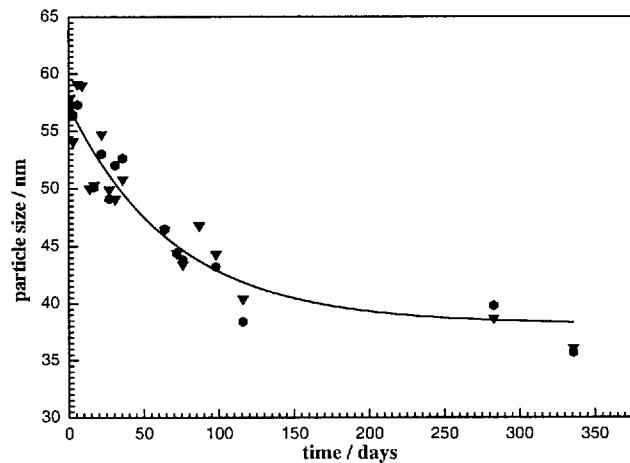


Fig. 2. Variation in particle size with aging time for diluted boehmite sols (2.5 (▼) and 5.0 (●) mass %).

The aim of this work is to investigate the aggregation of peptized boehmite particles in water at $\text{pH} \approx 2.5$ as a function of concentration and time. The relationship between their aggregation, resulting microstructure, and crystallization of $\alpha\text{-Al}_2\text{O}_3$ was also studied.

EXPERIMENTAL

The boehmite sol used in this work was prepared from commercial boehmite (Condea Pural SB-1), using the procedure described in [8, 14]. Water boehmite suspension (15 mass %) was peptized by mixing it with HNO_3 ($\text{pH} \approx 2.5$) at 55°C . Unpeptized part of boehmite (≈ 2 mass %) was removed from the sol by centrifugation ($10\,000\text{ min}^{-1}$). Obtained sol was softly turbid, transparent colloidal solution. Sols of chosen content

of boehmite (14.7, 5.0, and 2.5 mass %) were prepared either directly as described or by dilution (13.0, 10.0, 5.0, and 2.5 mass %) of the most concentrated solution (14.7 mass %). Aggregation of boehmite particles at 25°C in closed vessel was studied by dynamic-elastic light scattering using the Brookhaven Instrument BI-200SM goniometry system with argon ion laser. The autocorrelation function was measured using a BI-2030AT digital correlator. Particle diameters were determined by the second-order cumulative analysis [19]. The gel point was determined visually as a moment when sols lost their fluidity.

Thermal analyses (DTA, TGA) of dried crushed (0.8–1.0 mm) gel grains were carried out in air at a heating rate of $10^\circ\text{C min}^{-1}$ in the temperature range of $25\text{--}1250^\circ\text{C}$, using derivatograph, type 3427. The sur-

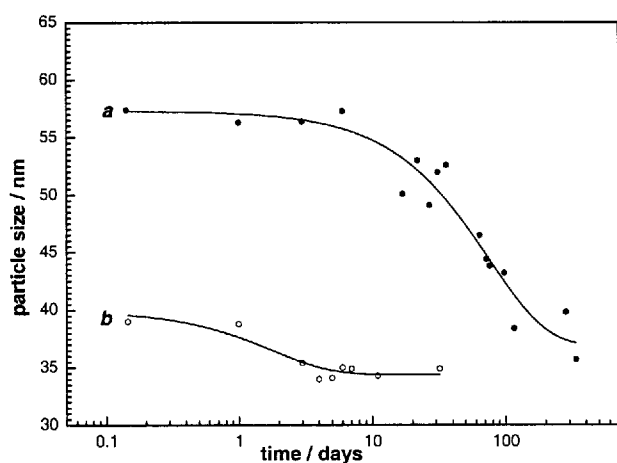


Fig. 3. Variation in particle size with aging time for 5 mass % boehmite sol: a) boehmite sol obtained by dilution of freshly prepared 14.7 mass % sol, b) boehmite sol prepared directly.

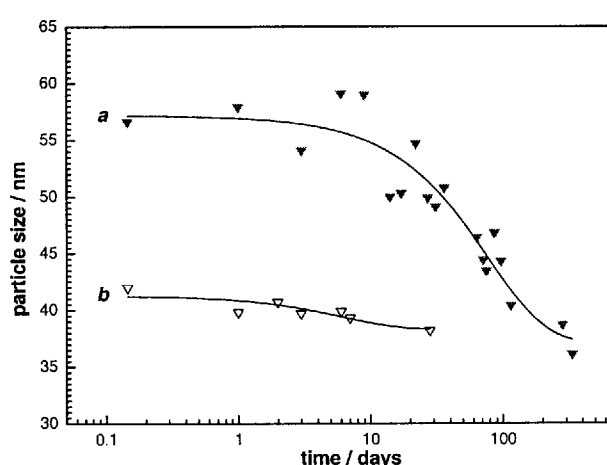


Fig. 4. Variation in particle size with aging time for 2.5 mass % boehmite sol: a) boehmite sol obtained by dilution of freshly prepared 14.7 mass % sol, b) boehmite sol prepared directly.

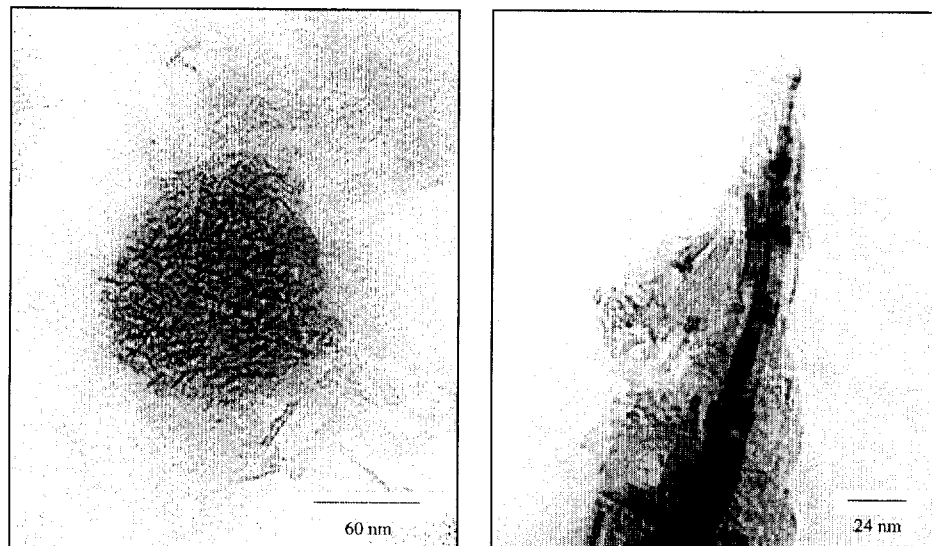


Fig. 5. TEM micrographs of boehmite crystals and their aggregates.

face area and the pore size distribution were measured by N_2 adsorption and desorption isotherms (BET) using Sorptomatic 1900 (Erba, Milan). The size of boehmite particles and microstructure of the gel were observed by TEM (ATEM 2000FX). The microstructures of the sintered samples were analyzed by SEM (Tesla BS 300). Bulk density of the sintered samples was measured by the Archimedes method.

RESULTS

The size of boehmite particle aggregates depends on the aging time and the composition of the sols (Figs. 1–4). All studied contents of boehmite in the sols (2.5, 5.0, 10.0, 13.0, and 14.7 mass %) were prepared by dilution of the most concentrated one (14.7 mass %). According to the growth of aggregates, sols can be divided into two groups. In more concentrated sols (10 mass % and more) aggregation takes place and in the less concentrated (2.5 and 5.0 mass %), on the contrary, deaggregation (peptization) occurs. There should be a defined content of boehmite in the sols at which the size of aggregates is stable for a long time.

The size of aggregates *vs.* time changes similarly for all observed sols (Fig. 1). The exponential growth of aggregates beyond of the gel point (GP) is caused by the aggregation of aggregates, *i.e.* multiple aggregations. The size of aggregates at a gelling point increases with decreasing content of boehmite in the colloidal solution. The growth of aggregates continued at the gel point. One part ($\approx 1/3$) [3] of aggregates is fixed into primary network of particles, but most of them can grow further in the limited areas. This tendency continues to a maximal size of aggregates and then, as larger aggregates are linked to the network, decrease of the size of free aggregates and free volume for motion of aggregates begins.

Continuous decrease of the size of aggregates is observed in the sols of 5.0 and 2.5 mass % of boehmite ob-

tained by dilution of freshly prepared 14.7 mass % sol (Fig. 2). The size of aggregates is after 300 d stabilized on a level of ≈ 35 nm in both cases. If sols of the content 5.0 and 2.5 mass % are prepared directly (Figs. 3 and 4), the size of aggregates is about 40 nm and changes slightly with aging time on the level of ≈ 35 nm after 20 d.

TEM micrographs (Fig. 5) of aggregates and gels show the individual particles of a size about 3–5 nm with nearly isometric shape and only with indication of edges. The rest of ordering of particles into fibres is evident also in the dry thin layers. Fineness of boehmite crystals observed by TEM is in agreement with broad XRD diffraction peaks of studied boehmite and respective $\gamma\text{-Al}_2\text{O}_3$ phase (Fig. 6).

Observed homogeneity of gels (Fig. 5) is in agreement also with their measured specific surface area

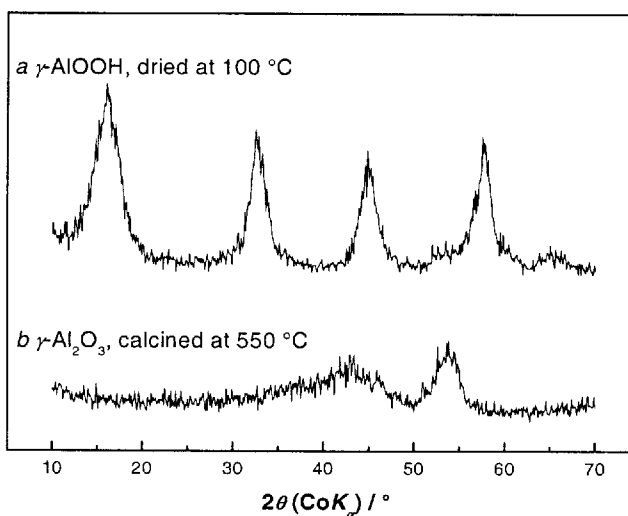


Fig. 6. XRD patterns of boehmite gels *a*) dried at 100 °C, *b*) calcined at 550 °C for 1 h, heating rate 10 °C min^{-1} .

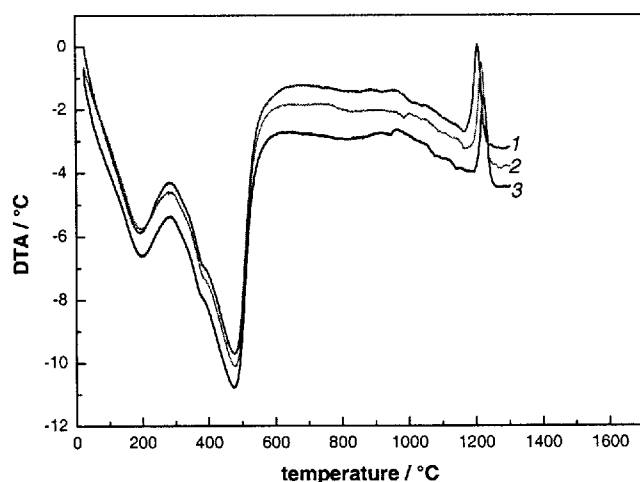


Fig. 7. DTA curves of boehmite gels (10.0 (3), 13.0 (2), and 14.7 (1) mass %) dried at 100 °C, heating rate 10 °C min⁻¹, atmosphere: air.

($\approx 250 \text{ m}^2 \text{ g}^{-1}$) and porosity. High porosity of gel ($\approx 43 \text{ vol. } \%$) is represented nearly by monomodal pores of the diameter $\approx 4 \text{ nm}$. Specific surface areas and parameters of pores are practically independent of the concentration of boehmite in original sols.

DTA patterns (Fig. 7) show only a small decrease of $\alpha\text{-Al}_2\text{O}_3$ crystallization temperatures (maximum of exothermic peaks) with composition of sols, *i.e.* that nucleation density of $\alpha\text{-Al}_2\text{O}_3$ increases a bit with concentration of boehmite in the original sols (Table 1).

Table 1. Bulk Density ρ after Sintering (1225 °C, 10 °C min⁻¹, without holding time), Relative Density ρ_r , Mean Size of Crystals L , and Nucleation Density N in Dependence on Boehmite (w_B) Content in Sols

w_B mass %	ρ g cm ⁻³	ρ_r g cm ⁻³	L μm	N cm ⁻³
10.0	3.27	81.95	11.96	6.1×10^8
13.0	3.29	82.25	9.95	1.0×10^9
14.7	3.35	83.96	6.96	3.1×10^9

Table 2. Content of Boehmite in Mass % and Vol. % in Sols and Time of Gelation

w_B mass %	φ_B vol. %	Gelation time
2.5	0.08	–
5.0	1.72	–
10.0	3.56	150 d
13.0	4.73	9 d

Direct measurements of nucleation density (Table 2) by counting of monocrystal colonies [16] per plane unit of fracture surfaces (Fig. 8) and recalculating the results per volume unit and bulk densities of samples support former results, both manifesting a little increase with the content of boehmite in sols.

In order to make the clarification of the mechanism of aggregation of boehmite particles in aqueous solution more reliable, it is important to know the proper volume of particles in sols or the skeletal volume of boehmite particles in the gel. This volume is calculated (Table 2) on the basis of boehmite density (3.01 g cm^{-3}) and content of boehmite in sols.

DISCUSSION

Boehmite sols of the 2.5 and 5.0 mass % content are probably infinitely stable in time, because they did not change their viscosity and the size of aggregates ($\approx 35 \text{ nm}$) during two years. The next of the examined sols with 10 mass % of boehmite content turned to a gel after 150 d. If we realize that this colloidal solution contains only 3.6 vol. % of boehmite particles, it is difficult to imagine the formation of gel by other way than by linking of fibrous aggregates of boehmite particles together. Fibre-likeness of aggregates is evident from TEM (Fig. 5) pictures. However, the strength of fibres is very low and they are easily destroyed during drying of gels. Primary aggregates formed in solutions by linking of individual particles should be exclusively fibre-like, because at so low solid volume content ($\approx 3.6 \text{ vol. } \%$) of boehmite, isometric aggregates would be led to flocculation and sedimentation. Fractal character with very low fractal dimension could be assumed already at aggregation of aggregates, *i.e.* multiple aggregation.

Formation of fibres from boehmite particles demonstrates the existence of attractive and repulsive sites on particles resulting in an identical orientation of particles in one direction. Mechanism of boehmite particle aggregation is governed by the surface properties of small boehmite crystals.

Raybaud et al. [20] recently published calculated (based on the density–function theory) surface properties of nanosized boehmite particles in water. Four different surface—OH groups on the four relevant crystallographic planes (010), (100), (001), and (101) with different surface-water interfacial energies were identified. The energy density is significantly lower for basal (010) planes (465 mJ m^{-2}) representing 67 % of the particle surface, than for the edge planes (650 mJ m^{-2} (hkl 100), 750 mJ m^{-2} (hkl 001), and 825 mJ m^{-2} (hkl 101)). —OH groups of edge planes are more reactive due to the high interface energies and they are the most preferable places for interparticle interaction. At used experimental conditions (pH = 3.3) all —OH groups are protonized to OH_2^+ . As properties of —OH are not the same, the same is true for OH_2^+ groups.

From the viewpoint of —OH groups, crystallographic planes differ by their frequency occurrence and prop-

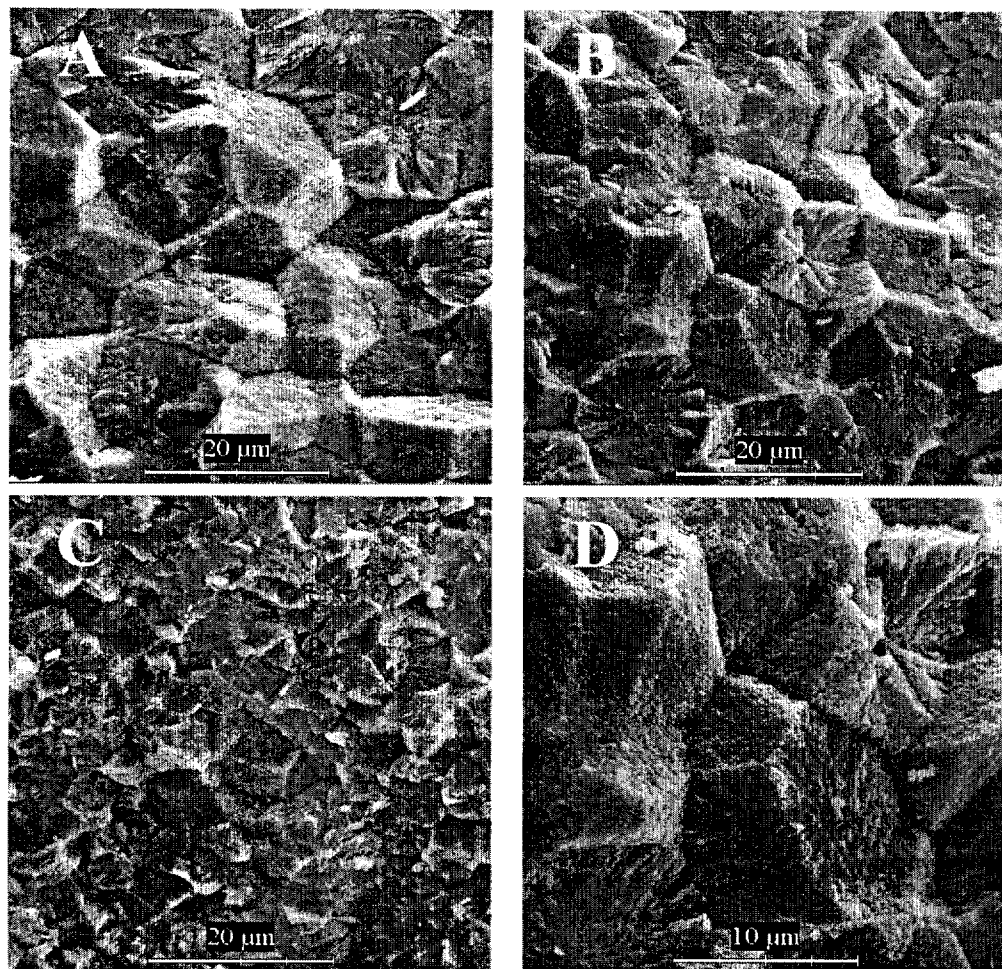


Fig. 8. SEM micrographs of the fracture surface of sintered (1250 °C, heating rate 10 °C min⁻¹ without holding time) samples: (A) 10.0 mass %, (B) and (D) 13.0 mass %, (C) 14.7 mass % of boehmite in original sols.

erties. This means that there are preferential sites for attraction and others for repulsion and then they are oppositely localized (uniformly *hkl*) as pairs. These localized attractive forces between particles associate uniformly oriented particles into fibre-like polycrystalline structures, as already observed under hydrothermal conditions by several authors [17, 18, 21]. These forces act further at drying of gel as long as the system contains liquid phase. Capillary forces control shrinkage of gels and the orientation of particles is a result of attractive and repulsive forces to minimize the free surface energy of the system. These processes result in stable microstructures with nearly monomial size of pores ≈ 4 nm dependent weakly on original composition of the sols. The size of these pores is similar to that of primary boehmite crystals. In such arrangement of particles, the coordination number of particles is defined and it does not change during heat treatment and therefore the nucleation density of α -Al₂O₃ is so stabilized.

The nucleation density may depend on properties of used boehmite and also on gelation process. If sols were

allowed to gel freely by aging in atmosphere, what is reported mostly in literature, it is difficult to remark weak effect of concentration of sols on nucleation density. In the present case, sols gelled in closed boxes without evaporation. It allowed us to observe slight effect of boehmite content in sols on α -Al₂O₃ nucleation density.

CONCLUSION

The size of studied boehmite particles is according to the TEM observation in the range from 3 to 5 nm.

Peptized (HNO₃, pH \approx 2.5) boehmite particles undergo aggregation and gelation in dependence on the sol composition. The size of aggregates grows and gelation time increases (14.7 mass %/8 h, 10.0 mass %/150 d) with the decrease of the boehmite content in sols.

Aggregation is a reversible process, deaggregation is observed at dilution of sols. Low concentrated sols (≤ 5 mass %) are stable more than two years.

Boehmite particles show preferential orientation at gelation resulting in fibre-like aggregates. Particles have preferential planes (edge planes) for the attraction (aggregation) and the other ones (based planes) for repulsion.

Due to weak attraction forces, fibre-like oriented structures are destroyed during drying of gels. The attractive and repulsive forces are still active at reorganization of particles into stable microstructure.

Microstructure, nucleation density of α -Al₂O₃, bulk density of sintered sample depends slightly on the content of boehmite in original sols.

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REFERENCES

1. Yoldas, B. E., *Am. Ceram. Soc. Bull.* 59, 479 (1980).
2. Leenaars, A. F. M., Keizer, K., and Burggraaf, A. J., *J. Mater. Sci.* 19, 1077 (1984).
3. Brinker, C. J. and Scherer, G. W., *Sol-Gel Science*. Chap. 7, 9, and 5. Academic Press, New York, 1990.
4. Wilson, S. J., *Proc. Br. Ceram. Soc.* 28, 281 (1979).
5. Poisson, R., Nortier, P., and Brunelle, J. P., in *Catalysts and Supported Catalysts*. (Stiles, A. B., Editor.) Pp. 11–55. Butterworths, Boston, 1987.
6. Burggraaf, A. J. and Cot, L., in *Fundamentals of Inorganic Membrane Science and Technology*. Chap. 7. Elsevier Science B. V., Amsterdam, 1996.
7. Shelleman, R. A., Messing, G. L., and Kumagai, M., *J. Non-Cryst. Solids* 82, 277 (1986).
8. Pach, L., Roy, R., and Komarneni, S., *J. Mater. Res.* 5, 278 (1990).
9. Suwa, Y., Komarneni, S., and Roy, R., *J. Mater. Sci. Lett.* 5, 21 (1986).
10. Huling, J. C. and Messing, G. L., *J. Am. Ceram. Soc.* 71, C-222 (1988).
11. Kákoš, J., Bača, L., Veis, P., and Pach, L., *J. Sol-Gel Sci. Technol.* 21, 67 (2001).
12. Pach, L., Bača, L., Holková, Z., and Plewa, J., *J. Porous Mater.* 9, 17 (2002).
13. Monroe, D. L. and Wood, P. W., *Eur.* 0228856 (1986).
14. Pach, L., Kovalík, Š., Majling, J., and Kozánková, J., *J. Eur. Ceram. Soc.* 12, 249 (1993).
15. Kumagai, M. and Messing, G. L., *J. Am. Ceram. Soc.* 68, 500 (1985).
16. Dynys, F. W. and Halloran, F. W., *J. Am. Ceram. Soc.* 65, 442 (1984).
17. Buining, P. A., Pathmamanoharan, Ch., Bosboom, M., Jansen, J. B. H., and Lekkerkerker, H. N. W., *J. Am. Ceram. Soc.* 73, 2385 (1990).
18. Buining, P. A., Pathmamanoharan, Ch., Jansen, J. B. H., and Lekkerkerker, H. N. W., *J. Am. Ceram. Soc.* 76, 1303 (1991).
19. Koppel, D. E., *J. Chem. Phys.* 57, 4814 (1972).
20. Raybaud, P., Digne, M., Iftimie, R., Wellens, W., Euzen, P., and Toulhoat, H., *J. Catal.* 201, 236 (2001).
21. Furuta, S., Katsuki, H., and Takagi, H., *J. Mater. Sci. Lett.* 13, 1077 (1994).