Journal of the European Ceramic Society 23 (2003) 659–666

www.elsevier.com/locate/jeurceramsoc

A critical role of pH in the colloidal synthesis and phase transformation of nano size α-Al_2O_3 with high surface area

Pramod K. Sharma*, V.V. Varadan, V.K. Varadan

Center for Engineering of Electronics of Acoustic Materials, 212 Earth and Engineering Science Building,
The Pennsylvania State University, University Park, PA 16802, USA

Received 5 November 2001; received in revised form 10 May 2002; accepted 25 May 2002

Abstract

This paper demonstrates the critical role of pH in the colloidal (i.e. sol-gel) synthesis of nano size α-Al_2O_3. Investigation, based on X-ray diffraction pattern, indicates that the transformation of α-Al_2O_3 from gels obtained at high $pH \geqslant 7$, undergoes via formation of boehmite (gel$\rightarrow$AlOOH$\rightarrow\gamma$-$Al_2O_3\rightarrow\alpha$-Al_2O_3). On the other hand, the transformation of α-Al_2O_3 at low pH ($\leqslant 6$) follows the gel$\rightarrow\gamma$-Al_2O_3 $\rightarrow\alpha$-Al_2O_3 sequence. The transmission electron microscopy reveals that the particle size of the α-Al_2O_3 decreases from $\approx$750 to $\approx$70 nm with decreasing pH from 12 to 2.5, respectively. The α-Al_2O_3 with large surface area ($\approx$130 m^2/g) is obtained when it is processed at low pH (2.5). The true powder density of the α-Al_2O_3 sample derived at $pH = 2.5$ is observed to be 3.92 g/cm^3 after sintering at 1450 °C, due to fine particles. The isoelectric point (iep) and ξ of the α-Al_2O_3 are found to be 8.7 and 9.2 when synthesized at pH 2.5 and 12, respectively.

Keywords: Al_2O_3; Powders-chemical preparation; Seeding; Sol–gel methods

1. Introduction

The Al_2O_3 exists in several distinct crystallographic phases (such as γ, δ, θ, α-Al_2O_3), and it can undergo a variety of transitions until the most stable corundum structure α-Al_2O_3 forms at high temperature.[1–2–3] α-Al_2O_3 is a ceramic material of industrial importance, due to its promising structural, chemical, and morphological properties.[1] Traditional method of fabricating α-Al_2O_3 includes direct sintering of the transitional alumina phases. This method requires very high temperature, which inevitably results in a considerable degree of particle coarsening with small surface area. Several wet chemical methods have been employed to synthesize the α-Al_2O_3 at low temperature. Bell et al. has reported a hydrothermal method for the fabrication of α-Al_2O_3, using 1,4-butanediol and has demonstrated how to control the particles size and morphology.[4] Additionally, the concept of seeding with α-alumina has also been employed in order to enhance the kinetics of transformation and to achieve the synthesis of α-alumina at a lower temperature. A fraction of ultrafine alumina crystallites, as seed materials, and the introduction of dopant (e.g. MnO_2) were tried by Messing and Gouvea, respectively, in order to reduce the temperature of transformation of stable alumina.[3,5] Sharma et al. has crystallized the α-Al_2O_3,which has a median particle size 60 nm, by hydrothermal method using a surface modifier.[6] Nevertheless, the colloidal method, using sol-gel processing, is another chemical approach that provides an alternative route to synthesis of α-Al_2O_3. In order to utilize chemical process for synthesis of nano sized powder, the control over thermodynamics of interfaces with in the reacting system has to be required as these fine particulate system tend to minimize their surface energy either by growing to large particles or agglomeration. One approach is to modify the surface of growing particles during precipitation process in a way that growth reaction can take place but a ‘‘growing together’’ is prevented. The surface free energy of these particulate can reduced to an appropriate level by using surface active compound (so called ‘‘surface modifier’’) which interact with the generated particle surface. The synthesis of pure alumina materials via organic or inorganic sol-gel method has been extensively studied over the past three decades. Yoldas has

---

* Corresponding author. Tel.: +1-814-865-0663; fax: +1-814-863-7967.

E-mail address: pk7@psu.edu (P.K. Sharma).

PII: S0955-2219(02)00191-7

carried out investigations on the hydrolysis of aluminum isopropoxide in the presence of various inorganic and organic acids as peptides.[7,8] The use of chelating agents has also been employed to control the hydrolysis and condensation rates during the sol-gel processing of alumina with desired physicochemical properties.[9] A number of papers discuss the effect of pH during the sol-gel process on pore size, pore volume, particle size, and surface area of SiO_2, Y_2O_3, TiO_2.[10,11] Rao and Ji have discussed the role of pH during the sol-gel processing of alumina. However, they did not mention the variation in particle size of the alumina with pH change.[9,12] Nevertheless, the surface area of the alumina reported in their investigations was <56 m^2/g. From the perspective of developing alumina based high temperature stable catalyst, high surface area of α-Al_2O_3 is very important. In recent years, the nanophase metal oxides, because of their fine particle size and large volume fraction of grain boundaries, exhibit superior properties over their larger polycrystalline counterparts.[13,14] Moreover, the surface area of the alumina depends on the size of the particle in the final product. Research has been continued in regard to control of the particle size of α-Al_2O_3 by means of reducing the temperature of phase transformation. Therefore, it is important that retention of the enhanced properties associated with smaller particle size requires the development of new processing routes that will drastically suppress the particle growth during densification, and leads to a high surface area.

In this paper, we are reporting a new colloidal method using a surface modifier, which not only produces α-Al_2O_3 at a low temperature, but also reduces the particle size to the nano range. A surface modifier and the seed of α-Al_2O_3 have been employed during the sol-gel process so that temperature for formation of α-Al_2O_3 can be lowered from 1300 to <1000 °C. In this work, we examine the effect of pH on the temperature of phase transformation of α-Al_2O_3 very carefully. Additionally, this paper also focuses on the fundamental aspects of hydrolysis and condensation of sol-gel processed alumina under the influence of pH. This method allows the variation in particle size and produces α-Al_2O_3 with unusually high surface area that may be valuable in catalytic applications.

2. Experimental procedure

A modifier solution was prepared by dissolving a measured amount (10 wt.% with respect to α-Al_2O_3) of surface modifier in 500 ml of methoxyethanol. A mixture of emulsogen OG and β-alanine was used as a surface modifier. The solution was stirred for an hour at room temperature. A known amount of (1 mol) aluminum iso-propoxide (AIIP) was added to the modifier solution. The minimum amount of acetic acid was added to the above solution in order to form a clear solution. The ratio of acetic acid and solvent to AIIP was 3:1 and 500:1 molar ratio (m.r.), respectively. The solution was reflux for three hours, with stirring. Water is required for the hydrolysis, therefore, 3 m.r. of water, with respect to AIIP, was added to the above solution. It was reflux for another three hours. This sol was divided equally into six parts. The pH of three samples was adjusted to 8, 10, and 12 by NH_4OH. Acetic acid was used to maintain the acidic pH (2.5, 4 and 6) of the remaining three sols. The 4 wt.% of α-Al_2O_3 particles (size 0.055 μm) was added to 30 ml of methoxyethannol and sonicated for 48 h in order to avoid the agglomeration in the seed particles. Then, the suspension of dispersed seed was transformed into the Al_2O_3 sol. This suspension was ball milled for 48 h. The slurry was then dried at 80 °C for 24 h. The sol was transformed to a thick mass (so called "gel"). The schematic diagram of the preparation of alumina gel, under the influence of pH, is shown in Fig. 1. The xerogel of Al_2O_3 was then grounded by mortar and pestle.

Differential thermal analysis (DTA) studies were carried out using Universal V2.5H TA thermoanalyzer, in air, from 25 to 1200 °C. The true powder density of materials was measured using Densitometer (Accu Pyc 1330). The crystalline phase was determined by powder X-ray diffraction, using Scintag diffractometer (DMC 105) with copper Kα radiation, for 2θ from 20° to 60°. The BET surface area of the powders was measured by Micromeritics ASAP 2000 after degassing the sample at 150 °C, for 24 h. Zeta potential values of the ceramic powder suspensions in water were measured with Zetasizer (Malvern Instrument, PCS V1.23, England) at (20 ± 1)°C without adding any electrolyte. This suspension was sonicated for 20 min before the measurement of zeta potential. During the potentiometric titration, constant agitation of the suspension was required. The microstructure of particles was investigated in a transmission electron microscope (TEM) (Philips, EM 420ST). High-resolution transmission electron microscopy (HRTEM) on the sample was carried out using a Hitachi-2000. The sample for the HRTEM study was prepared by grounding raw sample thoroughly with acetone. A 300-meshed copper grid was suspended in the suspension liquid, and kept for 30 min in an open atmosphere so that all of the acetone evaporated.

3. Results and discussion

The structural analysis of the powders derived from pH 2.5 and 12 is investigated by XRD and shown in Figs. 2 and 3. The critical processing parameter for sol-gel processing of any metal oxide is the pH, because that is what determines the phase formation, particle size, and morphology of the final product. Fig. 2 shows the XRD powder pattern of the products after heat

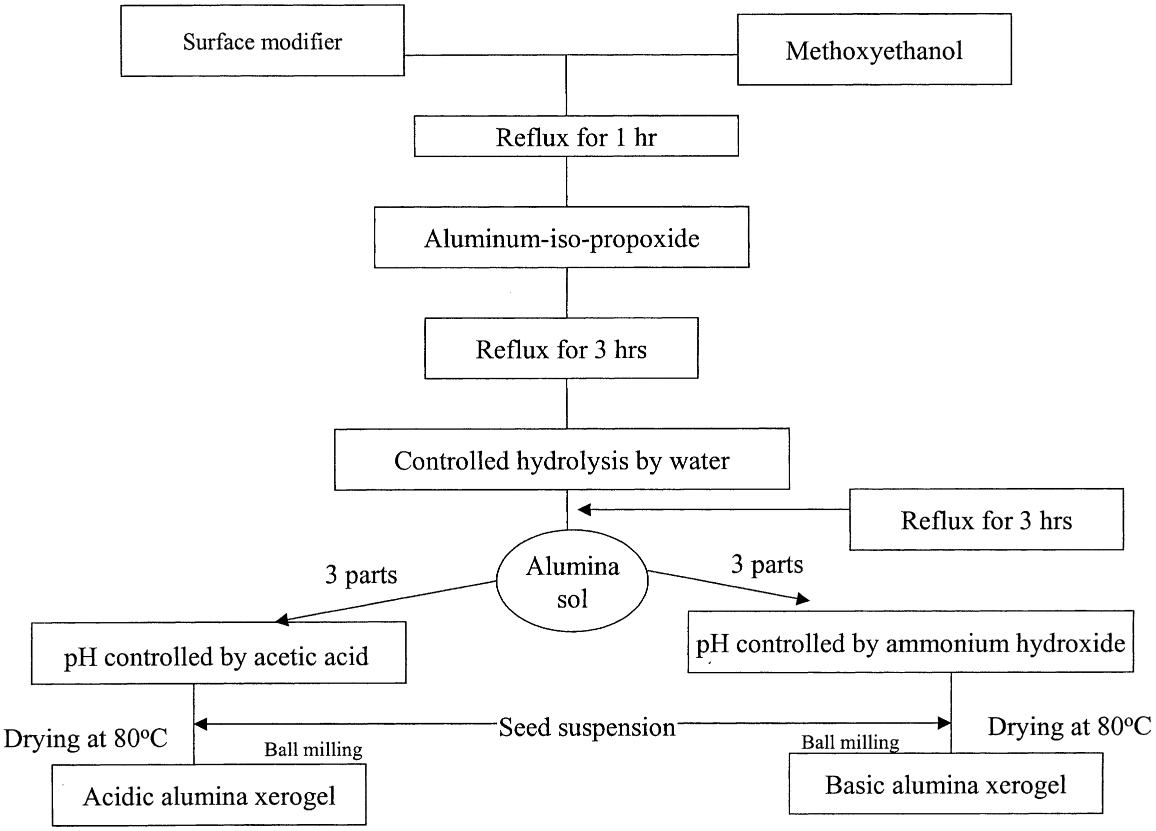


Fig. 1. Flow diagram of the preparation of alumina xerogel under the influence of pH.

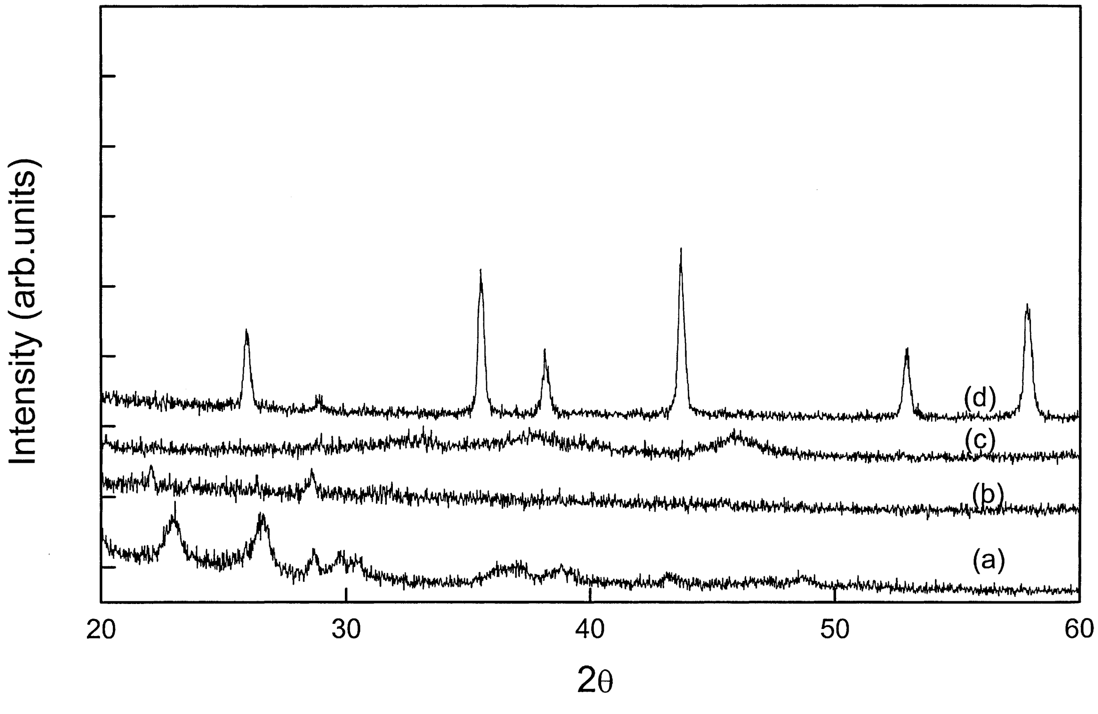


Fig. 2. X-ray diffraction pattern of powders synthesized from pH = 2.5 and heat treated at (a) 150 °C,(b) 450 °C, (c) 750 °C, and (d) 1050 °C.

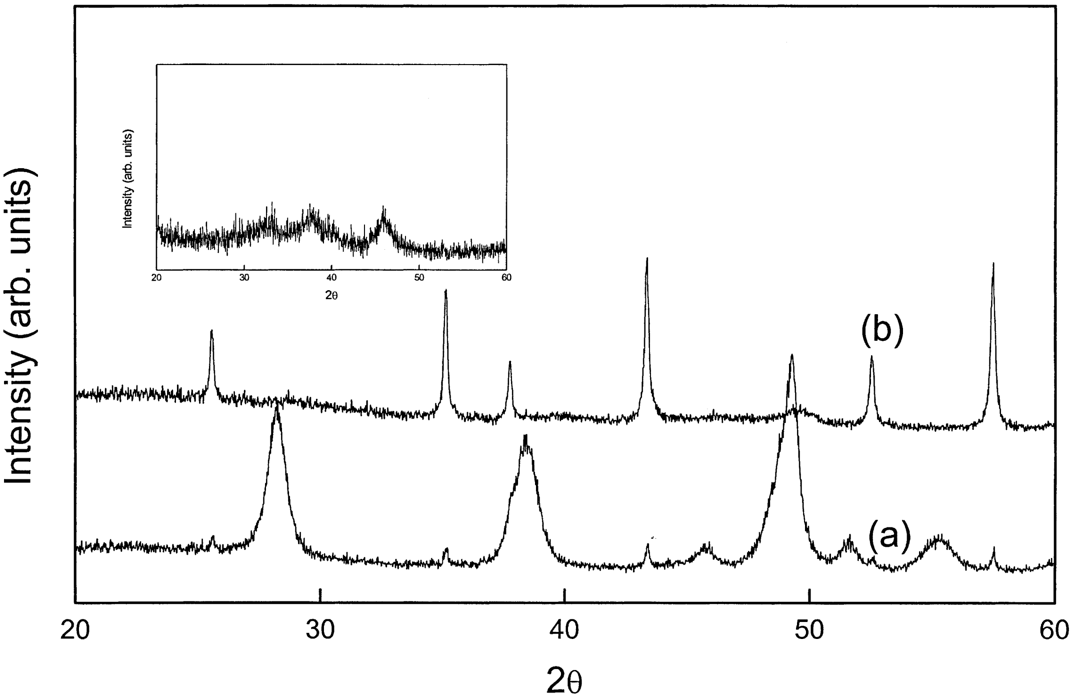
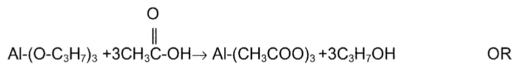
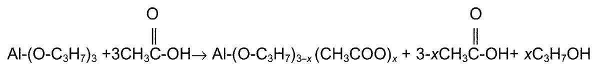


Fig. 3. X-ray diffraction pattern of powders synthesized from pH = 12 and heat treated at (a) 450 °C and (b) 1200 °C . Inset is the XRD pattern of the powder 850 °C.

treatment at 150, 450, 750, and 1050 °C obtained at pH 2.5. It has been observed that the XRD pattern of the powder is highly crystalline when the powder heat treated at 150 °C. Peaks appearing at a low value of 2θ are due to the formation of acetates of alumina in different forms. The powder was synthesized in the presence of a high concentration of acetic acid (i.e. 3 molar ratio with respect to AlIP) used during the preparation of alumina sol. Therefore, there may be a possibility of formation of acetates of alumina due to the following reactions



$$\mathrm{Al\text{-}(O\text{-}C_3H_7)_3 + 3CH_3\overset{\overset{O}{\|}}{C}\text{-}OH \rightarrow Al\text{-}(CH_3COO)_3 + 3C_3H_7OH} \qquad \text{OR} \qquad (1)$$



$$\mathrm{Al\text{-}(O\text{-}C_3H_7)_3 + 3CH_3\overset{\overset{O}{\|}}{C}\text{-}OH \rightarrow Al\text{-}(O\text{-}C_3H_7)_{3\text{-}x}(CH_3COO)_x + 3\text{-}xCH_3\overset{\overset{O}{\|}}{C}\text{-}OH + xC_3H_7OH} \qquad (2)$$

At 150 °C, the FTIR (not shown here) of the powder indicates the presence of peaks at ≈1700 cm and ≈1255 cm^{-1}, which are assigned to $\nu_{\mathrm{asym}}(\mathrm{COO})$ and $\nu_{\mathrm{asym}}(\mathrm{COO})$ vibrations of acetic acid.[9] The powder is found to exhibits amorphous characteristics at any temperature up to 750 °C. The appearance of amorphous characteristics is understood because the material is derived from the higher organic precursors. This powder does not show the formation of boehmite phase during the transformation of α-$\mathrm{Al_2O_3}$ accept a weak peak at $2\theta \approx 28.3°$. On the other side, the calcined product at 750 °C exhibits the distinct diffraction peaks of γ-$\mathrm{Al_2O_3}$. Peaks, due to γ-$\mathrm{Al_2O_3}$, disappear when the temperature increases from 750 to 1050 °C. The XRD pattern of the powder obtained at 1050 °C was similar to the one matched with α-$\mathrm{Al_2O_3}$. The XRD powder pattern does not show any impurities, due to incomplete transformation of any metastable phase of $\mathrm{Al_2O_3}$ e.g. θ-, γ-, α-, β at 1050 °C. These results show that the formation of α-$\mathrm{Al_2O_3}$ at low pH ($\leqslant 6$), occurs by the following steps: Gel $\rightarrow \gamma\mathrm{Al_2O_3} \rightarrow \alpha\mathrm{Al_2O_3}$. Nevertheless, the peaks referring to metastable alumina in the XRD patterns (at 750 °C), are weak compared with α-$\mathrm{Al_2O_3}$. Therefore, the power was further heated to high temperatures (e.g. 1100, 1150, 1200, and 1250 °C), to ensure no amorphous phase present in the powder. It has been observed that the intensity of d_{113} plane increases to 6% when the temperature increases from 1050 to 1150 °C. However, the enhancement in the intensity of d_{113} plane from 1150 to 1250 °C was observed $<2\%$. It indicates that the material at 1050 °C may contain a small amount of amorphous phase. Table 1 summarizes the DTA results, due to exothermic reactions of xerogels, obtained from sol-gel process in pH range from 2.5 to 12. The most important peak in Table 1 is the peak associated to the transformation of transition aluminas to α- phase, which is considered an exothermic reaction. The peak, which appears at 930 °C can be attributed to the formation of α-$\mathrm{Al_2O_3}$. However, it completes at 1050 °C; therefore, the samples were heated at 1050 °C. It is worth noting that the temperature of formation of such an exothermic peak is observed to be shifting to a higher temperature when the pH value increases.

Table 1
DTA and TEM results of xerogels derived at different pH

pH	Exothermic peak, transformation of α-Al_2O_3	Morphology	TEM particle size (nm)
2.5	930	Spherical	55–70
4	930	–	–
6	1020	–	–
8	1080	Irregular hexagonal	150–300
10	1150	–	–
12	1170	Hexagonal	450–750

Fig. 3 shows the XRD pattern of the powders derived at pH = 12 after heat treatment of 450, 850, and 1200 °C. However, the powder at 150 °C (not shown here) has a different XRD pattern than the one derived from pH-2.5. The powder synthesized at high pH ($\geqslant 7$) does not show any peak, due to the acetate formation of aluminum, unlike the powder derived at a low pH. Nonetheless, the powder exhibits an amorphous characteristic, which appears to exist up to the temperature $\approx$450 °C. The boehmite phase was observed when the powder was calcined at 450 °C. It has been observed that for boehmite, the transformation sequence, upon heating, is: boehmite→ γ→ δ→ θ→ α-Al_2O_3. In this study, boehmite transformation also occurs via γ phase. The γ phase appears at 950 °C and is shown in the inset of Fig. 3. Peaks, due to boehmite, are found to disappear when this powder is annealed at 1200 °C, as shown in the Fig. 3. This transformation is further confirmed by DTA analysis (refer to Table 1), which indicates an exothermic peak at 1170 °C at pH = 12. The formation of boehmite is seen in all the gels derived at pH$\geqslant$7 and is obvious because of the excess amount of hydroxyl groups (from NH_4OH). Hence, at a high pH the transformation sequence can be: gel→ boehmite→ γ→ α-Al_2O_3. On the contrary, the powders derived at low pH (6) do not show the presence of boehimte, due to the neutralization of hydroxl ions by acetate ions. Ji et al. has also reported that the alumina xerogel derived in presence of access nitric acid did not undergo boehmite formation during the transformation of α-Al_2O_3.[9]

The microstructure of the α-Al_2O_3 particles at pH = 12, is observed to be almost like irregular hexagonal, with particle size in the range of 450–750 nm. When pH decreases to 8, the particle size of α-Al_2O_3 is found to be 150–300 nm (refer to Table 1). Although, the morphology of the particles remain same, the phase transition to α-Al_2O_3 is accompanied by severe aggregates, because of sintering. On the other hand, the TEM particle size of the powder at pH = 2.5 is found to be bimodal (e.g. $\approx$70 and <30 nm) with spherical morphology. The fine particles (<30 nm) may belong either to any transitional alumina which was present in the small amount and remain undetected by XRD, or same phase crystallizes in two different kind of particle sizes. The fine grains of θ-Al_2O_3 are observed to exist in the sintered specimen of α-Al_2O_3 sintered at 1100 °C in the study of Deng et al.[15] Further studies are underway to clarify this fact. Here, the low pH seems to help in forming the spherical shape of the particles. The aggregate is also noticed in the particles derived at low pH. It is usual, because nano particles have large surface areas, and they tend to aggregate to minimize their total surface energy.[13,16,17]

The results described above are indicate that the variation in the initial pH has a significant effect on the physical properties of the final product. As sol-gel processing is based on several chemical processes, such as hydrolysis and polycondensaion, this needs to be further considered. Literature, indicates that at low pH ($\leqslant 6$), the rate of hydrolysis [refer to Eq. (3)] is governed by the hydronium ion in solution [Eq. (4)], therefore, the amount of water is small, due to rapid formation of H_3O^+.[11] Sharma et al. has demonstrated that hydrolysis/ condensation is controlled and selective during the sol-gel synthesis of Y_2O_3 at low pH, which leads to formation of linear polymer.[11]

$$\mathrm{Al(O-s-Pr)_3 + H_3O^+ \rightarrow (O-s-Pr)_{3-y} - Al - (OH)_y + H^+ + } y\mathrm{PrOH} \qquad (3)$$

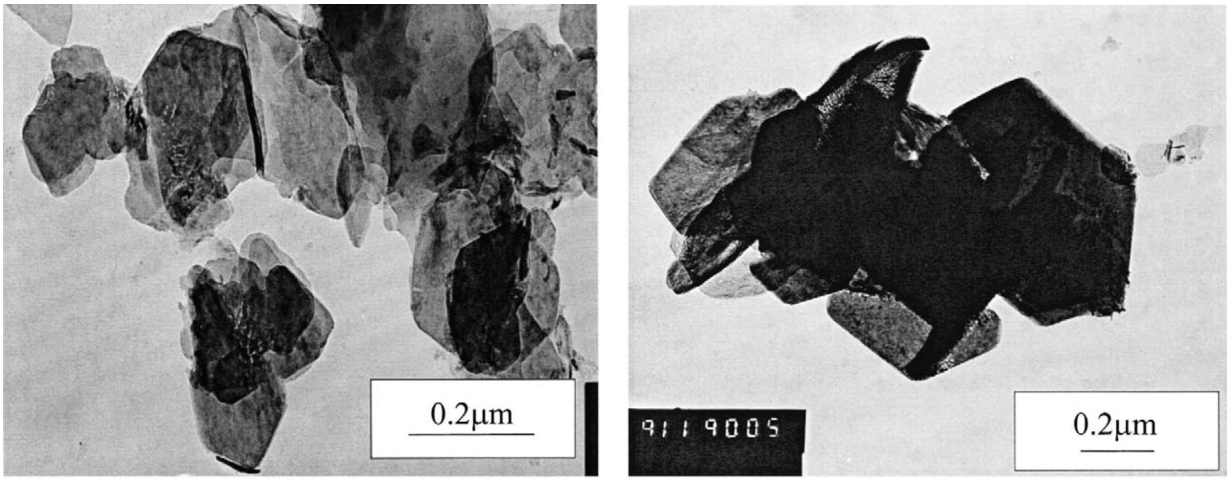
$$\mathrm{H_2O + H^+ \rightarrow H_3O^+} \qquad (4)$$

Condensation can take place by any of the following equations:

$$\mathrm{(O-s-Pr)_{y-1}-Al-(OH) + (OH) - Al - (O-s-Pr)_{y-1} \rightarrow (O-s-Pr)_{y-1}-Al-O-Al - (O-s-Pr)_{y-1} + H_2O} \qquad (5a)$$

$$\mathrm{(O-s-Pr)_{y-1} - Al - (OH) + (O-s-Pr)_{y-1}-Al-(OH) \rightarrow (O-s-Pr)_{y-1} - Al - O - Al - (OH) + PrOH} \qquad (5b)$$

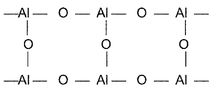
On the other hand, the reaction is controlled by the hydroxyl ions (OH) when powders are derived at pH$\geqslant$7. The reported work indicates that the initial growth leads to a linear chain, but due to the high concentration of OH ions, it results in the cyclization, since the probability of intermolecular reaction is higher than



(a) (b)

Fig. 4. TEM micrograph of powder derived at (a) pH = 12 and (b) pH = 8.

the interamolecular reaction.[10] Fig. 6 is a very simple illustration of behavior of gels under the influence of pH.



(6)

The hydrolysis and condensation are uncontrolled and undirectional which result in highly-branched polymers. The most probable meal-oxygen polymeric network, formed at high pH, is the structure (6). Nonetheless, the larger interstices at pH ⩾ 8 lead to larger grains. Hence, the particle size is observed (refer to Fig. 4) to be larger in the pH range from 8 to 12, than the one seen in pH range, from 2.5 to 6 (refer to Fig. 5).

Furthermore, the effect of pH on the surface modifier, and seed can not be ignored. Sharma et al. has demonstrated that the surface modifier layer that protects the particles, and prevents the grain growth during thermal treatment, is found to be more effective only in the acidic pH in the Eu doped Y_2O_3.[11] In the basic pH, the modifier layer is found to be less effective due to the presence of excessive OH^- ions in the system. It results in the aggregation and larger particle size in the $pH > 7$. On the other hand, the seed in the acidic pH may have distributed well enough that their seeding ability might have enhanced. Further study has to be required in order to understand the influence of pH solely on the seeding.

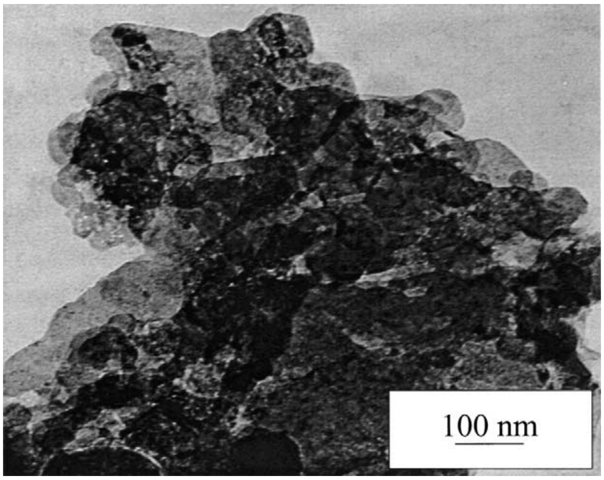


Fig. 5. TEM micrograph of the powder derived at pH = 2.5.

The influence of pH is, once again, found to be significant while considering the surface area and true density of the powders (as shown in Fig. 7). The surface area of the powder at 1050 °C is found to be ≈25 m^2/g at pH = 12, which increases to 130 m^2/g when the pH decreases to 2.5. It is worth noting that the surface area of the commercially available α-Al_2O_3 is < 35 m^2/g. As both the powders derived at low and high pH transformed to α-Al_2O_3 at 1200 °C. Therefore, a comparison has been made on the surface area and true density of the powders derived at different pH conditions after heat treatment at 1200 °C. In low pH regime, linear chain growth seems to be preferred, as discussed earlier, which results in higher reactivity at the chain ends. It is well known that the linear chains obtained at low pH

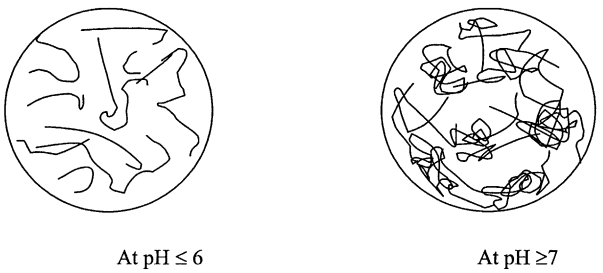


Fig. 6. Schematic diagram of the behavior of alumina gel under the influence of pH.

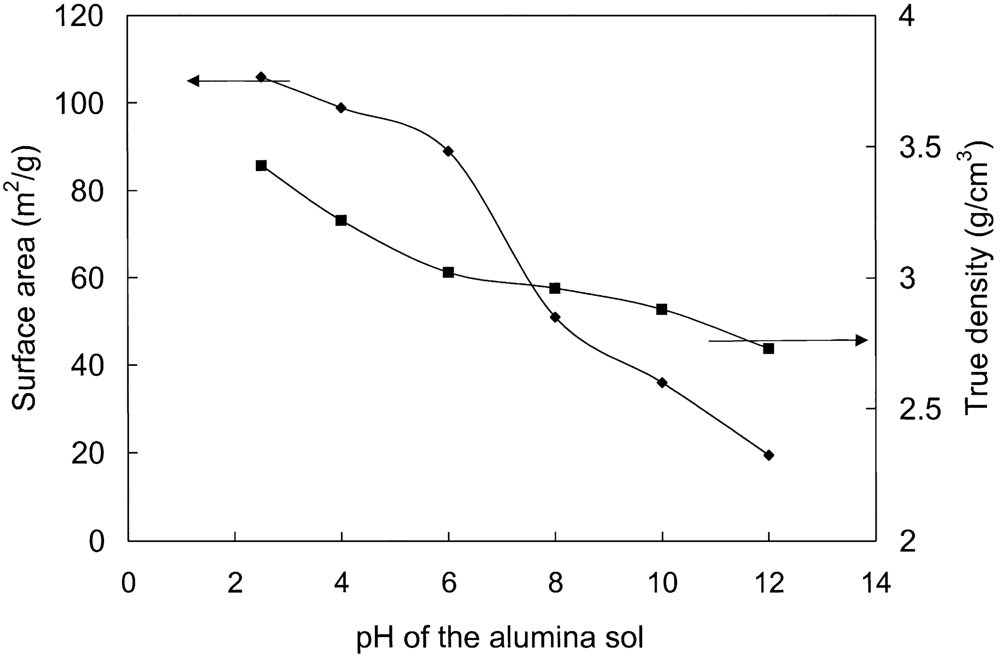


Fig. 7. Surface area and true density of the powders derived at different pH after heat treatment at 1200 °C.

leads smaller grains, since the relation between the particle size and surface area is inverse.[13] Therefore, the surface area increases when pH decreases from 12 to 2.5. The low pH (≤ 7) gives finer particles which can further to be attributed to the packing of the particles and leads to high-true powder density i.e. 3.43 g/cm^3 (≈86% of theoretical density). The true powder density decreases when the particles become coarser at high pH (≈68% at 12).[18] Furthermore, the maximum true powder density of the α-Al_2O_3 sample, derived at pH = 2.5 that can be achieved, is observed to be 3.92 g/cm^3 when sintered at 1450 °C, due to fine particle.

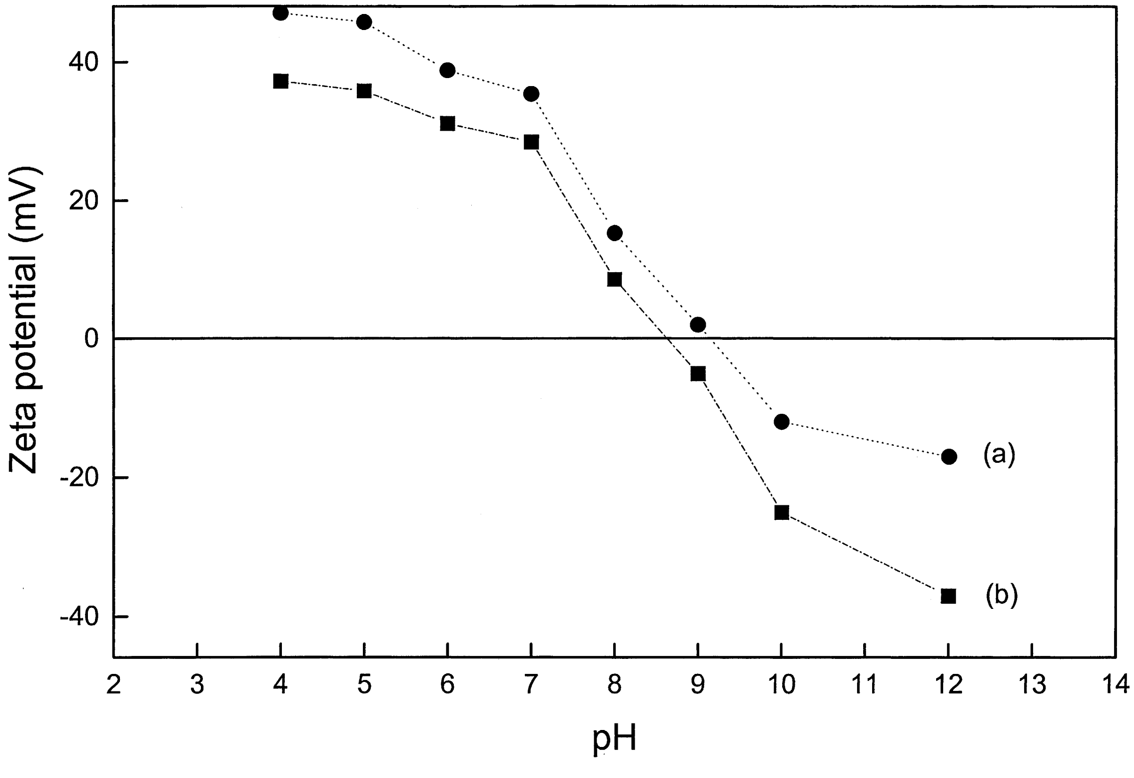


Fig. 8. Zeta potential of α-Al_2O_3 at (a) pH = 8 and (b) pH = 2.5.

The zeta potential (ξ) is an important parameter in colloidal stability, since it reflects the variation in surface potential for a specific material. These powders were derived from solution route at low temperature, therefore, it was necessary to understand the surface charge of these powders. Hence, zeta potential studies were done. Fig. 6 shows the zeta-potential data of an aqueous suspension of synthesized α-Al_2O_3 heat treated 1050 °C, as a function of pH (range 4–12). There is no addition of any electrolyte to control the ionic strength of the solutions. The Al_2O_3 particles are positively charged at $pH < 8.7$ with maximum $\xi = 47$ mV (at pH 4). Above this pH, the α-Al_2O_3 particles are negatively charged to increase the negative ξ values. The iep value of powder derived at $pH = 8$ is found to be 9.2, as shown Fig. 8(a). Nevertheless, the iep of the powder derived at $pH = 2.5$ is 8.7. The iep value is associated with several factors e.g. phase composition, OH-group content, calcinations temperature etc. It can be assumed that powder synthesized in presence of acid, has a positive charge on the surface even at the temperature of 1050 °C. Hence, a shift in iep was observed towards lower value of pH.

4. Summary

In summary, the particle size of α-Al_2O_3 can be tailored by controlling the pH of the modified alumina sol. TEM study confirms that at $pH = 2.5$, the α-Al_2O_3 with particle size 70 nm can be achieved due to linear chain polymerization. The particle size increases to 750 nm by increasing pH to 12 due to 3D network of polymer. Surface area and true powder density of α-Al_2O_3 are highly dependent on the reaction conditions of the alumina sol. The hexagonal morphology of the particles was obtained at $pH = 12$, which was changed to the spherical one at $pH = 2.5$. Hence, morphology can be altered by changing the pH of the alumina sol. The α-Al_2O_3 particles derived from low pH are observed to have a positive charge, which causes a shift in the value of iep in the powder.

References

1. Levin, I. and Brandon, D., Metastable Al_2O_3 polymorph: crystal structure and transition sequences. *J. Am. Ceram. Soc.*, 1998, **81**, 1995–2012.
2. Lippins, B. C. and DeBoer, J. H., Study of phase transformation during calcinations of aluminum hydroxides by selected area electron diffraction. *Acta Crystallogr.*, 1964, **17**, 1312–1321.
3. Kumagai, M. and Messing, G. L., Controlled transformation and sintering of a boehmite sol-gel by α-Al_2O_3 seeding. *J. Am. Ceram. Soc.*, 1985, **68**, 500–505.
4. Bell, N. S., Cho, S. B. and Adair, J. H., Size control of α- Al_2O_3 particles synthesized in 1,4 -Butanediol solution by α-Al_2O_3 and α-Hematite seeding. *J. Am. Ceram. Soc.*, 1998, **81**, 1411–1420.
5. Gouvea, D., Villalobos, R. L. and Capocci, J. D. T., Polymeric precursor synthesis of alumina containing manganese oxide. *Adv. Powder Technol.*, 1999, **299**, 91–96.
6. Sharma, P. K., Jilavi, M. H., Nass, R. and Schmidt, H., Hydrothermal synthesis of nanosize α-Al_2O_3 from seeded aluminum hydroxide. *J. Am. Ceram. Soc.*, 1998, **81**, 2732–2734.
7. Yoldas, B. E., Al_2O_3 sol preparation from alkoxides. *Am. Cer. Soc. Bull.*, 1975, **54**, 289–290.
8. Yoldas, B. E., A transparent porous Al_2O_3. *Am. Cer. Soc. Bull.*, 1975, **54**, 286–288.
9. Ji, L., Lin, J., Tan, K. L. and Zeng, H. C., Synthesis of high surface area Al_2O_3 using aluminum tri-sec-butoxide-2,4Pentanedione-2propanol-nitric acid precursors. *Chem Mater.*, 2000, **12**, 931–939.
10. Brinker, C. J. and Scherrer, G. W., *Sol-gel Science: The physics and Chemistry of Sol-gel Processing*. Academic Press Inc, New York, 1990.
11. Sharma, P. K., Jilavi, M. H., Varadan, V. K. and Schmidt, H., Influence of initial pH on the particle size and fluorescence properties of the nano scale Eu (III) doped yttria. *J. Phys. Chem. Sol.*, 2002, **63**, 171–177.
12. Rao, G. V. R., Venkadesan, S. and Saraswati, V., Surface area and pore size studies of alumina gels. *J. Non-Cryst. Solids*, 1989, **111**, 103–112.
13. Sharma, P. K., Jilavi, M. H., Nass, R. and Schmidt, H. K., Tailoring the particle size from microns to nanometer scale by using a surface modifier and theier size effect on the fluorescence properties of europium doped yttria. *J. Lum.*, 1999, **82**, 187–193.
14. Ramesh, S., Sominska, E., Cina, B., Chaim, R. and Gedanken, A., Nanocrystalline γ- Al_2O_3 synthesized by sonohydrolysis of alkoxide precursor in the presence of organics acids: Structure and Morphological properties. *J. Am. Ceram. Soc.*, 2000, **83**, 89–94.
15. Deng, Z. Y., Fukasawa, T., Ando, M., Zhang, G. J. and Ohji, T., High surface area alumina ceramics fabricated by the decomposition of $Al(OH)_3$. *J. Am. Ceram. Soc.*, 2001, **84**, 485–491.
16. Nair, J., Nair, P., Ommen, J. G. V., Ross, J. R. H., Burggraaf, A. J. and Mizukami, F., Influence of peptization and ethanol washing on the pore structure evolution of sol gel derived Al_2O_3 catalyst supports. *J. Am. Ceram. Soc.*, 1998, **81**, 2709–2712.
17. Keefer, K. D., Silicon-based polymer science; a comprehensive resource. In *Am. Chem. Soc*, ed. J. M. Zeigler and F. W. Gordon. Washington DC, 1990, pp. 228.
18. Sharma, P. K., Fishcer, H and Craievich, A. F., Chemical and structural properties of nickel hydroxide xerogels obtained by the sol-gel procedure in the presence of acetic acid. *J. Am. Ceram. Soc.*, 1999, **82**, 1020–1024.