JOURNAL OF MATERIALS SCIENCE 11 (1976) 465–470

Thermal stabilization of an active alumina and effect of dopants on the surface area

BULENT E. YOLDAS*
Owens-Illinois, Inc, Technical Center, 1700 N. Westwood Avenue, Toledo, Ohio, USA

The α-Al_2O_3 transformation of a monolithic active alumina has been increased from 1200 to ~1380° C through structural incorporation of silica. This shift is significant since α-Al_2O_3 transformation determines the limits of the usefulness of these materials as catalysts and catalyst carriers. The thermal stabilization effect is optimized at around 6% silica doping. At elevated temperatures, the material containing no silica rapidly loses surface area, primarily by α-Al_2O_3 transformation, whereas the material containing excess silica loses surface area by classical sintering.

1. Introduction

Transition aluminas have high surface areas and are well known for their catalytic properties [1-4]. The maximum temperature limits for the various forms of these high surface area aluminas have been reported as follows: gamma, 850° C; delta, 1150° C; theta, 1150° C, alpha being the only stable phase above 1150° C [5]. The transformation to the alpha phase marks the end of the useful catalytic properties of these materials since activated sintering (the Hedvall effect) causes a catastrophic decrease in surface area. Some of the recent application, particularly the high temperature catalytic carrier application for auto emission control, require service temperatures close to the thermal stability limit of these materials; therefore, there is an industrial need to stabilize the high surface area aluminas. Various investigators have studied the effect of dopants on the alumina transformations [6-15].

The monolithic active alumina which is employed in this investigation has been previously reported [16]. This material upon transforming to α-Al_2O_3 at 1200° C becomes opaque, without losing its monolithic nature. This makes it possible to follow the effect of dopants on the α-Al_2O_3 transformation visually, as well as with DTA and X-ray analysis. It is found that introduction of some dopants into the material, e.g. ThO_2, ZrO_2, and SiO_2 increases the α-Al_2O_3 transformation temperature while the introduction of certain others, e.g. TiO_2 and Na_2O decrease it. Since the primary goal of this investigation was the formation of a refractory high surface area material, only those dopants which contributed to the crystalline stability as well as minimized the sintering of the material were investigated. Among these, silica was found to be especially effective and was studied in greater detail.

2. Experimental procedure

2.1. Sample preparation

The high surface area monolithic alumina studied is produced from a clear sol of aluminium monohydroxide. The precursor sol was prepared by hydrolysis of aluminium-secondary butoxide, $Al(OC_4H_9^s)_3$, and peptization of the resultant monohydroxide with 0.07 mol nitric acid per mol alkoxide [17, 18]. The methods of introducing a second oxide into this system, the limits of such additions, and the rules governing the capability of these gels to remain monolithic during the drying and pyrolysis have been presented earlier [19, 20]. The method used provides intimate mixing of the constitutents; and in certain cases, e.g. with silica, a chemical bond formation and polymerization among the constituents also occurs. The method of preparation is particularly import-

---

*Present address: Westinghouse Electric Corporation, Research Laboratories, Beulah Road, Pittsburgh, PA 15235 USA.

ant in this system. In classical methods of sample preparation from oxide powder mixes, crystalline transformation may take place in either alumina or silica phase before a substantial reaction between these two refractory oxides occur.

The doped sols were gelled, dried, and pyrolized. The samples were heated together in the same furnace, and small portions were taken out at various temperatures and time intervals for investigation.

2.2. Test methods

The surface areas of samples were determined by the standard BET method, which makes use of nitrogen adsorption desorption isotherms. The temperature of the α-Al_2O_3 transformation of the active alumina studied can be identified by a sharp exothermic DTA peak [16]. The effect of doping on the transformation has, therefore, been investigated by differential thermal analysis as well as X-ray diffraction. The DTA equipment had a platinum/rhodium liquid-type sample holder with embedded Pt/Rh thermocouples. Samples of approximately 100 mg were heated 10° C min^{-1} in an air atmosphere. It was also possible to observe the crystalline transformation visually since as mentioned, it is accompanied by the loss of transparency in these monolithic samples.

3. Results and discussion

The effect of 4% doping of the material with various oxides on the exothermic DTA peak associated with the transformation of the undoped material at 1200° C was first surveyed. Oxides of the following elements were studied: K, Na, Li, Ba, Sr, Ca, B, La, Ti, Th, Zr and Si. Ba and Sr broaden this exothermic peak; Na, Ti, K and B progressively showed lower temperature DTA peaks; Ca and Li had endothermic DTA peaks around 700 and 1150° C respectively. All the above samples had a low surface area after the occurrence of the DTA peak. Only Th, Zr and Si had a thermal stabilization effect beyond 1200° C, thus no further work was done on the other dopants.

The surface area measurements of samples doped with 4% ThO_2, ZrO_2, and SiO_2 after a 24 h heat-treatment at 1000° C were 99, 98 and 151 m^2g^{-1} respectively. Undoped samples give a surface area of approximately 80 m^2g^{-1} for the same heat-treatment.

The thermal stabilizing effect of thoria, hafnia and silica on active aluminas has been reported elsewhere [10-14]; and a similar effect from zirconia is also expected. However, the magnitude of the stabilization effect of silica on this material was somewhat unexpected; therefore, further work was concentrated entirely on silica doping.

3.1. Effect of silica on the α-alumina transformation temperature

Since the primary cause of surface area loss in undoped alumina is the transformation to α-Al_2O_3 the effect of silica doping on this transformation was investigated. DTA runs show that an increase in the silica concentration initially causes a corresponding increase in α-Al_2O_3 transformation temperature (Fig. 1). When the DTA peak temperatures are plotted as a function of silica concentration, a curve showing the maximum stabilization temperature of about 1380° C is obtained around 6% SiO_2 (Fig. 2). With additions beyond 6%, a decrease in the temperature of the DTA peak as well as in its relative intensity is observed.

The sharp DTA peak of the undoped material occurring at 1200 C was previously determined to be the result of α-Al_2O_3 transformation [16]. There may be questions whether, with the silica doping, these DTA peaks still represent the α-Al_2O_3 transformation. The DTA peaks must still represent the α-Al_2O_3 transformation at low silica concentrations, e.g. below 6%, for several reasons. 2% silica-doped material gives a DTA peak at around 1360° C and no peak is observed at 1200° C (Fig. 1). If we assume, for example, that this new

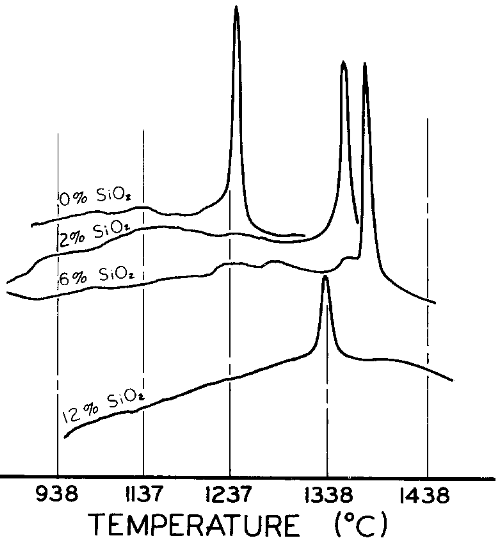

Figure 1 The DTA curves of the material doped with various amounts of silica (10° C min^{-1} heating rate, in air).

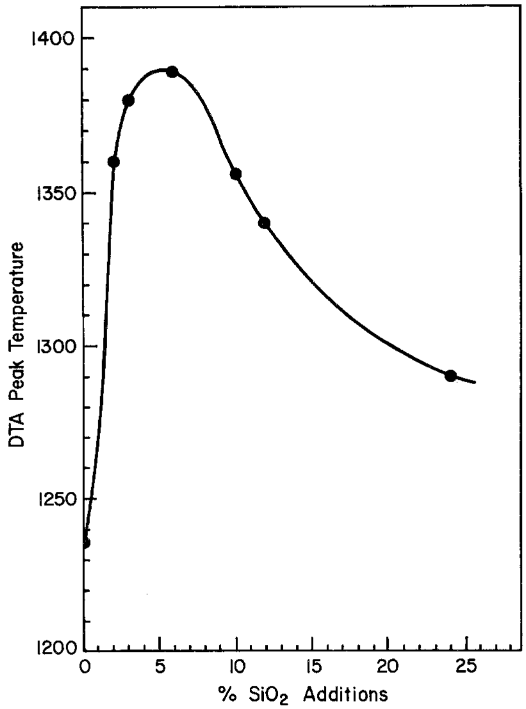

Figure 2 The effect of SiO_2 concentration on the DTA peak temperature. (For accuracy's sake the tip of the DTA peak rather than the starting point is used.)

DTA peak is due to mullite formation, then there has to be another peak at 1200° C, since over 90% of the active Al_2O_3 must still remain free and transform to α-Al_2O_3 (with 2% SiO_2 the maximum theoretical mullite formation can only be 7%). Under this condition any assumptions that perhaps the mullite stabilizes the material cannot be justified either, since the mullite formation temperature would be higher than the α-Al_2O_3 transformation temperature.

It is quite possible, that the DTA peaks occurring above 6% SiO_2 concentration are of entirely different origin and are due to mullite formation. Nevertheless, the fact that the DTA peaks represent the α-Al_2O_3 transformation below the 6% SiO_2 concentrations is established experimentally by making X-ray analysis of the material before and after the occurrence of the DTA peak (see X-ray diffraction section and Fig. 5).

3.2. Effect of silica on the thermal stability of the surface area

Table I gives the surface areas of samples doped with various amounts of silica as a function of concentration and time at 1100° C, along with the calculated percent of surface area retained between intervals of 30 to 400 h.

TABLE I Effect of incorporation of silica on the stability of the surface area after firing for various times at 1100° C

	Surface area (m^2g^{-1})			%Surface area retained
%SiO_2	30h	100h	400h	(30 to 400 h)
1	44.7	21.9	13.6	30
3	92.3	71.9	52.8	57
5	108.0	91.7	77.9	72
7	116.0	98.4	84.9	73
10	133.0	107.0	88.7	67

The reason the samples containing higher silica initially show higher surface area is largely due to the source of the silica and method of sample preparation. The silica obtained from hydrolyzed ethyl silicate has a high surface area; however, it sinters rather rapidly if not tied into the structure. The ability to retain surface area is greatest at 5 to 7% SiO_2. The optimizing effect of about 6% silica concentration on the thermal stability of the surface area becomes evident after sufficiently long periods of time at 1100° C, e.g. 400 h (Fig. 3). The 2000 h curve of Fig. 3, which was obtained by extrapolating the surface areas shown in Table I, to 2000 h at constant silica concentrations, makes this even more evident. Therefore, the surface stabilization effect of SiO_2 parallels its effect on the α-Al_2O_3 transformation.

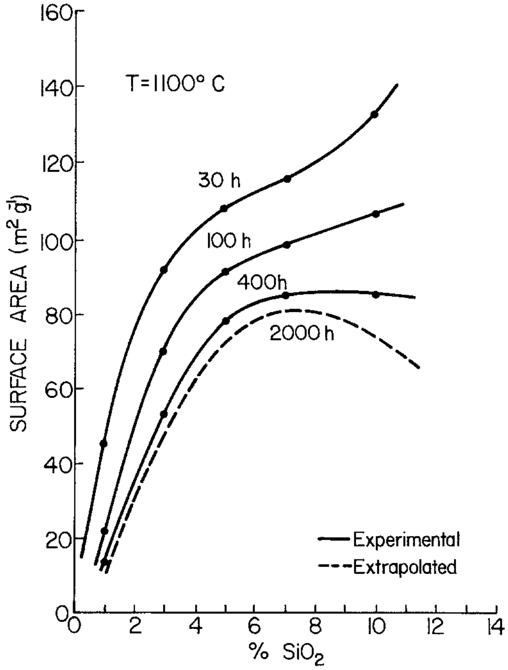

Figure 3 The surface area of the material as a function of SiO_2 content and time at 1100° C. (The 2000 h curve was obtained by extrapolating the data of Table I at constant silica concentrations in log time scale.)

3.3. X-ray diffraction studies

A detailed structural study of the undoped alumina including infra-red and electron spectroscopy, X-ray diffraction, and small-angle X-ray scattering has been presented earlier [16].

The X-ray diffraction pattern of undoped material gives agreement for δ-Al_2O_3 with respect to the number and position of reflections observed. However, relative intensities of these reflections are appreciably different from the reported values of δ-Al_2O_3 (ASTM pattern number 16-394). In monolithic samples this is generally an indication of preferred orientation of crystallites. However, our pulverized samples gave the similar results. This deviation may be an indication of a defect structure, e.g. having vacancies or displaced atoms in each unit cell [16]. Such variations are commonly observed in transition aluminas [21-24].

X-ray diffraction patterns of samples doped with various amounts of silica and heat-treated at 800° C for 1 h show that the relative areas under the two primary peaks occurring at 45.5 and 65.5° C do not change up to 5 to 6% silica concentration. Whereas, additions above this concentration cause a rapid decrease of the area under these peaks.

Fig. 4 shows X-ray patterns of samples heated 30 h at 1100° C. Only the 1% SiO_2-doped sample showed the presence of the α-alumina phase. Undoped material would have principally transformed to α-Al_2O_3. When the heat-treatment period was extended to 400 h still there was no indication of α-Al_2O_3 formation in the remaining samples (Table II).

3 and 6% silica-doped samples were heated at 1350 and 1400° C for 10 min–temperatures just

Figure 4 The X-ray diffraction patterns of various amounts of SiO_2-doped samples held at 1100° C for 30 h. (Only 1% SiO_2-doped samples show formation of α-Al_2O_3.)

TABLE II X-ray diffraction analysis of SiO_2-doped material

	Phases formed at 1100° C	
%SiO_2	30 h	400 h
1	α-Al_2O_3 P.P. α-Al_2O_3 T.P.	α-Al_3O_3 P.P. δ-Al_2O_3 T.P.
3	α-Al_2O_3	δ-Al_2O_3 P.P. A trace of cubic phase with lattice parameters 8.0 (spinel?)
5	δ-Al_2O_3	δ-Al_2O_3
7	δ-Al_2O_3	δ-Al_2O_3
10	δ-Al_2O_3	δ-Al_2O_3

before and after the DTA peaks. X-ray analysis of these samples indicates that the material has the active alumina phase with a trace amount of mullite at 1350° C; whereas, at 1400° C this active phase is entirely transformed to α-Al_2O_3. (See Fig. 5 for 6% SiO_2 doping).

The fact that a more stable phase of the transition alumina is formed by 6% silica-doping supports the view that, initially, silica goes into certain sites in the structure causing no disturbance in the lattice and remains essentially undetectable. When the sites are saturated the structure is more stable, requiring higher energy to transform. Additions of silica above 6% appear to be in excess, presumably having the effect of activating the sintering.

4. Conclusions

(1) Introduction of up to 6% silica into the structure of the monolithic active alumina significantly increases the structural stability. The α-Al_2O_3 trans formation temperature of the material is increased from about 1200° C to about 1380° C at 6% silica doping.

(2) Material containing no silica primarily loses surface area by sintering activated by transformation to α-Al_2O_3, whereas material containing excess silica appears to lose surface area by sintering promoted by the presence of silica. The capacity to retain the surface area at elevated temperatures in sustained use is optimized at about 6% SiO_2 doping.

Acknowledgement

The author expresses sincere thanks to G.F. Neilson, H.F. Pawlecki, and T.O. Miller for X-ray diffractometry; K.B. Andrus for BET surface area

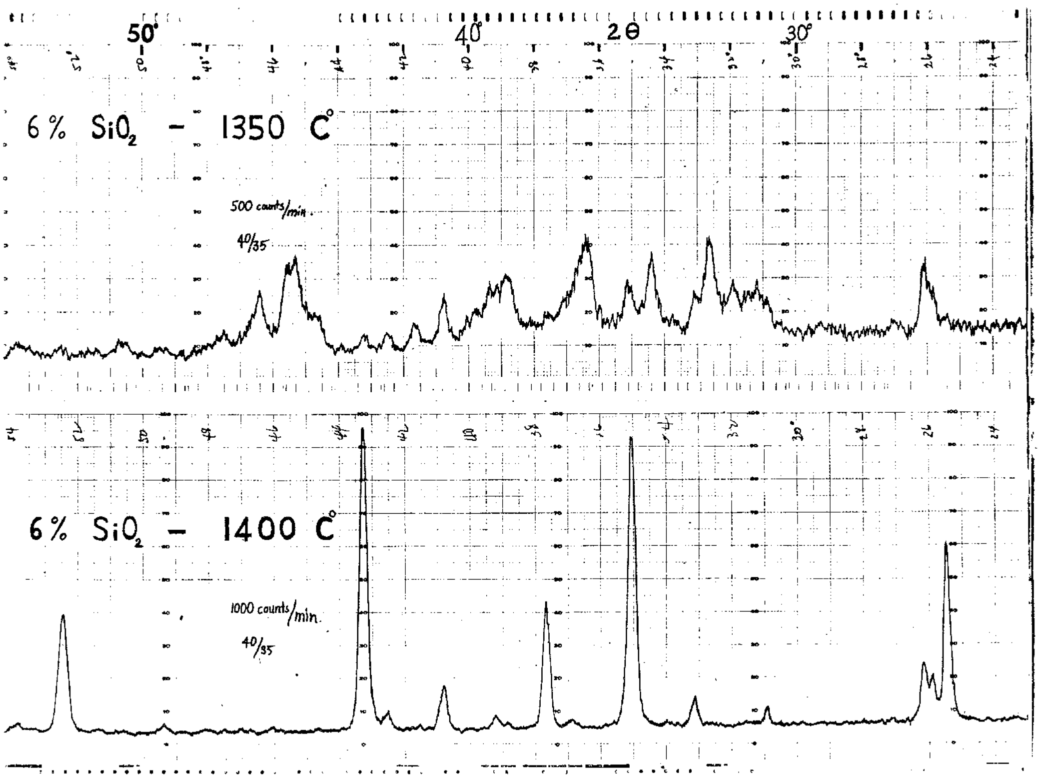

Figure 5 The X-ray diffraction patterns of 6% SiO_2-doped sample heat-treated at 1350 and 1400° C for 10 min (before and after the transformation DTA peak).

measurements, R.K. Ware for DTA studies, and D.M. Mattrox and L.A. Ivanycky in the preparation of the manuscript.

References

1. S. M. FRIDMAN, *Tresta Organizatsii i Ratsional Elektronstansii,* 9 (1954) 37; *Referat. Zhur. Khim.* (1956) Abstr. No. 48123.
2. J. C. GREAVES and J. W. LINNETT, *Trans Faraday Soc.* **54** (1958) 1323.
3. A.W. MILLER and S. W. ROBERTS, *Ind. Chem.* **34** (1958) 141.
4. Alcoa Brochure, "Activated and Catalytic Aluminas" June 1 (1970).
5. W. H. GITZEN, "Alumina as a ceramic material", The American Ceramic Society, Inc. Special Publication No. 4 (1970).
6. G. C. BYE and G. T. SIMPKIN, *J. Amer. Ceram. Soc.* **57** (1974) 367.
7. Y. WAKAO and T. HIBINO, *Nagoya Kogyo Gijutsu Shikensho Hokoku* **11** (1962) 588.
8. S. MUKHERJEE and H. ROY, *Technology* **3** (1966) 63.
9. M. D. EFROS *et al., Vetsi Akad. Nauk Belarus. SSR Ser. Khim. Nauk.* **1** (1971) 9.
10. G. FINK, *Natur.* **52** (1965) 32.
11. S. E. VOLTZ *et al.,* U.S. Patent 2,810,698, October 22 (1957).
12. *Idem,* U.S. Patent 2,810,699, October 22 (1957).
13. R. K. ILLER, *J. Amer. Ceram. Soc.* **47** (1964) 339.
14. W. H. GITZEN and L. D. HART, U.S. Patent 3,433,894, May 13 (1969).
15. *Idem,* U.S. Patent 3,433,895, May 13 (1969).
16. B. E. YOLDAS, *Amer. Ceram. Soc. Bull.* **54** (1975) 286.
17. *Idem, J. Appl. Chem. Biotech.* **23** (1973) 803.
18. *Idem, Bull. Amer. Ceram. Soc.* **54** (1975) 289.
19. *Idem,* "Methods of Forming Porous Transparent Alumina-Based Ceramics", Presentation at the Ceramic Society 77th Annual Meeting, Washington, D.C., May (1975).
20. *Idem, J. Mater. Sci.* **10** (1975) 1856.
21. GUY ERVIN, JUN., *Acta Crust.* **5** (1952) 103.
22. ROBERT TERTAIN, DENIS PAPEE and JACQUES CHARRIER, *Compt. Rend.* **238** (1954) 98.
23. H. P. ROOKSBY, *J. Appl. Chem.* **8** (1958) 44.
24. H. P. ROOKSBY and C. J. M. ROOYMANS, *Clay Miner. Bull.* **4** (1961) 234.

Received 3 June and accepted 28 August 1975.