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Sucrose synthesis of nanoparticulate alumina

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The synthesis of nanoparticulate α -Al₂O₃ at 600 °C using a sucrose-based polymer dispersion technique was reported recently by Das *et al.* [1]. This is of interest, as γ -Al₂O₃ is frequently an unwanted intermediate phase in the conversion of nanoparticulate amorphous alumina into nanoparticulate α -Al₂O₃. γ -Al₂O₃ has a relatively disordered structure, but usually requires temperatures in the order of 1100 °C to transform completely to the stable α -Al₂O₃ phase [2].

Dispersion of cations in a polymer matrix has been widely used as a “chimie douce” method for the production of oxide materials at low temperatures. The “Pechini” process, where citric acid and ethylene glycol are co-polymerized to form a resin is a particularly common variant [3]. A highly acidic sucrose solution can self-polymerize or cross-link with polyvinyl alcohol (PVA) to form a heavier and more 3 dimensional resin [4]. The charred polymer also acts as a fuel during calcination, raising the local temperature briefly to much higher temperatures than the equilibrium temperature in the furnace.

The extent of cation dispersion in a matrix has been seen to affect phase composition and crystallite size in other systems [3]. Consequently a study was undertaken to ascertain the effect of drastically increasing the dispersion of Al³⁺ cations in the matrix by increasing the sucrose content. This would be expected to increase the surface area of the material, but as the sucrose : Al³⁺ molar ratio is greater than 18 : 1, calcining at 600 °C should still produce α -Al₂O₃ according to the hypothesis of Das *et al.* [1].

The resin was produced by adding 250 ml of 10 M sucrose solution acidified to a pH of approximately 1 with nitric acid, to 3.75 g of Al(NO₃)₃ · 9H₂O. This formulation yielded a 250 : 1 molar ratio. The intimate mixture was caramelized on a hot plate at approximately 250 °C to reduce the aqueous solution to a thick syrup. Afterwards, it was placed in an air-circulating oven at 200 °C for 18 h resulting in a dehydrated charred resin. The resulting carbon-rich precursor was calcined in a muffle furnace at 600 °C for 24 h to produce the aluminum oxide material.

Samples of this material were further calcined in a zirconia crucible in air at temperatures of 1050, 1150 and 1250 °C to examine the ease of α -Al₂O₃ formation from this very high surface area γ -Al₂O₃.

X-ray diffraction data were obtained using a Bruker D8 diffractometer equipped with a HISTAR 2-dimensional area detector at a sample-detector distance of 15.3 cm. The tube angle was fixed at 10° using a

1 mm diameter snout collimator, and frames taken using Cu K α radiation at detector angles of 15, 30 and 45° for 30 min durations. The samples were mounted on a quartz zero background holder. 1-D powder patterns were obtained by integrating the 2-D data across a fixed chi range, and merging the three resulting patterns into one. The instrument broadening function was determined by obtaining frames from the NIST 660a LaB₆ standard, and crystallite size obtained by peak fitting with the Bruker TOPAS software [5].

Scanning electron microscope (SEM) micrographs were taken of the alumina using a Cambridge Stereoscan 250. Samples were prepared with carbon adhesives on aluminum stubs, and then sputter-coated with gold. The surface area values of the powders were obtained using BET analysis with nitrogen gas as the adsorbate. A Quantachrome Quantasorb system was used for the sorption measurements.

After calcination of the charred precursor at 600 °C, the material obtained was a white, fluffy powder with a very low density. On examination of this material by SEM, a foil-like microstructure (Fig. 1) was observed. This microstructure probably resulted from preferential growth around the resin pore surfaces. Attempts to resolve the individual particles with a high resolution Field emission gun (FEG) SEM tentatively suggested a particle size of 10–20 nm, however it was not possible to obtain well-resolved images due to charging of the sample.

The surface area of the material was found to be approximately 290 m²/g, as opposed to the 194 m²/g reported by Das *et al.* [1]. Given the greater organic content in this precursor, this increase was not unexpected, but may be of interest given the use of γ -Al₂O₃ as a catalyst support.

X-ray diffraction of the 600 °C material yielded a poor crystalline pattern (Fig. 2), which could be assigned as γ -Al₂O₃. Firing at 1050 °C for 30 min yielded a more ordered γ -Al₂O₃ pattern, while firing for 60 min gave rise to a number of spots corresponding to a few crystallites of α -Al₂O₃. The significance of spots in a frame is discussed below. Increasing the temperature to 1150 °C for 60 min led to the formation of a two phase mixture of γ -Al₂O₃ and nanocrystalline α -Al₂O₃ powder with a 17.5 nm crystallite size. Firing at 1250 °C for 60 min led to the formation of 25 nm α -Al₂O₃ with β -Al₂O₃ present as a minor phase. β -Al₂O₃ does not exist as a pure alumina polymorph [6], so the presence of β -Al₂O₃ could be due to trace sodium impurities, producing phases such as NaAl₁₁O₁₇.

Figure 1 SEM micrograph of the 600 °C calcined "as-prepared" alumina.

The transition to α - Al_2O_3 seemed to be more sluggish in this material than has been observed by other workers [7, 8]. This was not totally unexpected, as the material density of γ - Al_2O_3 has been shown to affect the transition, i.e. dense pellets transform to α - Al_2O_3 faster than a loose powder [9]. There are possible indications of the presence of the δ - Al_2O_3 and/or θ - Al_2O_3 phases in the 1050 and 1150 °C calcined materials from some peak broadening and "shoulders". These known intermediate phases, often seen in the γ - to α - Al_2O_3 phase transition, have similar diffraction patterns to γ - Al_2O_3 , but the experimental reflections are very diffuse, making it very difficult to assign peaks unambiguously.

Use of the area detector facilitated observation of a small number of large isolated nucleating crystallites that would probably have been overlooked by conventional powder diffraction. Such spots appear in a 2-D

frame effectively as a single crystal reflection spot. Rotating the sample moves the spot, while remounting the sample can give rise to different reflections. For example, a spot corresponding to the 52.6° [024] α - Al_2O_3 reflection was observed in the as-prepared powder as seen in Fig. 3. In this case the spot was within the range of chi integration, so a small reflection is present in Fig. 2 at the corresponding 2 theta. For comparison, Fig. 4 shows the 23–56° 2 theta frame of the 1150 °C calcined powder which shows a uniform, untextured powder with a good powder average.

In summary, a dispersed alumina with a very high surface area has been prepared by complexation and

Figure 2 1-D X-ray diffraction patterns of the "as-prepared" and calcined materials.

Figure 3 2-D frame from the as-prepared sample in the range 38–70° 2 theta.

Figure 4 2-D frame from the 1150 °C calcined sample in the range 23–56° 2 theta, showing the uniform sharp α -Al₂O₃ arcs with the more diffuse γ -Al₂O₃ also visible. There are no visible spots indicating a uniform sample.

dispersion in a sucrose solution, which was then charred and calcined to produce the final product. The material calcined at 600 °C in this study differed from that described by Das *et al.* [1], in that it was poor crystalline γ -Al₂O₃ and had a much higher surface area, although it did appear to contain isolated α -Al₂O₃ crystallites. These differences may be explained by the use of a much higher sucrose to cation ratio. The resin in this study was produced using more uniform heating than that attainable using a hotplate alone, which in turn produced a more homogeneous resin. The hypothesis proposed by Das *et al.* [1] is not supported by the re-

sults presented here, but the synthesis conditions used were far removed (over 1 order of magnitude increase in the sucrose excess) from those used by Das *et al.* The sluggish transition between γ - and α -Al₂O₃ may also be attributed to the extremely low density of the material [9]. Heating at 1050 °C yielded an increasing number of diffraction spots from α -Al₂O₃ crystallites, conventional α -Al₂O₃ powder diffraction arcs appearing at 1150 °C. Calcination at 1250 °C resulted in a fluffy powder of α -Al₂O₃ with a crystallite size of approximately 25 nm.

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References

1. R. N. DAS, A. BANDYOPADHYAY and S. BOSE, *J. Amer. Cer. Soc.* **84** (2001) 2421.
2. I. LEVIN and D. BRANDON, *ibid* **81** (1998) 1995.
3. P. A. LESSING, *Ceramic Bulletin* **68** (1989) 1002.
4. R. N. DAS, *Materials Letters* **47** (2001) 344.
5. User Manual, TOPAS V2.0: General profile and structure analysis software for powder diffraction data, Karlsruhe, Germany, (2000).
6. A. R. WEST, in "Solid State Chemistry and Its Applications" (Wiley, Chichester, 1984) p. 467.
7. A. JANBEY, R. K. PATI, S. TAHIR and P. PRAMANIK, *Journal of the European Ceramic Society* **21** (2001) 2285.
8. Y. WU, Y. ZHANG, G. PEZZOTTI and J. GUO, *Materials Letters* **52** (2002) 366.
9. J. -P. AHN, J. -K. PARK and H. -W. LEE, *Nanostructured Materials* **11** (1999) 133.

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