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The synthesis of nanoparticulate $\alpha$-$\text{Al}_2\text{O}_3$ at 600 °C using a sucrose-based polymer dispersion technique was reported recently by Das et al. [1]. This is of interest, as $\gamma$-$\text{Al}_2\text{O}_3$ is frequently an unwanted intermediate phase in the conversion of nanoparticulate amorphous alumina into nanoparticulate $\alpha$-$\text{Al}_2\text{O}_3$. $\gamma$-$\text{Al}_2\text{O}_3$ has a relatively disordered structure, but usually requires temperatures in the order of 1100 °C to transform completely to the stable $\alpha$-$\text{Al}_2\text{O}_3$ 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 sucrose content. This would be expected to increase the surface area of the material, but as the sucrose : Al ratio is greater than 18 : 1, calcining at 600 °C should still produce $\alpha$-$\text{Al}_2\text{O}_3$ 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(NO$_3$)$_3$ · 9H$_2$O. This formula 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 aluminium 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 $\alpha$-$\text{Al}_2\text{O}_3$ formation from this very high surface area $\gamma$-$\text{Al}_2\text{O}_3$.

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$_\alpha$ 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 LaB$_6$ 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 aluminium stubs, and then sputter-coated with gold. The surface area values of the powders were obtained using BET analysis with nitrogen gas as the absorbent. 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 m$^2$/g, as opposed to the 194 m$^2$/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 $\gamma$-$\text{Al}_2\text{O}_3$ as a catalyst support.

X-ray diffraction of the 600 °C material yielded a poor crystalline pattern (Fig. 2), which could be assigned as $\gamma$-$\text{Al}_2\text{O}_3$. Firing at 1050 °C for 30 min yielded a more ordered $\gamma$-$\text{Al}_2\text{O}_3$ pattern, while firing for 60 min gave rise to a number of spots corresponding to a few crystallites of $\alpha$-$\text{Al}_2\text{O}_3$. 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 $\gamma$-$\text{Al}_2\text{O}_3$ and nanocrystalline $\alpha$-$\text{Al}_2\text{O}_3$ powder with a 17.5 nm crystallite size. Firing at 1250 °C for 60 min led to the formation of 25 nm $\alpha$-$\text{Al}_2\text{O}_3$ with $\beta$-$\text{Al}_2\text{O}_3$ present as a minor phase. $\beta$-$\text{Al}_2\text{O}_3$ does not exist as a pure alumina polymorph [6], so the presence of $\beta$-$\text{Al}_2\text{O}_3$ could be due to trace sodium impurities, producing phases such as NaAl$_2$O$_4$.7.
The transition to $\alpha$-$\text{Al}_2\text{O}_3$ 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 $\gamma$-$\text{Al}_2\text{O}_3$ has been shown to affect the transition, i.e. dense pellets transform to $\alpha$-$\text{Al}_2\text{O}_3$ faster than a loose powder [9]. There are possible indications of the presence of the $\delta$-$\text{Al}_2\text{O}_3$ and/or $\theta$-$\text{Al}_2\text{O}_3$ phases in the 1050 and 1150 $^\circ$C calcined materials from some peak broadening and “shoulders”. These known intermediate phases, often seen in the $\gamma$- to $\alpha$-$\text{Al}_2\text{O}_3$ phase transition, have similar diffraction patterns to $\gamma$-$\text{Al}_2\text{O}_3$, 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 $^\circ$[024] $\alpha$-$\text{Al}_2\text{O}_3$ 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 $^\circ$ 2 theta frame of the 1150 $^\circ$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...
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 results 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

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