An investigation of commercial gamma-Al$_2$O$_3$ nanoparticles

Y Rozita$^{1,2}$, R Brydson$^1$ and A J Scott$^1$

$^1$ Institute for Materials Research, School of Process, Environmental and Materials Engineering, University of Leeds, Leeds LS2 9JT, UK
$^2$ Universiti Pendidikan Sultan Idris, Tanjung Malim 39500, Malaysia

E-mail: pmry@leeds.ac.uk

Abstract. We present an analysis of the morphology and crystal structure of commercial gamma-alumina nanoparticles. Characterisation was carried out with a combination of several techniques such as transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), selected area electron diffraction (SAED), in parallel with X-ray powder diffraction (XRD). TEM analysis of crystallite size and structure is in good agreement with XRD. HRTEM showed evidence for surface reconstruction on facetted cubeoctahedral nanoparticles. This is similar to results observed for cubeoctahedral nanoparticles of magnetite Fe$_3$O$_4$.

1. Introduction
Gamma-Al$_2$O$_3$ is isostructural with gamma-Fe$_2$O$_3$ and perhaps the most important nanomaterial used as a support for metal catalysts. It has been considered as one of the most promising advanced materials for a variety of applications due to its distinctive chemical, mechanical and thermal properties. The high surface area to volume ratio in nanoparticles can lead to modifications in structure and properties. There is great interest in the study of the surfaces of gamma-alumina nanoparticles as their catalytic activity is closely related to the structure of exposed crystalline faces. Inasmuch as gamma-alumina is widely used as a catalyst support, its structure and properties had been the subject of numerous studies. Gamma-alumina has been conventionally described as a defect spinel (Fd$ar{3}$m) with the idealized formula Al$_{21+1/3}$O$_{32}$, where $\bullet$ denotes a vacancy [1]. Extensive reviews have reported that when gamma-Al$_2$O$_3$ is derived from amorphous aluminas, it always has a cubic lattice [2]. Both a cubic lattice [3] and a tetragonal distortion [4] are found for boehmite [AlO(OH)]- or gibbsite [Al(OH)$_3$]- derived gamma-Al$_2$O$_3$. Other studies, however, have proposed the existence of only a tetragonal structure [5]. Using TEM, Jefferson [6] found evidence for enhanced surface contrast of exposed crystalline (111) surface facets of gamma-Al$_2$O$_3$ nanoparticles and similar results were observed for cubeoctahedral nanoparticles of magnetite Fe$_3$O$_4$ [7]. The principal difficulty in analysing the gamma-alumina structure is because it does not yield single crystals suitable for a standard structural analysis [8]. This study examines two commercial gamma-aluminas using a combination of XRD, SEM and TEM.
2. Methodology and Materials

2.1. Materials

Commercial gamma-alumina nanopowders were obtained from Alfa Aesar (99.97% purity - product code 39812: batch B17U053 labelled as AA1 and batch K16104 labelled as AA2) and from Johnson Matthey (99.99% purity - product code 37212 labelled as JM) with surface areas nominally between approximately 80-150 m²/g and were used without further treatment.

2.2 Methodology

The powder samples were stored in a desiccator until they were needed. Samples were analyzed using a Panalytical X’Pert ProMPD X-ray diffractometer with a Cu Kα source and an X’cellerator detector. The diffractometer was set up to measure in step-scan mode over the 2θ range (10° - 90°), the range was chosen because it covered all the important diffraction peaks for the crystal structures to be examined. A step size or sample interval of 0.05 degrees and a scan time of 0.01°/scan were used.

The characterisation of gamma-alumina nanoparticles with transmission electron microscopy (TEM) was carried out using a Philips CM200 thermally assisted field emission gun TEM operated at 197 kV (point resolution of 0.24nm) equipped with a UTW Oxford Instruments EDX detector running ISIS software and Gatan (GIF200) imaging filter. All TEM samples were examined using standard holey carbon films supported on 400 mesh copper grids. The sizes of the nanoparticles were determined by measuring the length and width (aspect ratio) of the crystals for at least 100 particles in each sample.

3.0 Results and Discussion

XRD analysis was carried out in order to characterize the phase and crystal structure of the bulk samples. The polycrystalline diffractograms of the JM, AA1 and AA2 samples (Figure 1) were compared to an XRD standard for gamma-alumina structure JCPDS reference no. 00-010-0425 in the International Centre for Diffraction Data (ICDD) database. The diffractograms for all samples in Figure 1 display three distinct reflections at 2θ = 37.2° ± 0.1° (311 reflection), 45.6° ± 1° (400) and 66.9° ± 1° (440) which is in agreement with the database standard and also the powder XRD studies of Lippens [8]. Generally, the XRD peak positions matched with the gamma-alumina standard apart from the absence of a (111) reflection in samples JM and AA1, while only a very diffuse (111) reflection was found at 2θ = 19.4° in AA2. Additional peaks are located at 2θ = 14.3° in JM and at 2θ = 44.7° in AA2 which correspond to delta-alumina peaks. There are also four sharp peaks in all samples located at 2θ=38.5°, 44.5°, 65.0° and 78.0° (labelled with an asterix) which were assigned to aluminium peaks (reference: JCPDS no. 00-004-0787) from the sample holder and provides an internal calibration. The gamma-alumina XRD relative peak intensities are similar for the three samples but do not agree with the standard which may due to differences in site occupancies within the unit cell. The widths of the XRD peaks allow us to calculate the average crystallite size by using the Debye-Scherrer equation: the results derived from the (400) and (440) reflections being averaged. This analysis shows the average crystallite size of JM, AA1 and AA2 to be approximately 10 nm, 5 nm and 16 nm respectively. The formation of gamma-alumina is expected, because it is reported to be the most thermodynamically stable phase when the specific surface area of alumina is larger than 125m²/g, or when the crystallite size (particle diameter) is less than about 13 nm. However, the fact that different peaks give different crystallite sizes suggests that there may be more than one alumina phase present or crystal shape anisotropy (e.g. preferential growth in certain directions).

Low magnification TEM images shown in Figure 2 were used to assess any agglomeration of the nanoparticles and to allow the measurement of the crystallite size. All of the nanoparticles were found to be agglomerated, although this was least for the AA2 sample. SEM and TEM image analysis revealed that the average agglomerate size was 550 nm ± 110 nm (JM), 535 ±140 nm (AA1) and 345
nm ± 120 nm (AA2). Both samples JM and AA1 clearly revealed a mixture of spherical and faceted particles while the AA2 sample possessed a mixture of ‘long needlelike’, ‘cubic’ and also faceted particles. The average projected particle diameter was 16 nm ± 6 nm (JM), 15 nm ±10 nm (AA1) and 31 nm ± 14 nm (AA2). The crystallite sizes from the TEM analysis are in agreement with those derived from XRD traces. EDX analysis of the samples demonstrates their purity with only aluminium and oxygen being detected. The average atom% of O and Al is (62.04 and 37.96) ± 0.08 respectively in JM, (62.72 and 37.28) ± 0.05 in AA1 and (64.28 and 35.72) ± 0.04 in AA2.

Figure 1. XRD diffractograms for JM, AA1 and AA2 together with ICDD database pattern for gamma-alumina JCPDS reference no. 00-010-0425

Figure 2. Bright Field TEM images of (a) AA2 and (b) JM
Black arrows showing the faceted particles in TEM micrographs of (c) AA2 (d) JM
The crystallinity of the nanoparticles was additionally confirmed by selected-area electron diffraction (SAED), which for all three samples revealed three broad diffraction rings corresponding to the (311), (400) and (440) reflections (Figure 2) and these d-spacings are consistent with the gamma-alumina structure. Additional proof for the crystallinity of the nanoparticles was obtained by high-resolution TEM investigations. The nanoparticles were found to be agglomerated on both the carbon film and also over the edges of holes within the film, complicating the process of acquiring high resolution images as the particles of interest are often obscured by overlapping particles. However, HRTEM imaging of all samples found evidence for surface reconstruction on single crystal facetted cubeoctahedral nanoparticles. The enhanced contrast is shown in figure 3 for the AA2 sample and was found to occur on facets that terminate with (111) planes \( \{d_{111}= 4.55\text{Å}\} \) and (400) planes \( \{d_{400}= 1.99\text{Å}\} \), the latter being a (100) surface. The angle between the (111) and (100) faces is \( \approx 55^\circ \). This enhanced contrast was similar to enhanced contrast observed at cation-terminated (111) surfaces of gamma-Al_2O_3 [6] and magnetite Fe_3O_4 [6, 7]. The difference in the scattering powers of oxygen and aluminium implies that the observed enhanced contrast at the (111) surface facets could be explained if the surface is cation-terminated with few or no surface oxygen atoms. Assuming that the enhanced surface contrast at the surfaces of the nanoparticles within the micrographs is a result of additional cations, in this case Al^{3+} ions from within the bulk of the nanoparticles, a disordered vacancy-containing layer should be apparent in the images just back from the edge. This defect structure is observed in TEM micrographs taken in [6, 7] and is also perhaps visible in Figure 3. The presence of excess cations at the nanoparticle’s surface is a modification of the structure from the bulk and a reconstructed surface may have significant implications for the role of gamma-alumina in enhancing the dispersion of fine metal particles in catalysts [6].

![Figure 3. HRTEM image of AA2 with black arrows showing the enhanced surface contrast on facets that terminate with (111) planes and (100) planes at the end of the edges and a disordered sub surface apparent in the image just back from the edges. White arrow showing ordered lattice fringes.](image)

References

[1] Verwey E J W 1935 Z. Krystallogr. 91 317
[2] Levin L A, Bendersky D G and Brandon M R 1997 Acta Mater. 45 3659
[3] Zhou S and Snyder R. L. 1991 Acta Crystallogr. 47 617
[4] Wilson S J 1979 J. Solid State Chem. 30 247
[5] Paglia G, Buckley C E, Rohl A L, Hart R D, Winter K, Studer A J, Hunter B A and Hanna J V 2004 Chem. Mater. 16 220
[6] Jefferson D.A 2000 Phil.Trans.R. Soc. Lond. A 358 2683
[7] Lovely G R, Brown A P, Brydson R, Kirkland A I, Meyer R R, Chang L, Jefferson D A, Falke M and Bleloch A 2006 Applied Physics Lett. 88 93124
[8] Lippens B C and Boer J H 1964 Acta Cryst. 17 1312