DOI: 10.1002/anie.201100668

Nanoparticles

Rapid One-Step Low-Temperature Synthesis of Nanocrystalline γ-Al_2O_3**

*Nina Lock, Mogens Christensen, Kirsten M. Ø. Jensen, and Bo B. Iversen**

γ-Al_2O_3 is a very widely used catalyst support for commercial applications, for example, in petrochemical industries and for petroleum refining.[1] The material is cheap and it also has a broad range of other applications, including use in mechanical parts and insulators because of its chemical, mechanical, and thermal properties.[2] For these reasons, synthesis and characterization of γ-Al_2O_3 is extremely important both in industry and academia. Facile low-temperature synthesis of γ-Al_2O_3 has been a challenge for a long time, and the interest can be exemplified by noting that more than 4500 papers have been published on γ-Al_2O_3 in the past decade alone.

Most batch-type synthesis methods involve two reaction steps to prepare γ-Al_2O_3. Typically, gibbsite (γ-$Al(OH)_3$), boehmite (γ-AlOOH), or an amorphous compound is first synthesized under hydrothermal or solvothermal conditions from aluminum chloride, nitrate, acetylacetonate (acac), or an alkoxide.[3] Other synthesis approaches can also be used for the initial reaction step. These include surfactant-stabilized reactions to obtain a nanocrystalline product or synthesis in supercritical CO_2/ethanol mixtures. In a second reaction step the intermediate product is calcined, typically at 500–850 °C for a few hours, which produces γ-Al_2O_3.[4] In 2007 phase-pure γ-Al_2O_3 was prepared at 200 °C over 6 days in a solvothermal reaction using $Al(acac)_3$ in benzylamine.[5] This was claimed to be the lowest temperature at which crystalline γ-Al_2O_3 had been synthesized. The single source precursor approach is another molecular method that has been used to synthesize Al/Al_2O_3 mixtures. In 2008 such mixtures resulted by heating *tert*-butoxyalane, $(CH_3)_3COAlH_2$, under anaerobic conditions and reduced pressure at temperatures higher than 300 °C.[6] In recent years, attention has also focused on continuous-flow synthesis as this allows production of large material quantities within a short time.[7] Amorphous Al_2O_3 was obtained in a flow reaction in supercritical NH_3/methanol using an $Al(acac)_3$ precursor.[7a] Mixtures of AlOOH and γ-Al_2O_3 were obtained under flow in supercritical water ($T > T_c = 374\,°C$, $p > p_c = 221$ bar) using aluminum nitrate as precursor.[8] In 2008 the first one-step synthesis of phase-pure γ-Al_2O_3 using this procedure was reported. This product was obtained under continuous flow in supercritical water at the high temperature of 500 °C; at lower temperature AlOOH/γ-Al_2O_3 mixtures were produced.[2a]

Herein, a facile low-temperature synthesis method for γ-Al_2O_3 is presented. The synthesis proceeds from $Al(IP)_3$ (IP = isopropoxide) in 2-propanol/water mixtures and is done at temperatures from as low as 250 °C and at a pressure of 100 bar. In situ synchrotron powder X-ray diffraction (PXRD) analysis in a batch reactor was used as the key tool to develop the new synthesis method. The parameter space for the chemical system was explored, and the particle nucleation and growth was followed. Subsequently, proof-of-principle continuous flow synthesis was used to produce γ-Al_2O_3 at a mixing point temperature of 215 °C and a pressure of 200 bar in a laboratory reactor.

Figure 1 a shows the time evolution of in situ PXRD data collected at 300 °C/100 bar. The first 200 frames are shown, and the onset of the supercritical state is clearly seen as a

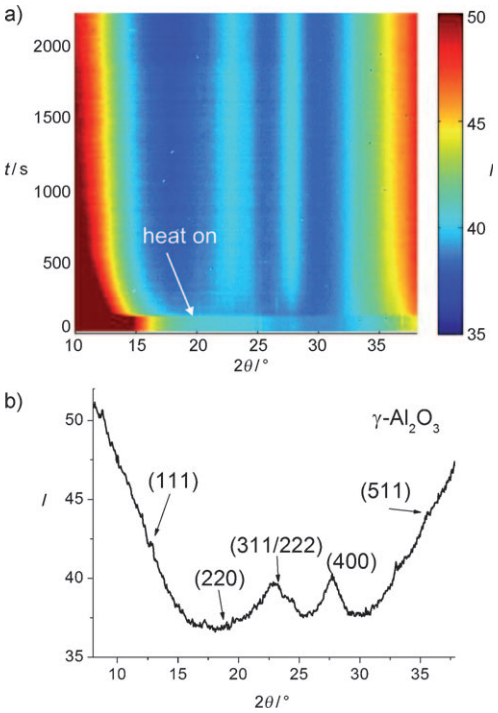

Figure 1. a) In situ PXRD data ($\lambda = 0.95$ Å) for a batch-type reaction carried out at 300 °C/100 bar (the first 200 data sets are shown). The background changes dramatically upon heating. No crystalline phases are formed prior to γ-Al_2O_3. b) PXRD data from the last frame, in which γ-Al_2O_3 is indexed with JCPDS card no. 29-0063.

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[*] Dr. N. Lock, Dr. M. Christensen, K. M. Ø. Jensen,
Prof. Dr. B. B. Iversen
Center for Materials Crystallography and Center for Energy Materials
Department of Chemistry and iNANO, Aarhus University
8000 Aarhus C (Denmark)
E-mail: bo@chem.au.dk

[**] We gratefully acknowledge beamtime obtained at MAX-lab and experimental support by Dr. Dörthe Haase. The work was supported by the Danish Strategic Research Council (Center for Energy Materials), the Danish National Research Foundation (Center for Materials Crystallography), and the Danish Research Council of Nature and Universe (Danscatt).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201100668.

dramatic change in the background intensity. The reactions were carried out in a purpose-built reactor (see the Supporting Information)[9] using a precursor mixture containing 7 vol% water. The last powder pattern in the data series collected at 300 °C/100 bar is shown in Figure 1 b. In situ PXRD data for an identical experiment (7 vol% water) carried out at 250 °C/100 bar also reveal γ-Al_2O_3 formation. The time evolution of the width of the (400) γ-Al_2O_3 Bragg reflection at 27.5° was determined by fitting a Lorentz function to the peak. The instrumental broadening, given by the width of a standard LaB_6 reflection, was subtracted, and the corresponding particle size was determined using the Scherrer equation. Figure 2 shows the γ-Al_2O_3 crystallite size in the direction along the [400] direction as a function of time. The experiments suggest a critical crystalline primary particle size of 1.5–2.0 nm or less, as no particles smaller than 1.5–2.0 nm were observed in these powder diffraction experiments. The thermodynamic primary particle size, however, may be smaller than 1.5 nm, but simply not detectable by this technique. The 1.5–2.0 nm particles formed after 56 s at 300 °C/100 bar and after 256 s at 250 °C/100 bar. The particle growth rate decreases after a reaction time of approximately 500 s, and the particle size after 2000 s is 2.5–3.0 nm and 3.5–4.0 nm, respectively, for particles formed at 250 °C/100 bar and 300 °C/100 bar (see the Supporting Information). The zero point in time in Figure 2 corresponds to the time the heat was turned on (as also shown in Figure 1) for the 300 °C/100 bar reaction. By ascribing the full peak width to size broadening, the size of the alumina particles is likely to be underestimated, as strain or defect broadening may contribute to the peak width. The γ-Al_2O_3 structure is known to contain defects,[10] but size broadening exceeds the contribution from strain broadening in small particles. Instead of considering the particle sizes shown in Figure 2 as absolute sizes, they should be considered as relative sizes, as the error bars may not reflect the actual uncertainty of the particle size. Application of a spherical size model is appropriate for small particles. The PXRD data are very similar to those reported by Noguchi et al., who prepared 6 nm particles in supercritical water according to TEM.[2a] Plots of the cell parameter, extracted from the position of the (400) reflection, as a function of the particle size are shown in Figure 3 for the 300 °C/100 bar reaction (see also the Supporting Information). There is a clear correlation between the sizes of the unit cell and the particle. Effects of the particle size on the cell parameters and lattice symmetry have been observed for several other oxides including Fe_3O_4 for which a similar trend is observed.[11a] For Al_2O_3 and Fe_2O_3, the unit cell, phase, and size are correlated.[11b] A general proposed physical explanation is that going towards smaller particles corresponds to applying a negative pressure on the lattice, resulting in expansion of the unit-cell volume.[11]

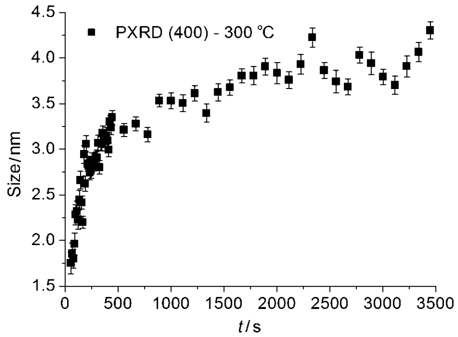

Figure 2. Spherical size of γ-Al_2O_3 synthesized at 300 °C/100 bar. In the early stage of the experiment, fits were made to all data sets, whereas only one in ten data sets were analyzed in the slow-growth period.

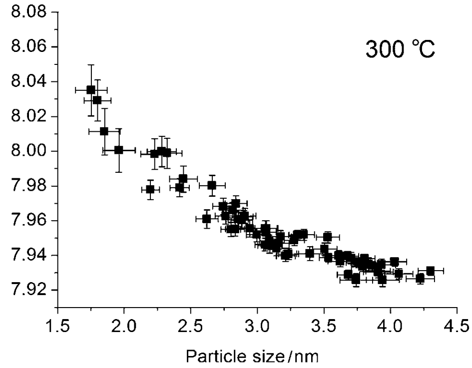

Figure 3. The cubic unit-cell parameter of γ-Al_2O_3 as a function of the particle size for the reaction at 300 °C/100 bar. In the early stage of the experiment fits were made to all data sets, whereas only one in ten data sets were analyzed in the slow-growth period.

The concentration of water has a remarkable influence on the reaction, as no crystalline product is formed in the absence of water. In contrast, AlOOH was formed in an in situ experiment at 300 °C/100 bar using a precursor mixture with a total water concentration of 13 vol% (Supporting Information). Thus, the reaction window for obtaining phase-pure γ-Al_2O_3 is narrow. This is similar to the synthesis of $BaTiO_3$, which is also strongly influenced by the water concentration.[12]

Proof-of-principle continuous-flow synthesis of γ-Al_2O_3 was carried out on a home-built reactor using a mixing point temperature of 215 °C and at a pressure of 200 bar. Figure 4

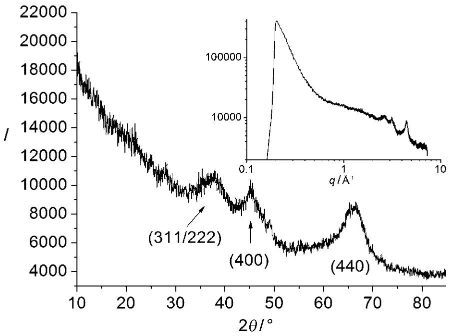

Figure 4. Ex situ PXRD data ($Cu_{K\alpha_1}$ radiation, $\lambda = 1.54$ Å) collected on a sample prepared at 215 °C/200 bar in a continuous-flow reactor using 0.1 M $Al(IP)_3$ in 2-propanol as precursor and 2-propanol with 5 vol% water as solvent. The inset is a double logarithmic plot of the intensity as a function of q including the SAXS region. The intense SAXS signal reveals globular particles with smooth surfaces. The beamstop causes the abrupt intensity decrease on the low-q site of the SAXS signal.

shows ex situ PXRD data collected on the 215 °C/200 bar sample, for which the Bragg reflections are indexed according to the γ-Al_2O_3 JCPDS card no. 29-0063. The broad peaks suggest small and imperfect crystals. The extremely intense small-angle X-ray scattering (SAXS) signal in the inset of Figure 4 is characteristic for globular nanosized particles with a smooth surface, as the Porod region 0.2–0.4 $Å^{-1}$ nearly follows a q^{-4} dependency (see the Supporting Information).

On the basis of observations from our in situ experiments, a formation mechanism can be proposed. Dry AlOOH is thermodynamically favored over alumina at temperatures below 470 °C, above which it dehydrates to γ-Al_2O_3.[13] Under hydrothermal conditions, however, the conversion from AlOOH to different alumina phases occurs at higher temperatures.[14] In a supercritical 2-propanol/water mixture, the thermodynamics and kinetics with respect to phase stability are expected to differ from those of dry powders and those under hydrothermal conditions. Furthermore, they are likely to be pressure-dependent. Since the precursor is an alkoxide in an alcohol/water mixture, we suggest that $Al(IP)_3$ is initially hydrolyzed to an $Al(OH)_3$ gel, which subsequently dehydrates to alumina similarly to the dehydration steps proposed by Noguchi et al. for γ-Al_2O_3 in supercritical water.[2a] It should be stressed that we do not have direct experimental evidence for the details of the suggested reaction mechanism, which is summed up in Equations (1–3).

$$\mathrm{Al(IP)_3 + 3\,H_2O \rightarrow Al(OH)_3 + 3\,HIP} \tag{1}$$

$$\mathrm{Al(OH)_3 \rightarrow AlOOH + H_2O} \tag{2}$$

$$\mathrm{AlOOH \rightarrow {}^1\!/_2\,\gamma\text{-}Al_2O_3 + {}^1\!/_2\,H_2O} \tag{3}$$

If the water concentration is too high, the reaction essentially stops after Equation (2). If the alumina formation follows this mechanism, Equation (1) is rate-determining, as no crystalline $Al(OH)_3$ is formed. Future studies are needed to cover the parameter window for alumina formation and to determine if alumina is the kinetic or the thermodynamic product formed using the $Al(IP)_3$ synthesis.

In summary, the present work introduces a novel low-temperature and low-pressure synthesis method of nanocrystalline γ-Al_2O_3. In situ PXRD studies suggest a reaction mechanism that does not involve crystalline intermediates. The synthesized nanocrystalline particles show changes in the unit-cell size with particle growth. As proof of concept for potential large-scale production, γ-Al_2O_3 was prepared at low temperature in a continuous-flow reactor using $Al(IP)_3$ in 2-propanol without subsequent calcination.

Experimental Section

In situ powder X-ray diffraction data were collected at the wiggler beamline I711 at MAX-lab in Sweden ($\lambda = 0.95$ Å). The reactions were carried out in a purpose-built reactor with fast heating, reaching its set point temperature within 10 s.[9] Water was added to a 1.5 M suspension of $Al(IP)_3$ in 2-propanol to obtain a total concentration of 7 vol % water. The alumina formation and growth was monitored by continuous collection of PXRD data on a MAR CCD detector. An exposure time of 4.0 s and subsequent readout resulted in a time resolution of 11.1 s.

The pressurized reactor used for continuous flow synthesis has T-piece mixing and a vertical reaction tube (see the Supporting Information). A hot solvent mixture of 2-propanol with 5 vol % water was combined with the reactant, a 0.1 M suspension of $Al(IP)_3$ in 2-propanol, in a volume ratio of 1:1. The solvent and the reaction tubes were kept at 375 °C leading to a mixing point temperature of 215 °C.

Received: January 26, 2011

Keywords: alumina · nanoparticles · supercritical fluids · X-ray diffraction

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