Effect of particle size on phase transitions in metastable alumina nanoparticles: A view from high-resolution solid-state $^{27}$Al NMR study

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Abstract

Detailed knowledge of the atomic structures of diverse metastable/stable polymorphs in alumina nanoparticles with varying particle size is essential to understand their macroscopic properties and their phase transition behaviors. In this study, we report high-resolution solid-state $^{27}$Al 2D triple-quantum (3Q) magic-angle spinning (MAS) and 1D MAS nuclear magnetic resonance (NMR) spectra for alumina nanoparticles with varying temperature and particle size with an aim to explore the nature of phase transitions in alumina nanoparticles. Although the $^{27}$Al MAS NMR spectra of alumina nanoparticles cannot fully resolve all the crystallographically distinct Al sites for metastable aluminas such as $\gamma$-, $\delta$-, and $\theta$-$\text{Al}_2\text{O}_3$, the simulation of $^{27}$Al MAS NMR spectra collected at different magnetic fields following the Czjzek model allows us to obtain the quantitative fractions of alumina polymorphs in nanoparticles and the NMR characteristics of their Al sites. The $^{27}$Al 3QMAS NMR spectra resolved crystallographically distinct [6]Al and [4]Al sites in ($\gamma$, $\delta$)- and $\theta$-$\text{Al}_2\text{O}_3$ in the isotropic dimension for the first time. The fraction of $\theta$-$\text{Al}_2\text{O}_3$ gradually increases up to ~1473 K at the expense of a decrease in ($\gamma$, $\delta$)-$\text{Al}_2\text{O}_3$. The onset of formation of $\alpha$-$\text{Al}_2\text{O}_3$ from metastable aluminas is observed above ~1493 K. Several phase transitions in alumina nanoparticles observed in the current study include, $\gamma$, $\delta$ $\rightarrow$ $\theta$-$\text{Al}_2\text{O}_3$, $\gamma$, $\delta$ $\rightarrow$ $\alpha$-$\text{Al}_2\text{O}_3$, and $\theta$ $\rightarrow$ $\alpha$-$\text{Al}_2\text{O}_3$. Although the phase transition $\gamma$, $\delta$ $\rightarrow$ $\theta$-$\text{Al}_2\text{O}_3$ occurs gradually with increasing annealing temperature from 873 K to 1473 K, the phase transitions $\gamma$, $\delta$ $\rightarrow$ $\alpha$-$\text{Al}_2\text{O}_3$ and $\theta$ $\rightarrow$ $\alpha$-$\text{Al}_2\text{O}_3$ occur dramatically within a narrow temperature range between 1473 K and 1573 K. The observed difference in temperature range (gradual vs. dramatic) for phase transition $\gamma$, $\delta$ $\rightarrow$ $\theta$-$\text{Al}_2\text{O}_3$ and $\gamma$, $\delta$, $\theta$ $\rightarrow$ $\alpha$-$\text{Al}_2\text{O}_3$ originates from the different structural disorder in the metastable aluminas (i.e., $\gamma$-, $\delta$-, $\theta$-) and $\alpha$-$\text{Al}_2\text{O}_3$. The effect of particle size on the phase transition ($\gamma$, $\delta$) $\rightarrow$ $\theta$-$\text{Al}_2\text{O}_3$ between 298 K and ~1473 K is not observed significantly. On the other hand, the transition temperature for $\gamma$, $\delta$, $\theta$ $\rightarrow$ $\alpha$-$\text{Al}_2\text{O}_3$, where the 50 % for alumina is $\alpha$-$\text{Al}_2\text{O}_3$, apparently
increases as the particle size increases (as evidenced by TEM observation), indicating a larger energy penalty for phase transitions into $\alpha$-Al$_2$O$_3$ in larger alumina nanoparticles. This could be due to higher surface energy of $\theta$-Al$_2$O$_3$ than that of $\alpha$-Al$_2$O$_3$ and/or the fact that transition from $\theta$-Al$_2$O$_3$ to $\alpha$-Al$_2$O$_3$ is kinetically favored for smaller nanoparticles. The mechanistic details of phase transitions among alumina polymorphs provided in the current study yield insights into the nature of the phase transition mechanisms for other oxide nanoparticles ubiquitous in the earth’s surface environment.

1. Introduction

The atomic structure of alumina and the phase transition mechanism have long been investigated in many experimental and theoretical studies due to its fundamental interest as one of the simplest covalent oxides (Fitzgerald et al., 1997; Gan et al., 2009; Hagaman et al., 2010; John et al., 1983; Kryukova et al., 2000; Levin and Brandon, 1998; MacKenzie and Smith, 2002; O’Dell et al., 2007; Ollivier et al., 1997; Perander et al., 2007; Pinto et al., 2004; Repelin and Husson, 1990). Alumina also has diverse industrial uses, for example, in catalysts, adsorbents, and gate microelectronic devices (e.g., Kresse et al., 2005). Given these important roles of alumina, the atomic structures of diverse alumina polymorphs are relatively well known (Levin and Brandon, 1998 and references therein). However, the nature of phase transitions among alumina polymorphs is not fully understood due to manifested configurational disorder and their pronounced metastability (see below for further discussion), which leads to broad ranges of transition temperatures rather than a single well-defined transition temperature between polymorphs. Additionally, the effect of particle size on phase transitions among metastable phases in nanoparticles has not been fully investigated. Because the large surface area of nanoparticles plays an essential role in controlling their phase transition behaviors, it is necessary to explore the effect of particle size on the transition
temperature of alumina nanoparticles. The objective of this study is to investigate the effect of particle size on the nature of phase transitions among alumina polymorphs including metastable phases in alumina nanoparticles.

In addition to the well-known stable $\alpha$-Al$_2$O$_3$ with a corundum structure, diverse metastable polymorphs have also been reported. These include $\gamma$-, $\delta$-, $\theta$-, $\chi$-, and $\eta$-Al$_2$O$_3$, and are often called metastable aluminas with their stability fields depending on the annealing temperature, time, and types of precursor (Levin and Brandon, 1998 and references therein). For instance, $\gamma$-AlOOH (i.e., boehmite) transforms to $\alpha$-Al$_2$O$_3$ via $\gamma$-, $\delta$-, and $\theta$-Al$_2$O$_3$. The transition temperatures between $\gamma$- and $\delta$-Al$_2$O$_3$, between $\delta$- and $\theta$-Al$_2$O$_3$, and between $\theta$- and $\alpha$-Al$_2$O$_3$ are ~ 700–800, 900–1000, and 1000–1100°C, respectively (Levin and Brandon, 1998; Santos and Santos, 1992 and references therein). Extensive studies of temperature-induced phase transitions of alumina have revealed that the temperature of the transition from metastable alumina such as $\gamma$- and $\theta$-Al$_2$O$_3$ into stable $\alpha$-Al$_2$O$_3$ varied with the particle size (Bokhimi et al., 2001; Gan et al., 2009), defects density (Liu et al., 2005), and presence of seeds (Nordahl and Messing, 2002; Rajendran, 1994).

In particular, the particle size (i.e., surface area) of alumina nanoparticles has been identified as one of the crucial factors controlling the relative stability of $\gamma$-Al$_2$O$_3$ and its phase transitions (McHale et al., 1997a; Navrotsky, 2001). The effect of particle size on the nature of the phase transitions among alumina polymorphs is due to an increased role of the surface energy with decreasing particle size (e.g., Navrotsky, 2001). An alumina polymorph with lower surface energy becomes more stable than one with higher surface energy as the particle size decreases (i.e., the surface area increases). A molecular dynamics simulation demonstrated that surface energy of $\alpha$-Al$_2$O$_3$ is larger than that of $\gamma$-Al$_2$O$_3$, which is consistent with calorimetric data for nanocrystalline alumina (Blonski and Garofalini, 1993; McHale et al., 1997b). Additional differential thermal analysis for phase transition from boehmite into $\alpha$-
Al₂O₃ showed that transition temperature for $\gamma \rightarrow \alpha$-Al₂O₃ decreases from 1565 K to 1465 K as the crystallite size of boehmite decreases (Bokhimi et al., 2001). The systematic, spectroscopic study of the effect of particle size of $\gamma$-Al₂O₃ nanoparticles and other alumina polymorphs remains to be explored.

The atomic structure and phase transitions of alumina polymorphs have been studied mainly using X-ray diffraction (XRD), transmission electron microscopy (TEM), and solid-state nuclear magnetic resonance (NMR) spectroscopy. XRD and TEM studies have successfully provided the atomic structure of crystalline alumina of the $\gamma$-, $\theta$-, and $\alpha$-Al₂O₃, (Figure 1). These studies using TEM and XRD studies have furthered our understanding of the atomic structure and phase transition mechanism of metastable aluminas (Gan et al., 2009; Levin et al., 1997; Lin et al., 2004; Macedo et al., 2007; Ollivier et al., 1997; Yang et al., 1988). Its application to heterogeneous metastable aluminas can, however, be limited because the XRD patterns for those alumina phases are not well distinguished due to low crystallinity and significant degree of disorder in the metastable aluminas, (e.g., $\gamma$- and $\delta$-Al₂O₃). Furthermore, because the temperature ranges of stability of each metastable alumina overlap, two or more phases can coexist in a sample within a given temperature range. It is often difficult to obtain the quantitative fractions of alumina polymorphs using either XRD or TEM (Levin et al., 1997; Ollivier et al., 1997; Yang et al., 1988).

NMR spectroscopy providing short-range structures around a specific nuclide of interest has been particularly effective in exploring the atomic structure of disordered oxide materials. Previous $^{27}$Al magic-angle spinning (MAS) NMR studies have provided the atomic configuration of oxygen and aluminum atoms in crystalline alumina (Fitzgerald et al., 1997; John et al., 1983; MacKenzie and Smith, 2002; Mastikhin et al., 1981; O’Dell et al., 2007; Piedra et al., 1996) as well as amorphous alumina thin films (Lee et al., 2009b; Lee et al., 2010b). The atomic scale structure of quadrupolar nuclei (e.g., $^{27}$Al) in alumina can be described by
structurally relevant NMR parameters such as the quadrupolar coupling constant ($C_q$), asymmetry parameter ($\eta$), and isotropic chemical shift ($\delta_{iso}$). Simulation of the 1D MAS NMR spectra with these NMR parameters allows us to obtain the quantitative fraction of each phase in a sample with heterogeneous mixtures of multiple phases (as is the case for the current nanoparticles) (Ashbrook and Duer, 2006; Ashbrook and Smith, 2006; Duer, 2004; Lee and Stebbins, 2003; Lee et al., 2003; Lee and Weiss, 2008; Phillips, 2000). To confirm the NMR characteristics of Al sites in alumina polymorphs, previous $^{27}$Al NMR studies of alumina have analyzed the spinning sideband and simultaneously simulated $^{27}$Al MAS NMR spectra $\theta$- and $\alpha$-$\text{Al}_2\text{O}_3$ collected at different magnetic fields (O’Dell et al., 2007; Pecharroman et al., 1999; Perander et al., 2007; Sabarinathan et al., 2010). The analysis of spinning sideband patterns in $^{27}$Al MAS NMR spectra has yielded excellent results and confirmed the NMR parameters of Al sites in $\alpha$-$\text{Al}_2\text{O}_3$ (Pecharroman et al., 1999; Sabarinathan et al., 2010). A simulation of the central transition peak in $^{27}$Al MAS NMR spectra measured at different magnetic fields (e.g., 8.4 T and 14.1 T) also successfully obtained the NMR parameters for Al sites in $\theta$-$\text{Al}_2\text{O}_3$ (O’Dell et al., 2007). A recent study also reported the simulation of $^{27}$Al MAS NMR spectra for $\gamma$-$\text{Al}_2\text{O}_3$ using the Czjzek model that have been effective in resolving Al sites in the disordered oxides (de Lacaillerie et al., 2008; Lee et al., 2009a; Massiot et al., 2002; Neuville et al., 2004).

Recent progress in 2D triple-quantum (3Q) MAS also provide much improved resolution among the different sites for quadrupolar nuclides (e.g., $^{27}$Al, $^{17}$O) (Lee, 2005; Lee et al., 2010a; Massiot et al., 1996; Neuville et al., 2004; Stebbins et al., 2000; Stebbins et al., 1999; Tangeman et al., 2004; Xue et al., 2010). $^{27}$Al 3QMAS NMR method has been used to elucidate the atomic scale structures of a single phase of crystalline and amorphous alumina (e.g., $\gamma$-$\text{Al}_2\text{O}_3$ or $\alpha$-$\text{Al}_2\text{O}_3$) as well as aluminum (oxy)hydroxides (e.g., boehmite, bayerite, gibbsite) (Chupas et al., 2001; Damodaran et al., 2002; Hagaman et al., 2010; Lee et al., 2009b; Lee et al., 2010b), and thus it may also be useful to resolve crystallographically distinct Al sites in...
multiple phases of alumina with varying temperature. Here, we explore the atomic structure of alumina polymorphs and the effect of particle size on the nature of phase transitions in alumina nanoparticles using high-resolution solid-state NMR. The NMR characteristics as well as fractions of Al sites in metastable aluminas are obtained by simulating $^{27}$Al MAS NMR spectra measured at different magnetic fields. We also report the first $^{27}$Al 3QMAS NMR spectra of resolved alumina nanoparticles resolving alumina polymorphs including ($\gamma$, $\delta$), $\theta$- and $\alpha$-Al$_2$O$_3$. On the basis of the data from these NMR results, we provide an improved insight into the nature of phase transitions of alumina nanoparticles with emphasis on the effect of particle size.

2. Experimental Methods

2.1. Sample Preparation and Characterization

Three types of alumina nanoparticles, FA51, FA81, and FA100 (Cabot Co., SpectAl series) with surface areas of 55±10, 79±10, and 97±19 m$^2$/g, respectively, were used. The particle sizes (i.e., diameters) of the alumina nanoparticles calculated using a spherical approximation ($d = 6/S_0\rho$, where $d$ is the average particle size, $S_0$ is the specific surface area, and $\rho$ is the true density of the material) are 27, 19, and 15 nm for FA51, FA81, and FA100, respectively. Here, we refer to FA51, FA81, and FA100 as 27, 19, and 15 nm alumina nanoparticles, respectively. The alumina nanoparticles were heated for 2 h at temperatures ranging from 873 to 1473 K in a vertical tube furnace. As for standard metastable alumina, the crystalline $\gamma$-alumina was also purchased from Sigma Aldrich (product no. 544833).

2.2. X-ray Diffraction Spectroscopy and Transmission Electron Microscopy

The X-ray diffraction patterns were collected on New D8 Advance (Bruker) using Cu
Kα X-rays, a 2θ range of 15–75°, a step width of 0.02°, and a scan rate of 1°/min. The transmission electron microscopy (TEM) study was performed on a 300 kV JEM-2100 instrument (JEOL Ltd.) with a Gatan digital camera. The specimens for electron microscopy were prepared by suspending them in ethanol and placing a few droplets of the suspension on a carbon-coated film.

2.3. 27Al NMR Spectroscopy

27Al MAS spectra were collected at various magnetic fields on Varian 400 MHz (9.4 T), Bruker 500 MHz (11.7 T), and Varian 600 MHz (14.1 T) spectrometers with a triple resonance 4 mm Bruker probe, 4 mm Doty Scientific MAS probe, and 2.5 mm Varian probe, respectively. Single-pulse acquisition with a pulse length of 0.2 μs [radio frequency tip angle of about 15° for solids] was used with a recycle delay of 1 s and spinning speeds of 15 kHz at 9.4 and 11.7 T and 20 kHz at 14.1 T. The simulation of 27Al MAS spectra was performed with the Dmfit program (Massiot et al., 2002). 27Al 3QMAS NMR spectra were collected on the Varian 400 MHz (9.4 T) spectrometer using a fast amplitude modulation- (FAM-) based shifted-echo pulse sequences (1 s relaxation delay–3.0 μs pulse for 3Q excitation–t1 delay–FAM pulse train with a 0.6 μs pulse-echo delay–15 μs soft pulse for echo reconversion–t2 acquisition) with a spinning speed of 15 kHz (Kentgens and Verhagen, 1999; Madhu et al., 1999). An AlCl3 solution of 2 mol% was used as an external frequency standard.

3. Results and Discussion

3.1. Characterization of Alumina Nanoparticles

Figure 2 shows TEM images of alumina nanoparticles of several sizes with increasing annealing temperature. The as-received alumina nanoparticles are mostly spherical and aggregated. Although the particle sizes varies (from ~16 to ~50 nm for FA51, from ~14 to ~26
nm for FA81, and from ~8 to~16 nm for FA100), the average particle sizes are similar to the calculated sizes (i.e., 27, 19, and 15 nm for FA51, FA81, and FA100, respectively). The particle size of \( \gamma \), \( \delta \), and \( \theta \) phases seems invariant upon annealing and drastically increases up to ~100 nm with phase transition into \( \alpha \)-Al\(_2\)O\(_3\) above 1473 K. This result is consistent with the result from previous electron microscopic observation [e.g., TEM and scanning electron microscope (SEM) images] (Nordahl and Messing, 2002; Wu et al., 1996).

Figure 3 presents the XRD patterns of as-received alumina nanoparticles and \( \gamma \)-Al\(_2\)O\(_3\). The results show that the multiple phases of alumina exist in the samples: the XRD pattern for 27 nm alumina nanoparticles shows diffraction peaks for crystalline \( \gamma \)-, \( \delta \)-, and \( \theta \)-Al\(_2\)O\(_3\), and those for 15 and 19 nm alumina nanoparticles mainly consists of \( \gamma \)- and \( \delta \)-Al\(_2\)O\(_3\). We note that the quantitative estimation of the fractions of alumina polymorphs in the nanoparticles using XRD is often difficult because metastable alumina phases are not well distinguished (Cava et al., 2007; Macedo et al., 2007). Furthermore, the diffraction peak positions (i.e., 2\( \theta \) values) for metastable aluminas are similar (for instance, see diffraction peaks for \( \delta \)- and \( \theta \)-Al\(_2\)O\(_3\) in Figure 3). Thus, we attempt to yield quantitative fraction of each alumina phase using NMR (see results and discussion below).

### 3.2. \(^{27}\)Al MAS NMR Spectra

Figure 4A shows the \(^{27}\)Al MAS NMR spectra at 11.7 T for 27, 19, and 15 nm alumina nanoparticles. The \(^{1}\)Al and \(^{6}\)Al peaks are well resolved at 0~20 and 50~80 ppm, respectively, showing unique quadrupolar peak shapes. The \(^{27}\)Al MAS NMR spectrum for 27 nm alumina nanoparticles differs from those for 15 and 19 nm alumina nanoparticles and shows an additional sharp feature at ~10 ppm that is due to \(^{6}\)Al peak for \( \theta \)-Al\(_2\)O\(_3\) (in addition to \( \gamma \)- and \( \delta \)-Al\(_2\)O\(_3\)) in the 27 nm alumina nanoparticles, as also indicated by the XRD result.

Figure 4B shows the \(^{27}\)Al MAS NMR spectra for 27 nm alumina nanoparticles collected...
at 9.4, 11.7, and 14.1 T. As the magnetic field \( (B_0) \) increases, the widths of the \(^{[4]}\)Al and \(^{[6]}\)Al peaks decrease because the contribution of quadrupolar broadening in the peak decreases with static magnetic field (i.e., quadrupolar broadening \( \propto 1/B_0 \)) (Ashbrook and Duer, 2006; Duer, 2004; MacKenzie and Smith, 2002). Crystallographically distinct aluminum sites in \( \gamma-, \delta-, \) and \( \theta-\)Al\(_2\)O\(_3\) are not fully resolved in the \(^{27}\)Al MAS NMR spectra even at 11.7 T, mainly due to their similar peak positions for \(^{[4,6]}\)Al sites and disordered structure of \( \gamma-\) and \( \delta-\)Al\(_2\)O\(_3\). In the current \(^{27}\)Al MAS NMR results, \( \gamma-\) and \( \delta-\)Al\(_2\)O\(_3\) are not well distinguished from each other. The lack of resolution between \( \gamma-\) and \( \delta-\)Al\(_2\)O\(_3\) in alumina nanoparticles is due to their similar atomic environments and pronounced topological disorder and thus to similarities in the peak positions of \( \gamma-, \delta-, \) and \( \theta-\)Al\(_2\)O\(_3\) (Pecharroman et al., 1999): the \( \delta-\)Al\(_2\)O\(_3\) consists of a superlattice of the \( \gamma-\)Al\(_2\)O\(_3\) structure with ordered cation vacancies (Jayaram and Levi, 1989). Simulation of the central transition peaks in these \(^{27}\)Al MAS NMR spectra collected at varying static magnetic field allows us to quantitatively discriminate crystallographically distinct Al sites in metastable alumina nanoparticles (see section 3.3. below for further information).

Figure 5A–C present the \(^{27}\)Al MAS NMR spectra at 11.7 T for 27, 19, and 15 nm alumina nanoparticles, respectively, with increasing annealing temperature up to 1573 K. The spectra show subtle, gradual changes in the quadrupolar peak shapes for the \(^{[4]}\)Al and \(^{[6]}\)Al sites. With increasing temperature up to 1473 K, an increase in the intensity of the sharp feature at \( \sim 10 \) ppm, the \(^{[6]}\)Al site in \( \theta-\)Al\(_2\)O\(_3\), is obvious. Though slight, changes in \(^{[4]}\)Al peak shape are indeed observed with increasing temperature, which may indicate changes in the atomic environment around Al during the phase transition \( \gamma \to \delta \to \theta-\)Al\(_2\)O\(_3\) (see Figure 5D).

Above 1473 K, a new \(^{[6]}\)Al peak for \( \alpha-\)Al\(_2\)O\(_3\) appears at \( \sim 14 \) ppm. The peak is partially resolved from the \(^{[6]}\)Al peaks for metastable aluminas owing to its symmetric shape and distinct peak position. The peak intensity for \(^{[6]}\)Al in \( \alpha-\)Al\(_2\)O\(_3\) increases dramatically with increasing temperature from 1473 K up to 1573 K: the peak intensity for \(^{[4]}\)Al decreases with increasing
temperature above 1473 K because the structure of $\alpha$-Al$_2$O$_3$ has only a [6]Al site.

Figure 5D compares the [6]Al peaks in the $^{27}$Al MAS NMR spectra of alumina nanoparticles with varying particle size at various temperatures. The fraction of $\alpha$-Al$_2$O$_3$ in alumina nanoparticles annealed between 1473 K and 1573 K varies with the particle size. For instance, the phase transition into $\alpha$-Al$_2$O$_3$ is apparently complete at 1523 K for 15 nm nanoparticles, with $\alpha$-Al$_2$O$_3$ being the only Al site in the nanoparticles. Thus, the 15 nm alumina nanoparticles consist only of $\alpha$-Al$_2$O$_3$ after annealing at 1523 K. However, the 19 and 27 nm nanoparticles still have a significant fraction of metastable aluminas at 1523 K. The phase transition into $\alpha$-Al$_2$O$_3$ is apparently complete at ~1573 K for 27 and 19 nm alumina nanoparticles. These results indicate that transition temperature for $\theta \rightarrow \alpha$-Al$_2$O$_3$ decreases with decreasing particle size.

3.3. Quantification of Metastable Alumina Phases in Nanoparticles

The quantitative fraction of each alumina polymorph in nanoparticles can be estimated from the analysis of the unique quadrupolar peak shape for each Al sites with NMR parameters including $C_q$, $\eta$, and $\delta_{iso}$. The NMR parameters for [4,6]Al sites in the metastable aluminas studied in previous and current studies are given in Table 1. Although the NMR parameters for the [4,6]Al sites of $\theta$- and $\alpha$-Al$_2$O$_3$ were generally confirmed, those for $\gamma$-Al$_2$O$_3$ show a wide range of variation (Hagaman et al., 2010; Kraus et al., 1996; O'Dell et al., 2007; Pecharroman et al., 1999; Sabarinathan et al., 2010; Skibsted et al., 1991): reported $C_q$ values for the [6]Al site in $\gamma$-Al$_2$O$_3$ varies from 4±1 to 7.5±1 MHz (Hagaman et al., 2010; Kraus et al., 1996; Perander et al., 2007). Additionally, the NMR parameters for the [4,6]Al sites in $\delta$-Al$_2$O$_3$ have not been reported. The simultaneous simulation of $^{27}$Al NMR spectra collected at different magnetic fields allows us to obtain robust NMR parameters (O'Dell et al., 2007; Perander et al., 2007). In the current study, following protocols has been used to obtain NMR parameters for
the Al sites in the alumina phases. First, we roughly simulated the spectra at 11.7 T using the previously reported NMR parameters for each phase (Table 1). Then, we adjusted the detailed NMR parameters by simulating the spectra collected at 9.4 T, 11.7, and 14.1 T simultaneously, with a constraints of intensity ratio between [4]Al and [6]Al for each alumina phase. Detailed information on the NMR parameters for alumina nanoparticles studied in the current study is also given in Table 2.

Figure 6 shows the $^{27}$Al MAS NMR spectra that were simulated simultaneously at 9.4, 11.7, and 14.1 T. The simulation of the [4]Al and [6]Al peaks for ($\gamma$, $\delta$)-Al$_2$O$_3$ in the $^{27}$Al MAS NMR spectrum were performed using the Czjzek model (de Lacaille et al., 2008; Lee et al., 2009a; Massiot et al., 2002; Neuville et al., 2004). Taking into consideration expected similarity between NMR parameters for [4,6]Al sites in ($\gamma$, $\delta$)-Al$_2$O$_3$, we consider a single [4]Al and [6]Al peak for ($\gamma$, $\delta$)-Al$_2$O$_3$. The average $C_q$ and $\delta_{iso}$ for [4]Al in ($\gamma$, $\delta$)-Al$_2$O$_3$ are $5.7\pm1.0$ MHz and $72\pm3$ ppm, respectively, and those for [6]Al are $4.2\pm1.0$ MHz and $14\pm3$ ppm. We also collected the $^{27}$Al MAS NMR spectrum for standard $\gamma$-Al$_2$O$_3$ [single phase, Sigma Aldrich, product no. 544833, mixture of nanorods ($\sim$ 50 nm length) and nanoparticles ($\sim$ 10 nm diameter)]. The spectrum was also simulated well with similar approach: $\delta_{iso} = 72.5\pm3.0$ ppm, $C_q = 5.7\pm1.0$ MHz for the [4]Al site and $\delta_{iso} = 14\pm2$ ppm, $C_q = 4.7\pm1.0$ MHz for the [6]Al site. These NMR parameters for the [4,6]Al sites in ($\gamma$, $\delta$)-Al$_2$O$_3$ show intermediate value between those reported in previous studies of $\gamma$-Al$_2$O$_3$ (Hagaman et al., 2010; Kraus et al., 1996; O'Dell et al., 2007; Pecharroman et al., 1999; Perander et al., 2007).

We note that there is a minor but detectable difference in NMR line shape for [6]Al sites and relative peak intensity ([4]Al/[6]Al) in the standard $\gamma$-phase (from Sigma Aldrich, 544833) and the $\gamma$-Al$_2$O$_3$ in the mixed phases, indicating that the particle size and morphology of the particles may lead to a slight change in structural distortion and thus NMR parameters. Similar particle size effect on NMR parameters, particularly $C_q$, has been observed for $\alpha$-
alumina nanoparticles (Sabarinathan et al., 2010). Currently, the changes in these NMR parameters are relatively small (see Table 2) and thus are within uncertainty. Yet this potentially interesting effect of particle size remains to be explored.

The $^{27}$Al NMR parameters for $\theta$-Al$_2$O$_3$ are $\delta_{\text{iso}} = 80.5$ ppm, $C_q = 6.0$ MHz, and $\eta_q = 0.7$ for the $[4]$Al site and $\delta_{\text{iso}} = 10.5$ ppm, $C_q = 3.45$ MHz, and $\eta = 0.0$ for the $[6]$Al site, respectively. These results are consistent with those from previous studies (O'Dell et al., 2007; Pecharroman et al., 1999). Note that the quadrupolar NMR parameters are correlated with deviation from perfect tetrahedral or octahedral symmetry (Ghose and Tsang, 1973). The current results imply that deviation from perfect cubic symmetry for Al site in $\theta$-Al$_2$O$_3$ is larger than those for $\gamma$-Al$_2$O$_3$. In contrast, as also deduced from XRD patterns, the dispersion of NMR parameters for Al sites in $\gamma$- and $\delta$-Al$_2$O$_3$ phases indicate a moderate degree of structural disorder around Al sites in $\gamma$- and $\delta$-Al$_2$O$_3$ as previously reported (Lippens and Deboer, 1964). $\theta$-Al$_2$O$_3$ shows less disordered structures as indicated by narrow dispersions in the NMR spectra and XRD patterns (Figures 3 and 5).

Figure 7 shows the simulated $^{27}$Al MAS NMR spectra for alumina nanoparticles with varying particle size and annealing temperature, which provides the quantitative changes in the fractions of each alumina phase in the nanoparticles (see supporting on-line materials for the complete sets of NMR spectra with varying temperature). For the NMR parameters of the $[6]$Al site in $\alpha$-Al$_2$O$_3$, we follow the previously reported values (i.e., $\delta_{\text{iso}} = 15.9$ ppm, $C_q = 2.4$ MHz, and $\eta_q = 0$) (Kraus et al., 1998; O'Dell et al., 2007; Sabarinathan et al., 2010; Skibsted et al., 1991). The intensity ratio between the $[4]$Al and $[6]$Al sites in $\theta$-Al$_2$O$_3$ is $\sim 50\pm 5:50\pm 5$, which is consistent with the previously reported ratio for the ideal structure of $\theta$-Al$_2$O$_3$ (O'Dell et al., 2007; Pecharroman et al., 1999). Though indirect, $[4]$Al and $[6]$Al ratio in the ($\gamma$, $\delta$)-Al$_2$O$_3$ may provide quantitative fraction of $\gamma$- and $\delta$-Al$_2$O$_3$. The ratios between $[4]$Al and $[6]$Al for ($\gamma$, $\delta$)-Al$_2$O$_3$ in 15, 19, and 27 nm alumina nanoparticles are $\sim 26\pm 8:74\pm 8$, $30\pm 8:70\pm 8$, and $32\pm 8:68\pm 8$, respectively.
respectively. These are intermediate between the values for the ideal structures of $\gamma$- and $\delta$-
$\text{Al}_2\text{O}_3$: the [4]Al:[6]Al ratios in ideal $\gamma$- and $\delta$-$\text{Al}_2\text{O}_3$ are about 25:75 and 38:62, respectively
(Pecharroman et al., 1999; Repelin and Husson, 1990). The current result may indicate that the
fraction of $\gamma$-$\text{Al}_2\text{O}_3$ is more significant in a smaller nanoparticles, because the [4]Al:[6]Al ratio in
($\gamma$, $\delta$)-$\text{Al}_2\text{O}_3$ approaches the ideal ratio for $\gamma$-$\text{Al}_2\text{O}_3$ as the particle size decreases from 27 nm to
15 nm. The fraction of each alumina phase in alumina nanoparticles based on NMR results in
the current remains to be tested with other quantitative experimental techniques.

Figure 8A–C show the variations in the population of each alumina phase in 27, 19,
and 15 nm alumina nanoparticles, respectively, with increasing annealing temperature up to
1573 K, which demonstrates the effect of particle size on the stability field for alumina
polymorphs. The population of alumina polymorphs in as-received alumina nanoparticles
varies with the particle size. The ($\gamma$, $\delta$)-$\text{Al}_2\text{O}_3$: $\theta$-$\text{Al}_2\text{O}_3$ ratio is approximately 99±0.5:1±0.5,
96±2:4±2, and 80±3:20±3 for the 15, 19, and 27 nm alumina nanoparticles, respectively. With
increasing temperature above ~873 K, the population of $\theta$-$\text{Al}_2\text{O}_3$ gradually increases up to
~1473 K at the expense of ($\gamma$, $\delta$)-$\text{Al}_2\text{O}_3$. The fractions of $\theta$-$\text{Al}_2\text{O}_3$ after annealing at 1473 K are
~16±5%, 18±5%, and 38±5% for 15, 19, and 27 nm alumina nanoparticles, respectively, and
thus a major fraction (62%~84%) of the alumina nanoparticles exist as ($\gamma$, $\delta$)-$\text{Al}_2\text{O}_3$. The error
bar in the fraction of each alumina phase stems from the deviation from a perfect match
between experimental and simulated spectra (~3%), the contribution from the uncertainties in
estimated NMR parameters (~3%), and possible artifacts introducing fixed value for NMR
parameters upon simulations (~3%). Taking into consideration of those uncertainties, the total
error bar of ±5 % is estimated. The significant fraction of ($\gamma$, $\delta$)-$\text{Al}_2\text{O}_3$ in the nanoparticles at
1473 K is somewhat unexpected, considering the previously known transition temperatures
for $\gamma \rightarrow \delta$-$\text{Al}_2\text{O}$ (700–800°C) and $\delta \rightarrow \theta$-$\text{Al}_2\text{O}$ (900–1000°C) (Levin and Brandon, 1998 and
references therein). However, the presence of $\gamma$-$\text{Al}_2\text{O}_3$ above 1473 K also has been reported in
previously XRD studies for both nanocrystalline and bulk alumina (heating rate of 3-50 K/min) (Bokhimi et al., 2001; Gan et al., 2009). Note that kinetic broadening upon phase transition among nanoparticles may contribute to the presence of larger fractions of (γ, δ)-Al₂O₃. This effect of kinetic broadening on phase transition needs to be explored using further NMR studies with varying annealing time.

Figure 8D–F (enlarged plots of Figure 8A–C) shows the variation in the population of alumina phases between ~1400 and ~1600 K for alumina nanoparticles. Multiple phases of alumina including γ-, δ-, θ-, and α-Al₂O₃ coexist in alumina nanoparticles from ~1473 K to the temperature at which all phase transitions into α-Al₂O₃ are complete (i.e., ~1573 K for 27 and 19 nm nanoparticles and ~1523 K for 15 nm nanoparticles). With increasing temperature from ~1473 K to ~1573 K, the population of α-Al₂O₃ increases dramatically at the expense of the metastable aluminas. The transition temperature for γ, δ, θ → α-Al₂O₃ decreases with decreasing particle size. In this study, the transition temperature for γ, δ, θ → α-Al₂O₃ is defined by the temperature of which the 50 % of alumina nanoparticles exist in form of α-Al₂O₃. Although the phase transition γ, δ → θ-Al₂O₃ occurs gradually with increasing annealing temperature from 873 K to 1473 K, the phase transitions γ, δ → α-Al₂O₃ and θ → α-Al₂O₃ occur dramatically within a narrow temperature range between 1473 K and 1573 K.

3.4. ²⁷Al 3QMAS NMR Spectra

Figure 9A and 9B show the ²⁷Al 3QMAS NMR spectra for 27 nm alumina nanoparticles before and after annealing at 1497 K for 2 h; the resolution is considerably better than that of the ²⁷Al MAS NMR spectra. The crystallographically distinct [6]Al and [4]Al sites in (γ, δ)- and θ-Al₂O₃ as well as α-Al₂O₃ are resolved in the isotropic dimension. For robust peak assignment, we calculated the expected position for the center of gravity of the [4,6]Al sites in γ-, θ-, and α-Al₂O₃ using previously reported NMR parameters shown in Table 1. Figure 9C shows the
expected position of the center of gravity of the \([4,6]\)Al sites for \(\gamma\), \(\theta\), and \(\alpha\)-\(\text{Al}_2\text{O}_3\) in \(\text{Al}\) 3QMAS NMR spectra (Hagaman et al., 2010; Kraus et al., 1996; O’Dell et al., 2007; Pecharroman et al., 1999; Perander et al., 2007; Sabarinathan et al., 2010; Skibsted et al., 1991).

On the basis of plots in figure 9C, the peak at -10 ppm in the isotropic dimension is assigned to the \([6]\)Al site in \(\alpha\)-\(\text{Al}_2\text{O}_3\), which appears after annealing at 1497 K (Hagaman et al., 2010; Kraus et al., 1996; O’Dell et al., 2007; Sabarinathan et al., 2010; Skibsted et al., 1991). The peaks at -8 ppm and -53 ppm in the isotropic dimension are assigned to the \([6]\)Al and \([4]\)Al sites in \(\theta\)-\(\text{Al}_2\text{O}_3\), respectively (O’Dell et al., 2007; Pecharroman et al., 1999). These \([6]\)Al and \([4]\)Al peak intensities for \(\theta\)-\(\text{Al}_2\text{O}_3\) increase after annealing at 1497 K, following the \(\gamma, \delta \rightarrow \theta\) phase transition. The broad peaks ranging from -10 to -20 ppm and at ~ -45 ppm are assigned to unresolved \([6]\)Al and \([4]\)Al sites in \(\gamma\)- and \(\delta\)-\(\text{Al}_2\text{O}_3\), respectively as their intensities decrease significantly after annealing at 1497 K (Hagaman et al., 2010; Kraus et al., 1996; Perander et al., 2007). These results are consistent with the temperature-induced phase transition sequence of alumina (i.e., \(\gamma \rightarrow \delta \rightarrow \theta \rightarrow \alpha\)-\(\text{Al}_2\text{O}_3\)).

Figure 10 shows the \(\text{Al}\) 3QMAS NMR spectra for alumina nanoparticles with varying particle size and annealing temperature; the \([4]\)Al and \([6]\)Al peaks for \((\gamma, \delta)\)-, \(\theta\)-, and \(\alpha\)-\(\text{Al}_2\text{O}_3\) are resolved (see supporting on-line materials for the complete sets of NMR spectra with varying temperature). The \([4,6]\)Al peaks for \(\theta\)-\(\text{Al}_2\text{O}_3\) are observed in the \(\text{Al}\) 3QMAS NMR spectra for the 15 and 19 nm alumina nanoparticles as well as the 27 nm alumina nanoparticles. We note that the presence of \(\theta\)-\(\text{Al}_2\text{O}_3\) is not clear in the XRD patterns for 15 nm and 19 nm alumina nanoparticles (see Figure 3). The discrepancy may be due to that small fraction (~3±2 %) of \(\theta\)-\(\text{Al}_2\text{O}_3\) is not detected using XRD. As the annealing temperature increases to ~1473 K, the peak intensities for the \([4,6]\)Al sites in \((\gamma, \delta)\)-\(\text{Al}_2\text{O}_3\) decrease, whereas those for \(\theta\)-\(\text{Al}_2\text{O}_3\) increase. Above 1473 K, the \([6]\)Al peak for \(\alpha\)-\(\text{Al}_2\text{O}_3\) is observed, indicating the onset of the \(\theta \rightarrow \alpha\) phase transition. These results are consistent with those of the \(\text{Al}\) MAS NMR spectra.
3.5. Effect of Particle Size on Phase Transitions of Metastable Alumina

Several phase transitions in alumina nanoparticles observed in the current study include, (1) $\gamma, \delta \rightarrow \theta$-$\text{Al}_2\text{O}_3$, (2) $\gamma, \delta \rightarrow \alpha$-$\text{Al}_2\text{O}_3$, and (3) $\theta \rightarrow \alpha$-$\text{Al}_2\text{O}_3$. Although the phase transition $\gamma, \delta \rightarrow \theta$-$\text{Al}_2\text{O}_3$ occurs gradually within a broad temperature range between $\sim 873$ K and $1473$ K, both phase transitions, $\gamma, \delta \rightarrow \alpha$-$\text{Al}_2\text{O}_3$ and $\theta \rightarrow \alpha$-$\text{Al}_2\text{O}_3$ occurs within narrow temperature range between $\sim 1473$ K and $1573$ K. The different temperature range between phase transition $\gamma, \delta \rightarrow \theta$ and $\gamma, \delta, \theta \rightarrow \alpha$-$\text{Al}_2\text{O}_3$ may originate from the different structural disorder between the metastable aluminas (i.e., $\gamma$-, $\delta$-, $\theta$-) and $\alpha$-$\text{Al}_2\text{O}_3$. The configurational disorder of $\gamma$- and $\delta$-$\text{Al}_2\text{O}_3$ may induce a gradual $\gamma, \delta \rightarrow \theta$ phase transition from $873$ K to $1473$ K as has been observed for structural transitions in compressed amorphous oxides (see (Lee et al., 2008).

Figure 11 presents the normalized variation in the ($\gamma, \delta$)-, $\theta$- and $\alpha$-$\text{Al}_2\text{O}_3$ population with varying particle size and annealing temperature. The normalized variations of ($\gamma, \delta$)- and $\theta$-$\text{Al}_2\text{O}_3$ population in 27, 19, and 15 nm nanoparticles between $298$ K and $\sim 1473$ K are similar to each other, indicating that the effect of particle size on the phase transition ($\gamma, \delta \rightarrow \theta$-$\text{Al}_2\text{O}_3$ is not significant. On the other hand, effect of particle size on the variation of $\alpha$-$\text{Al}_2\text{O}_3$ population is obvious between $\sim 1473$ K and $\sim 1673$ K. The transition temperature for $\gamma, \delta, \theta \rightarrow \alpha$-$\text{Al}_2\text{O}_3$, where a 50 % for alumina is $\alpha$-$\text{Al}_2\text{O}_3$, is $1523\pm10$, $1518\pm10$, and $1490\pm10$ K for 27, 19, and 15 nm alumina nanoparticles, respectively. This result indicates that the phase transition $\gamma, \delta, \theta \rightarrow \alpha$-$\text{Al}_2\text{O}_3$ occurs at lower temperatures for smaller alumina nanoparticles. Although the transition temperature in this study may change with the annealing time because the equilibrium or steady state for phase transitions of alumina may not be reached with an annealing duration of 2 h, the current results can yield insights into the relative difficulty for phase transition $\gamma, \delta, \theta \rightarrow \alpha$-$\text{Al}_2\text{O}_3$. This could be due to higher surface energy of $\theta$-$\text{Al}_2\text{O}_3$ than that of $\alpha$-$\text{Al}_2\text{O}_3$ and/or it could be due to the fact that transition from $\theta$-$\text{Al}_2\text{O}_3$ to $\alpha$-$\text{Al}_2\text{O}_3$ is
kinetically favored for smaller nanoparticles. A detailed study for surface energy of $\theta$-Al$_2$O$_3$
phase remains to be explored.

In this study, we quantified the fractions of alumina polymorphs in nanoparticles and reported the NMR characteristics of their Al sites using both high-resolution 1D $^{27}$Al MAS and 3QMAS NMR. Particularly, first 2D NMR spectra for complex nanoparticles resolved crystallographically distinct $[^6]$Al and $[^4]$Al sites in ($\gamma$, $\delta$)- and $\theta$-Al$_2$O$_3$. The results show that phase transition $\gamma$, $\delta \rightarrow \theta$-Al$_2$O$_3$ occurs gradually with increasing annealing temperature from 873 K to 1473 K and the phase transitions $\gamma$, $\delta$, $\theta \rightarrow \alpha$-Al$_2$O$_3$ occur dramatically within a narrow temperature range between 1473 K and 1573 K. In addition to that, the results clearly demonstrate that phase transition $\gamma$, $\delta$, $\theta \rightarrow \alpha$-Al$_2$O$_3$ occurs at lower temperatures for smaller alumina nanoparticles. The current results may be helpful to account for a transition behavior in other simple and complex oxide nanoparticles. Nanoparticles with complex compositions are produced through geochemical (Banfield and Zhang, 2001; Foissner et al., 2009; Hochella et al., 2008) and mechanical processes (Han et al., 2007) in diverse geological settings.

Although the alumina nanoparticles in this study are not ubiquitous in the earth, they are the simplest compound that exhibits the complexities of diverse earth materials. In addition to Al$_2$O$_3$, other minerals including Fe$_2$O$_3$, TiO$_2$, and ZrO$_2$ also exhibit different surface energies among stable and metastable polymorphs, indicating a similar effect of particle size on their relative stability in nanoparticles (Navrotsky, 2004). The potential metastability of earth materials in nano-sized domain may induce heterogeneity of mantle (e.g., nanoscale spinel phases at the olivine-spinel transition at 400 km depth) (Banfield and Zhang, 2001). The structural information on alumina polymorphs and the mechanistic details obtained from the experiments described here provide insights into the nature of the phase transitions of other oxide nanoparticles, highlighting the effects of particle size.
Acknowledgment

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Atomic structure of alumina nanoparticle


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Atomic structure of alumina nanoparticle


Kim, Hyun Na & Lee, Sung Keun

Atomic structure of alumina nanoparticle


McHale, J.M., Navrotsky, A., and Perrotta, A.J. (1997b) Effects of increased surface area and


Kim, Hyun Na & Lee, Sung Keun  

Atomic structure of alumina nanoparticle


### Table 1. $^{27}$Al NMR parameters for metastable and α alumina

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Table 2. $^{27}$Al NMR parameters for simulation of $^{27}$Al NMR spectra. $\delta_{\text{iso}}$ is the isotropic chemical shift, $C_q$ is the quadrupolar coupling constant, $\eta$ is the asymmetry parameter. The $\Delta\delta_{\text{iso}}$ is the full width at half-maximum of the distribution of the isotropic chemical shift in the Czjzek model, which is used for simulation of the $[4]$Al and $[6]$Al peaks for ($\gamma$, $\delta$)-$\text{Al}_2\text{O}_3$. The $[4]$Al:$[6]$Al ratio in ideal $\gamma$-, $\delta$-, $\theta$- and $\alpha$-$\text{Al}_2\text{O}_3$ is 25:75, 38:62, 50:50, and 0: 100, respectively (Pecharroman et al., 1999; Repelin and Husson, 1990).

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* The quadrupolar NMR parameters, such as $\nu_q$, $\eta$ and $\sigma$ are correlated among each other. The relations among them can be described with the following equation (de Lacaille et al., 2008):

$$\left\langle C_q^2 \right\rangle = \left( \frac{2}{3} I(2I-1) \right)^2 \left\langle \nu_q^2 (1 + \frac{\eta^2}{3}) \right\rangle = \left( \frac{2}{3} I(2I-1) \right)^2 5\sigma^2$$
In Dmfit program (version released in 2011) used in the current study, therefore, $C_q$ is used as an input parameter and the $\sigma$ value is automatically adjusted depending on $C_q$ value: the estimated $\sigma$ is $\sim 380 \pm 60$ kHz and $280 \pm 50$ kHz for $^{[4]}\text{Al}$ and $^{[6]}\text{Al}$ sites in ($\gamma, \delta$)-$\text{Al}_2\text{O}_3$, respectively.

† The Gaussian or Lorentzian broadening factor ($\sim 300$Hz to 2000 Hz) is applied to simulate Al sites in ($\gamma, \delta$)-, $\theta$-$\text{Al}_2\text{O}_3$ and $\alpha$-$\text{Al}_2\text{O}_3$, respectively.
Figure captions

**Figure 1.** Crystal structure of (A) $\gamma$-Al$_2$O$_3$, (B) $\theta$-Al$_2$O$_3$, and (C) $\alpha$-Al$_2$O$_3$ with crystallographically distinctive aluminum sites.

**Figure 2.** TEM images of (A) 27 nm, (B) 19 nm, and (C) 15 nm alumina nanoparticles before and after annealing at various temperatures.

**Figure 3.** XRD patterns for $\gamma$-Al$_2$O$_3$ and alumina nanoparticles. Red, blue, and purple vertical lines correspond to the peak positions and intensities of $\gamma$-Al$_2$O$_3$ (JCPDS file no.00-050-0741), $\delta$-Al$_2$O$_3$ (JCPDS file no.00-016-0394), and $\theta$-Al$_2$O$_3$ (JCPDS file no.00-23-1009), respectively.

**Figure 4.** (A) $^{27}$Al MAS NMR spectra at 11.7 T for as-received alumina nanoparticles with varying particle size. (B) $^{27}$Al MAS NMR spectra for 27 nm alumina nanoparticles at various magnetic fields.

**Figure 5.** $^{27}$Al MAS NMR spectra at 11.7 T for (A) 27 nm, (B) 19 nm, and (C) 15 nm alumina nanoparticles with increasing annealing temperature up to 1573 K. (D) Comparison of $^{63}$Al peaks in $^{27}$Al MAS NMR spectra for alumina nanoparticles with varying particle size.

**Figure 6.** Simulation of $^{27}$Al MAS NMR spectra for as-received 27 nm alumina nanoparticles at 9.4, 11.7, and 14.1 T and for $\gamma$-Al$_2$O$_3$ at 11.7 T.
Figure 7. Simulation of $^{27}$Al MAS NMR spectra at 11.7 T for (A) 27 nm, (B) 19 nm, and (C) 15 nm alumina nanoparticles with increasing annealing temperature.

Figure 8. Variation in populations of ($\gamma$, $\delta$)-, $\theta$-, and $\alpha$-$\text{Al}_2\text{O}_3$ in (A) 27 nm, (B) 19 nm, and (C) 15 nm alumina nanoparticles with increasing annealing temperature up to 1573 K. (D–F) show enlarged plots of Figure 8A–C at temperatures of 1400 and 1600 K.

Figure 9. $^{27}$Al 3QMAS NMR spectra for 27 nm alumina nanoparticles (A) as-received and (B) annealed at 1497 K for 2 h. (C) Expected center of gravity for $\gamma$-, $\delta$-, $\theta$-, and $\alpha$-$\text{Al}_2\text{O}_3$ calculated on the basis of previous works: solid square (Kraus et al., 1996); solid triangle (Perander et al., 2007); solid circle (Hagaman et al., 2010); solid diamond (O’Dell et al., 2007); open circle (Sabarinathan et al., 2010); open diamond (Skibsted et al., 1991); open square (Pechyroman et al., 1999). Red, blue, and purple symbols refer to ($\gamma$, $\delta$)-, $\theta$-, and $\alpha$-$\text{Al}_2\text{O}_3$, respectively.

Figure 10. $^{27}$Al 3QMAS NMR spectra for 15, 19, and 27 nm alumina nanoparticles after annealing at various temperatures.

Figure 11. Normalized variation in the (A) ($\gamma$, $\delta$)- and $\theta$-$\text{Al}_2\text{O}_3$, (B) $\alpha$-$\text{Al}_2\text{O}_3$ population in particles of several sizes annealed at several temperatures.
Figure 1

Atomic structure of alumina nanoparticle
Figure 2

A. 27 nm particle

B. 19 nm particle

C. 15 nm particle
Atomic structure of alumina nanoparticle

Figure 3
Figure 4
Figure 5
Figure 6
Figure 7

Atomic structure of alumina nanoparticle
Figure 8
Figure 9
Figure 10

Isotropic dimension (ppm)

MAS dimension (ppm)

as-received
Figure 11

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 Atomic structure of alumina nanoparticle
Supporting Materials

We present the complete set of $^{27}$Al MAS NMR spectra, which is not shown in the manuscript. Figure S1 presents the simulated $^{27}$Al MAS NMR spectra for alumina nanoparticles with varying particle size and annealing temperature up to 1573 K.

![Simulated 27Al MAS NMR spectra](image)
Figure S1. Simulation of $^{27}$Al MAS NMR spectra at 11.7 T for (A) 27 nm, (B) 19 nm, and (C) 15 nm alumina nanoparticles with increasing annealing temperature.
Figure S2 presents the $^{27}$Al 3QMAS NMR spectra for alumina nanoparticles with varying particle size and annealing temperature.

Figure S2. $^{27}$Al 3QMAS NMR spectra for 15, 19, and 27 nm alumina nanoparticles with increasing annealing temperature.