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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

Nanoparticles are known to have physical properties different from their bulk analogs, a characteristic that bears wide technological potential. 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 the behavior of their phase transitions. 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 γ-, δ-, and θ-Al_2O_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 (γ,δ)- and θ-Al_2O_3 in the isotropic dimension for the first time. The fraction of θ-Al_2O_3 gradually increases up to ~1473 K at the expense of a decrease in (γ,δ)-Al_2O_3. The onset of formation of α-Al_2O_3 from metastable aluminas is observed above ~1493 K. Several phase transitions in alumina nanoparticles observed in the current study include, γ,δ → θ-Al_2O_3, γ,δ → α-Al_2O_3, and θ → α-Al_2O_3. Although the phase transition γ,δ → θ-Al_2O_3 occurs gradually with increasing annealing temperature from 873 to 1473 K, the phase transitions γ,δ → α-Al_2O_3 and θ → α-Al_2O_3 occur dramatically within a narrow temperature range between 1473 and 1573 K. The observed difference in temperature range (gradual vs. dramatic) for phase transition γ,δ → θ-Al_2O_3 and γ,δ,θ → α-Al_2O_3 originates from the different structural disorder in the metastable aluminas (i.e., γ-, δ-, θ-) and α-Al_2O_3. The effect of particle size on the phase transition (γ,δ) → θ-Al_2O_3 between 298 and ~1473 K is not observed significantly. On the other hand, the transition temperature for γ,δ,θ → α-Al_2O_3,where the 50% for alumina is α-Al_2O_3, apparently increases as the particle size increases (as evidenced by TEM observation), indicating a larger energy penalty for phase transitions into α-Al_2O_3 in larger alumina nanoparticles. This could be due to higher surface energy of θ-Al_2O_3 than that of α-Al_2O_3 and/or the fact that the transition from θ-Al_2O_3 to α-Al_2O_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.

Keywords: Metastable alumina, nanoparticles, solid-state NMR, phase transition among metastable polymorphs