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Probing the transformation paths from aluminum (oxy)hydroxides (boehmite, bayerite, and gibbsite) to metastable alumina: A view from high-resolution ^{27}Al MAS NMR

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Abstract

Detailed knowledge of the structural evolution of diverse aluminum (oxy)hydroxides with varying temperatures up to ~300 °C provides insights into the dehydration processes involving transitions among metastable phases on Earth's surface and in the crust. Here, we report the high-resolution solid-state ^{27}Al NMR spectra for three different types of aluminum (oxy)hydroxides (i.e., boehmite, bayerite, and gibbsite) with varying annealing temperatures up to 300 °C, revealing the effect of distinct precursor minerals on the stability of metastable alumina. ^{27}Al MAS NMR results allow us to obtain the quantitative fractions and NMR parameters for each phase during transformation. The results demonstrate that each aluminum (oxy)hydroxide phase follows a unique transformation path to metastable alumina. The ^{27}Al MAS and 3QMAS NMR spectra of boehmite show that a minor but observable $^{[4]}$Al signal (~2%) is detected at ~50 °C, and the $^{[4]}$Al fraction gradually increases up to 300 °C (~16%), indicating that the phase transformation from boehmite to γ-/η-Al_2O_3 occurs at a temperature as low as ~50 °C, significantly lower than earlier estimations based on XRD. Together with the $^{[4]}$Al fraction, the $^{[5]}$Al fraction increases from <1% at 50 °C to ~2.3% at 300 °C, whereas the NMR results of bayerite and gibbsite do not show the presence of $^{[5]}$Al. In addition, the ^{27}Al 3QMAS NMR spectra resolved the $^{[6]}$Al site in boehmite and that in γ-/η-Al_2O_3, which could not be uniquely determined from 1D NMR spectra. The population of bayerite abruptly decreases from 100% (at 150 °C), through ~47% (at 200 °C), to 0% (at 250 °C), indicating that the phase transition from bayerite to boehmite + γ-/η-Al_2O_3 occurs within a narrow temperature range. As for gibbsite, while $^{[4]}$Al is not observed in the spectra up to 200 °C, the $^{[4]}$Al fraction of ~2% is observed in the spectra for gibbsite annealed at 250 °C, and the $^{[4]}$Al fraction increases rapidly to ~15% as the annealing temperature increases to 300 °C, suggesting that the phase transformation into γ-/η-Al_2O_3 occurs at ~250 °C. The results confirm that the phase transformation paths (gradual vs. dramatic) depend on the type of precursor minerals. Particularly, the onset temperature of the phase transformation from boehmite to metastable alumina (~50 °C) is lower than those from other precursor minerals (>150 °C). Furthermore, the phase transformation from boehmite to γ-/η-Al_2O_3 occurs gradually within broad temperature ranges from ~50 °C. This is due to their configurational disorder as evidenced by the presence of $^{[5]}$Al. The observed structural evolution in aluminum (oxy)hydroxides in the low-temperature range facilitates our understanding of the nature of phase transformation and dehydration of oxides and hydroxides in the Earth's surface environments.

Keywords: Metastable (transition) alumina, aluminum (oxy)hydroxide, solid-state NMR, γ-/η-Al_2O_3, phase transformation, extent of disorder