SUPPORTING INFORMATION

Effect of Impurities on Radical Formation in Gibbsite Radiolysis

Supporting Information

Hanna Hlushko,[a] Alejandro Ramos-Ballesteros,[a] Ping Chen, [b] Xin Zhang,[b] Kevin M. Rosso,[b] Carolyn I. Pearce,[b,c] and Jay A. LaVerne[a,d]

[a.] Radiation Laboratory, University of Notre Dame, Notre Dame, 46556
[b.] Pacific Northwest National Laboratory, Richland, WA, 99354
[c.] Washington State University, Pullman, WA, 99163
[d.] Department of Physics and Astronomy, University of Notre Dame, Notre Dame, IN, 46556

Corresponding Author
laverne.1@nd.edu

1. Materials

Aluminum chloride, aluminum nitrate, magnesium nitrate, and sodium hydroxide were purchased from Sigma Aldrich. Boehmite was purchased from Apyral®.

Before use, boehmite was heated under applied vacuum at 300C to remove all organic impurities and stored in humidity chamber to reinstate hydration of the material. Synthesized gibbsite was heated under vacuum at 250°C. Humidity was kept at 75% by a magnesium nitrate slurry. All other materials were used as received.

2. Experimental Procedures

2.1. Gibbsite particles synthesis

Gibbsite was synthesized from aluminum nitrate or aluminum chloride precursors. $AlCl_3$ (anhydrous) or $Al(NO_3)_3 \cdot 9H_2O$ were dissolved in deionized water with 0.25 M concentration, and the solution pH was adjusted to ~5 with 3M NaOH solution. After ~1 hour, amorphous $Al(OH)_3$ nanoparticles (AAH) were produced, separated by centrifugation and washed with DI water at least three times to remove soluble species. Further, amorphous $Al(OH)_3$ nanoparticles were re-dispersed in DI water to prepare 0.25 M (based on Al ions) AAH suspensions, and 500 mL of suspension was transferred into a 1000 mL glass bottle, which was then put into an electric oven at 80 °C for 7 days. Crystallized gibbsite particles were cooled down to the room temperature, washed with DI water, centrifuged at 9,000 rpm out of the solution, and dried at 50 °C for two days.

2.2. **Powder X-ray diffraction (pXRD)** was performed at Materials Characterization Facility at University of Notre Dame, using high-resolution D8 Discover XRD, Bruker. Scans were taken in the range 2θ of 10-60° with the increment of 0.023°.

2.3. **Scanning Electron Microscopy (SEM)**

SEM was performed at Notre Dame Integrated Imaging Facility with the Magellan 400 - field emission scanning electron microscope using the beam current of 25 pA and the beam voltage of 5 kV. The samples were dispersed on conductive carbon tape and pre-sputtered with 3 nm of Pt/Pd coating.

2.4. **Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)**

DRIFTS were collected with Bruker Vertex 70 spectrometer with DGTS detector and Harrick Praying Mantis high temperature cell. Gibbsite and boehmite were mixed with pre-cleaned KBr, resulting in samples with 10% of aluminum compounds, which were analyzed in reflectance mode at 30, 100, 200, 300, and 400°C. Spectra were obtained in the range of 4000-400 cm^{-1} wavenumbers with a resolution of 4 cm^{-1}, using the signal from KBr collected at 400°C as a background.

2.5. **Irradiation**

Samples were sealed under vacuum in Suprasil® quartz tubes samples and irradiated with ^{60}Co γ-radiation at a dose rate of 55 Gy/min, until the samples received 1, 5, 10, and 20 kGy. The dose was determined with Fricke dosimetry and corrected for natural decay.

2.6. **Electron paramagnetic resonance (EPR)**

EPR spectra of the samples before irradiation and after they received 1, 5, 10, and 20 kGy of γ-radiation. EPR spectra (5 scans averaged, 300-400 mT) were obtained at room temperature on irradiated gibbsite with a Bruker EMX spectrometer at X-band frequency (~9.8 GHz), 30 dB attenuation, 1 G modulation amplitude, and 2 mW power. Origin software was used to deconvolute peaks in collected spectra.

2.7. **X-ray Photoelectron Spectroscopy (XPS)**

XPS was used for surface analysis of gibbsite and boehmite before irradiation. XPS measurements were done with PHI VersaProbe II, equipped with Al-Kα X-ray source with a photon energy of 1486.6 eV. High-resolution scans for each element of interest were taken with a pass energy of 23 eV and energy steps of 0.1 eV. Sample charging during the measurement was minimized by flooding with 10 eV Ar^{2+} ions and low-energy electrons. Energy shifts were applied to all spectra after they were collected using the standard position of the carbon impurity at 284.8 eV for C 1s peaks.

3. Additional Figures

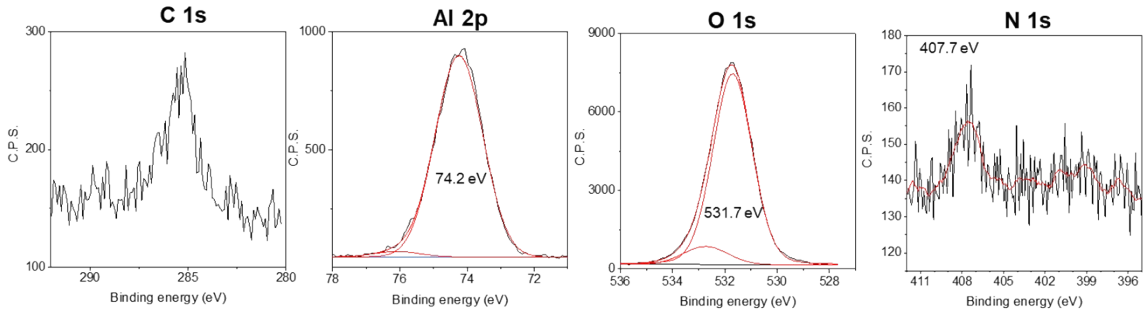

Figure S1. High-resolution XPS spectra of C, Al, O, and N, collected for gibbsite, made from $Al(NO_3)_3$

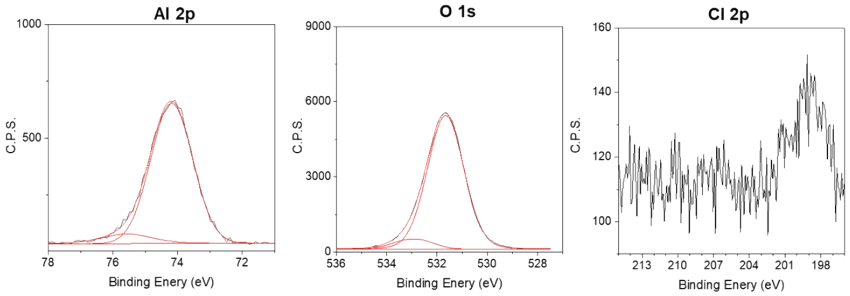

Figure S2. High-resolution XPS spectra of C, Al, O, and N, collected for gibbsite, made from $AlCl_3$

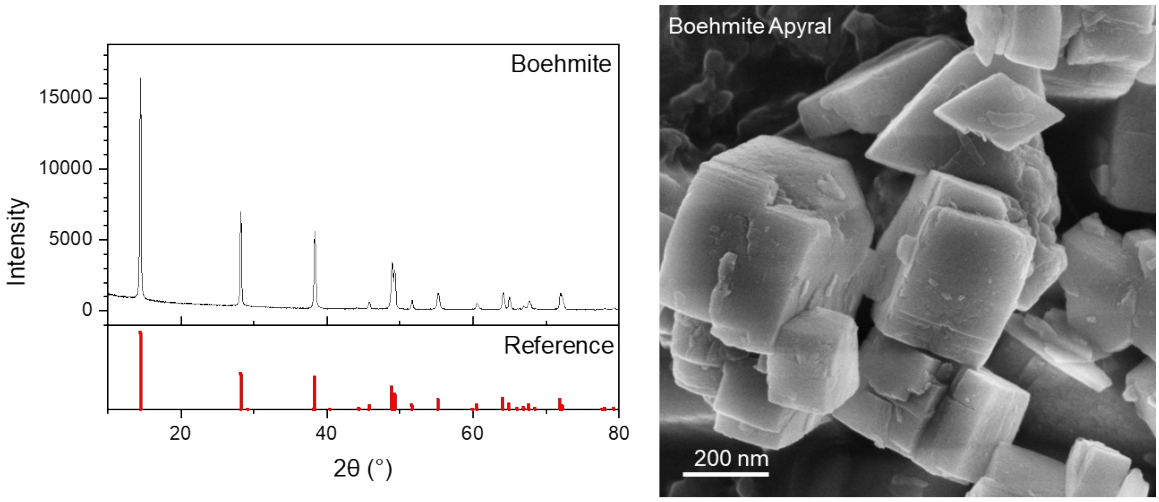

Figure S3. pXRD pattern and SEM image of boehmite used in these studies