Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

A Multi-Faceted Structural, Thermodynamic, and Spectroscopic Approach for Investigating Ethanol Dehydration over Transition Phase Aluminas

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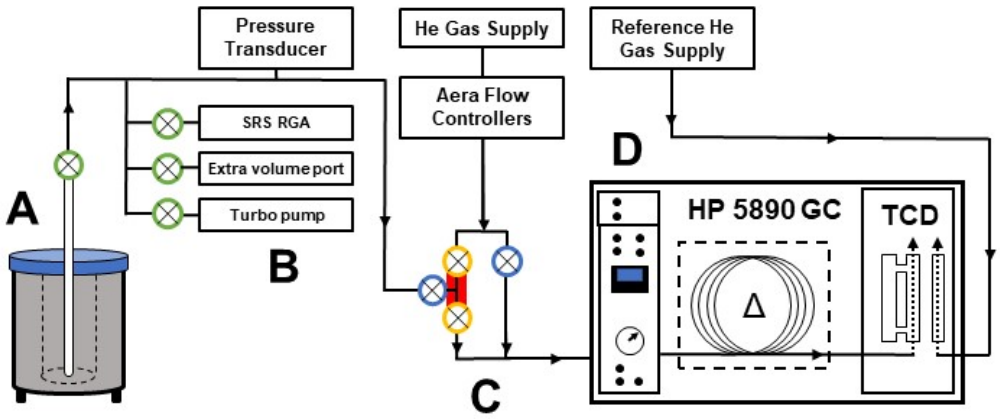

Figure S1. Schematic of the TPD apparatus coupled to a GC-TCD. The individual components are labeled as: A – sample cell, B – ancillary equipment ports, C – sample manifold, and D – GC-TCD.

The green valves represent manual bellows valves. Blue and yellow valves are pneumatically actuated (by color) bellows valves and are operated by a double-pole double-throw switch. When actuated together (by color), the valves turn the gas line outlined in red into a flow cell at the interface between the manifold and GC. The TCD detector produces a 0-1 VDC signal which is fed into an analog-to-digital converter whereby the signal can be read by a computer.

Table S1. Relevant parameters for GC-TCD

Gas Chromatography Parameters	Value
Stationary Phase	Hayesep T porous polymer (packed)
Column dimensions	L = 2 m, i.d. = 2.2 mm
Mobile Phase	UHP Helium
Mobile Phase flow rate (mL/sec)	0.529
Inlet Head Pressure (kPa)	58
Reference Gas flow rate (mL/sec)	2.53
Initial Oven Temperature (°C)	140
Initial Oven Hold Time (min)	1.5
Temperature Ramp Rate (°C/min)	40
Final Oven Temperature (°C)	250
Final Oven Hold Time (min)	5
Detector Temperature (°C)	175

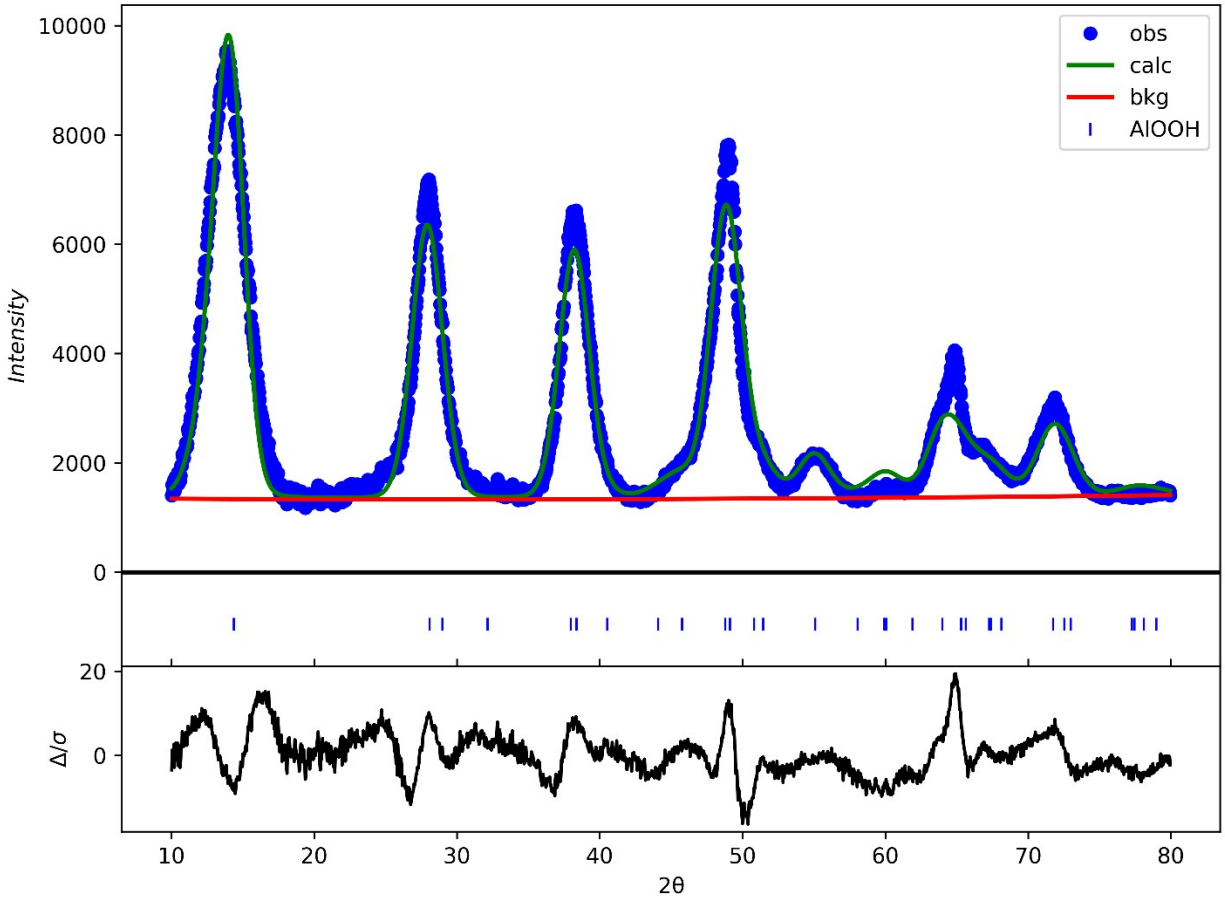

Figure S2. Rietveld refinement of the boehmite starting material XRD data. The initial orthorhombic structural model for boehmite was obtained from ICSD (59610) and converged with lattice parameters, a = 2.8551 Å, b = 12.3111 Å, and c = 3.7059 Å. The refinement converged with R_w = 0.1014 and R = 0.0809.

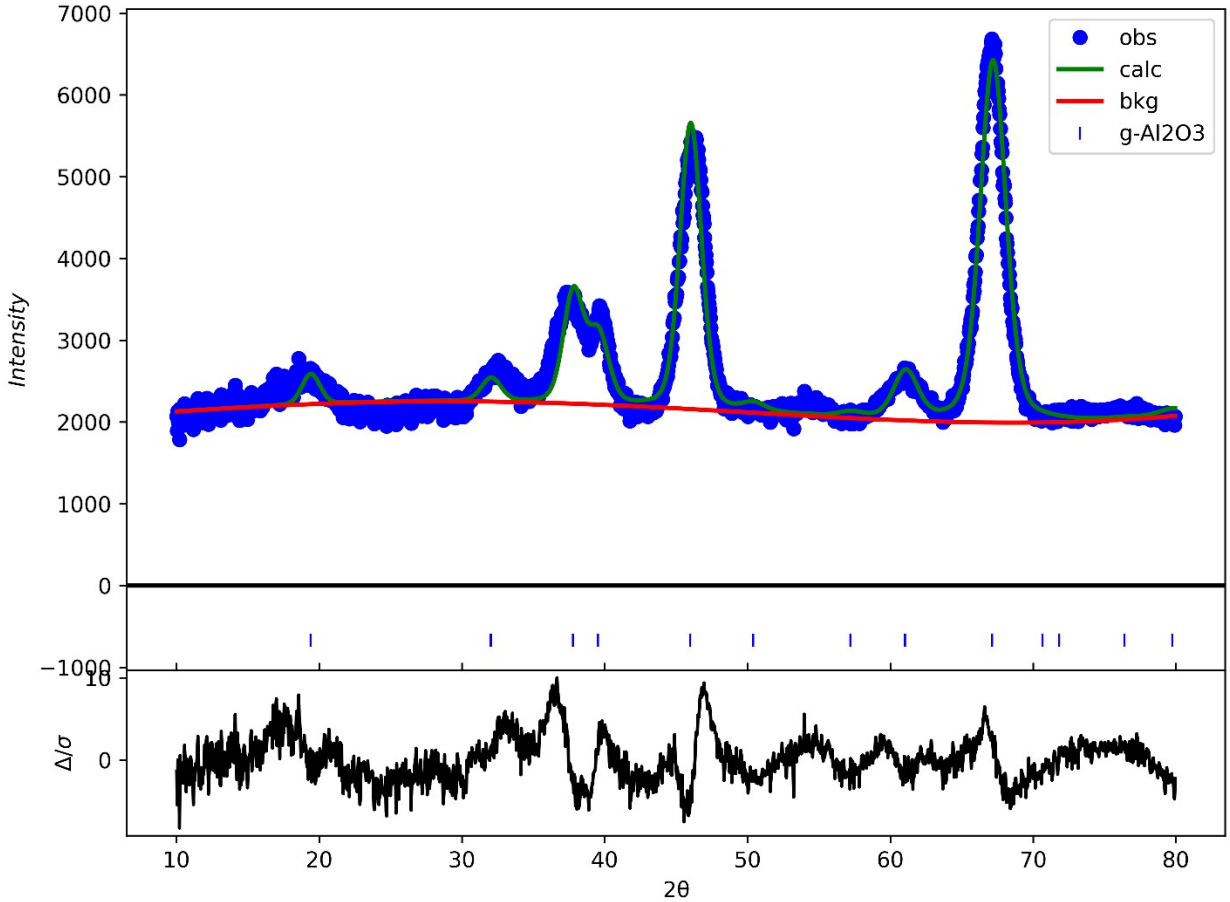

Figure S3. Rietveld refinement of the γ-alumina XRD data derived from heating boehmite at 600 °C for 8 hours. The initial cubic structural model for θ-alumina was obtained from ICSD (66559) and converged with lattice parameter, a = 7.8705 Å. The refinement converged with R_w = 0.0537 and R = 0.0430.

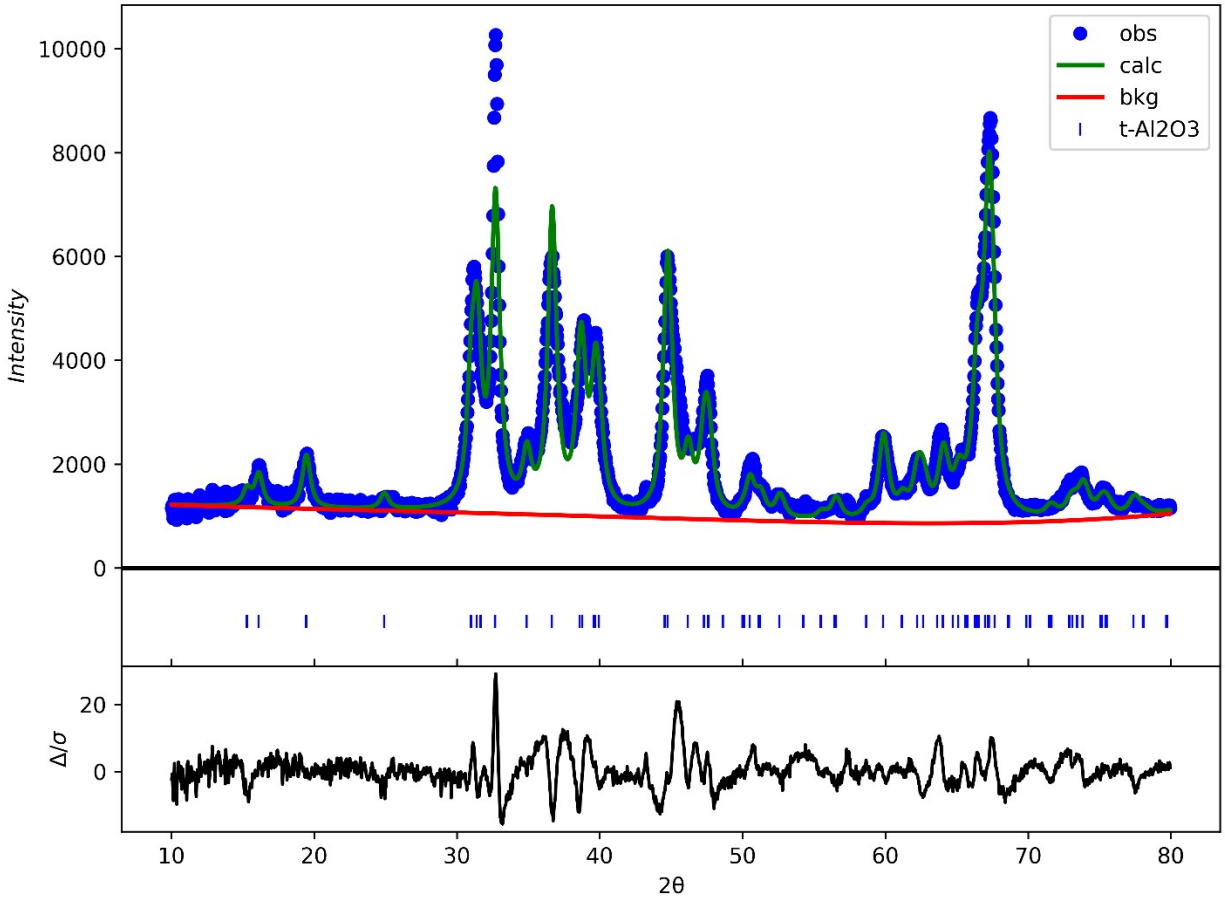

Figure S4. Rietveld refinement of the θ-alumina XRD data derived from heating boehmite at 1050 °C for 8 hours. The initial monoclinic structural model for θ-alumina was obtained from ICSD (82504) and converged with lattice parameters, a = 11.8401 Å, b = 2.9018 Å, c = 5.6190 Å, and β = 103.817°. The refinement converged with R_w = 0.1039 and R = 0.0791.

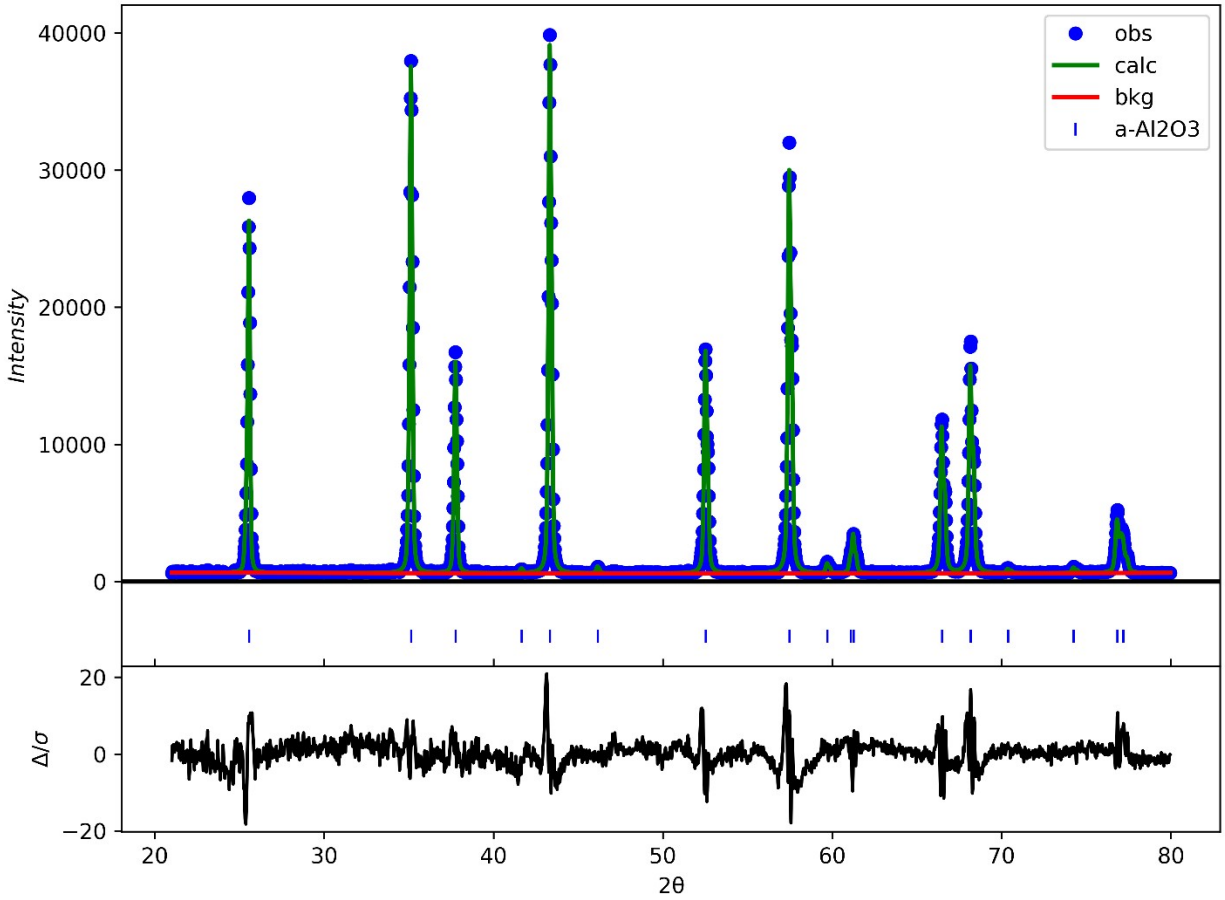

Figure S5. Rietveld refinement of the α-alumina XRD data derived from heating boehmite at 1200 °C for 12 hours. The initial trigonal structural model for α-alumina was obtained from ICSD (10425) and converged with lattice parameters, a = 4.76102 Å and c = 12.9985 Å. The refinement converged with R_w = 0.0862 and R = 0.0650.

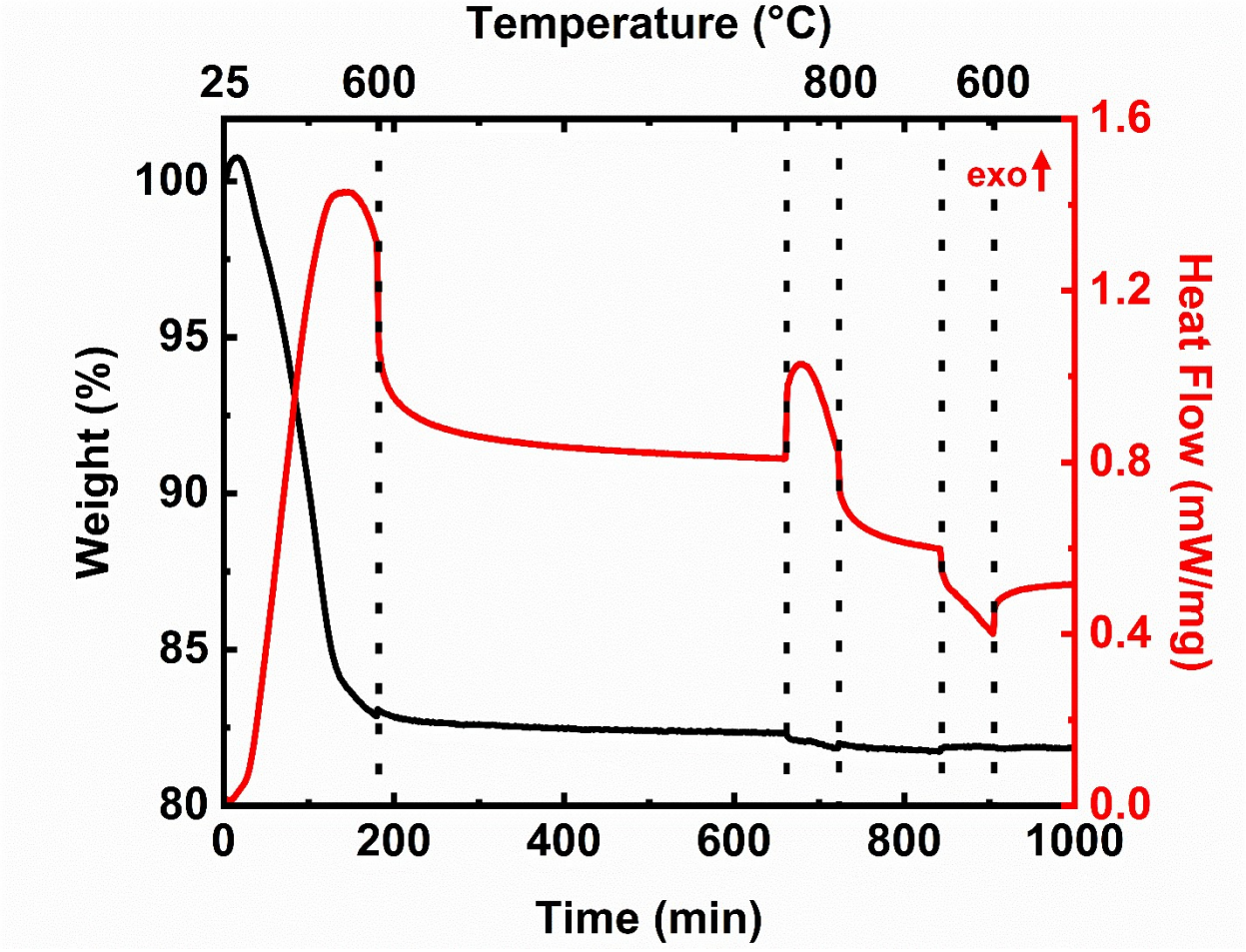

Figure S6. TGA-DSC for the calcination of boehmit to δ-alumina. The black trace (left axis) represents the fractional weight of the starting material. The corresponding DSC is shown in red (right axis).

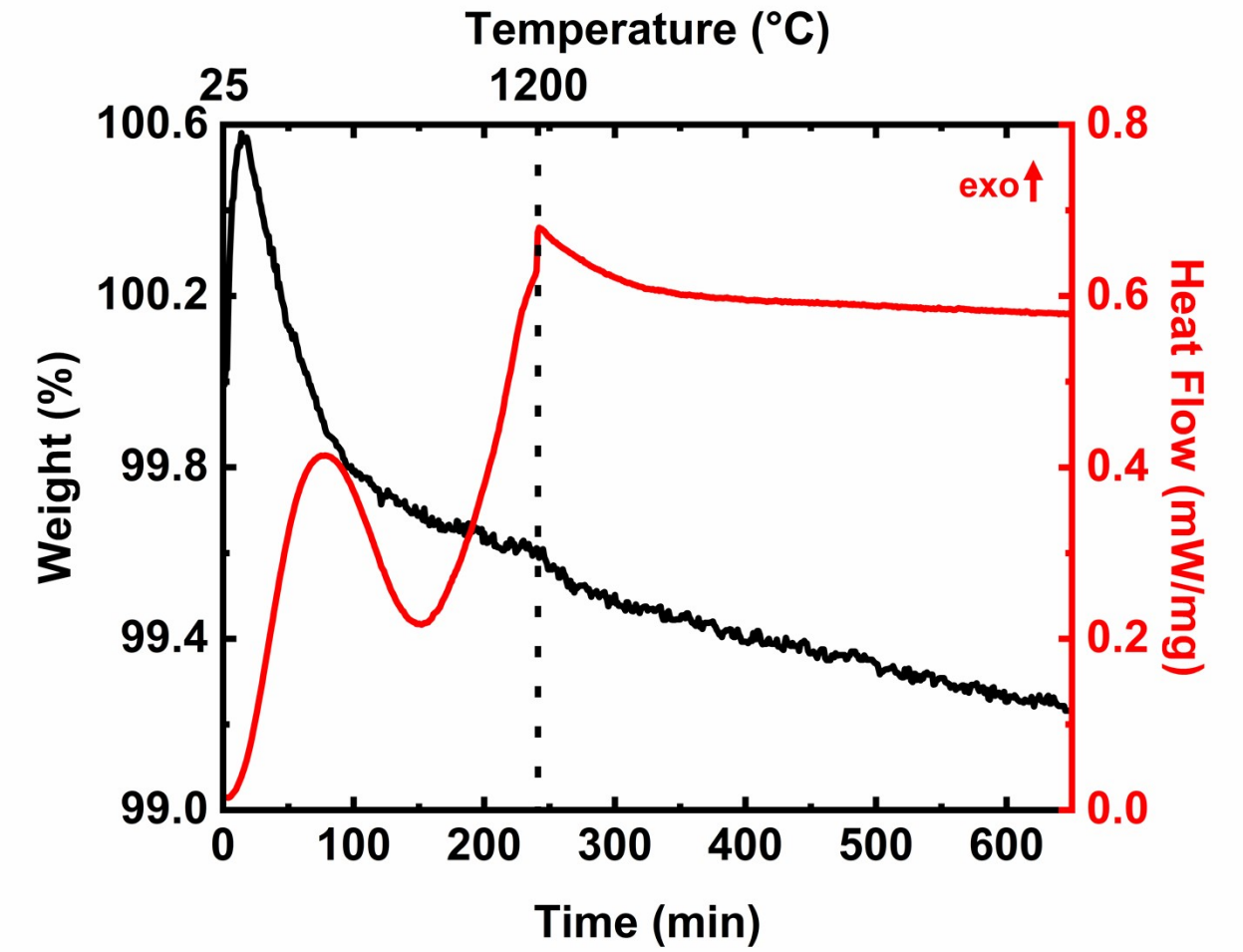

Figure S7. TGA-DSC for the calcination of θ- to α-alumina. The black trace (left axis) represents the fractional weight of the starting material. The corresponding DSC is shown in red (right axis).

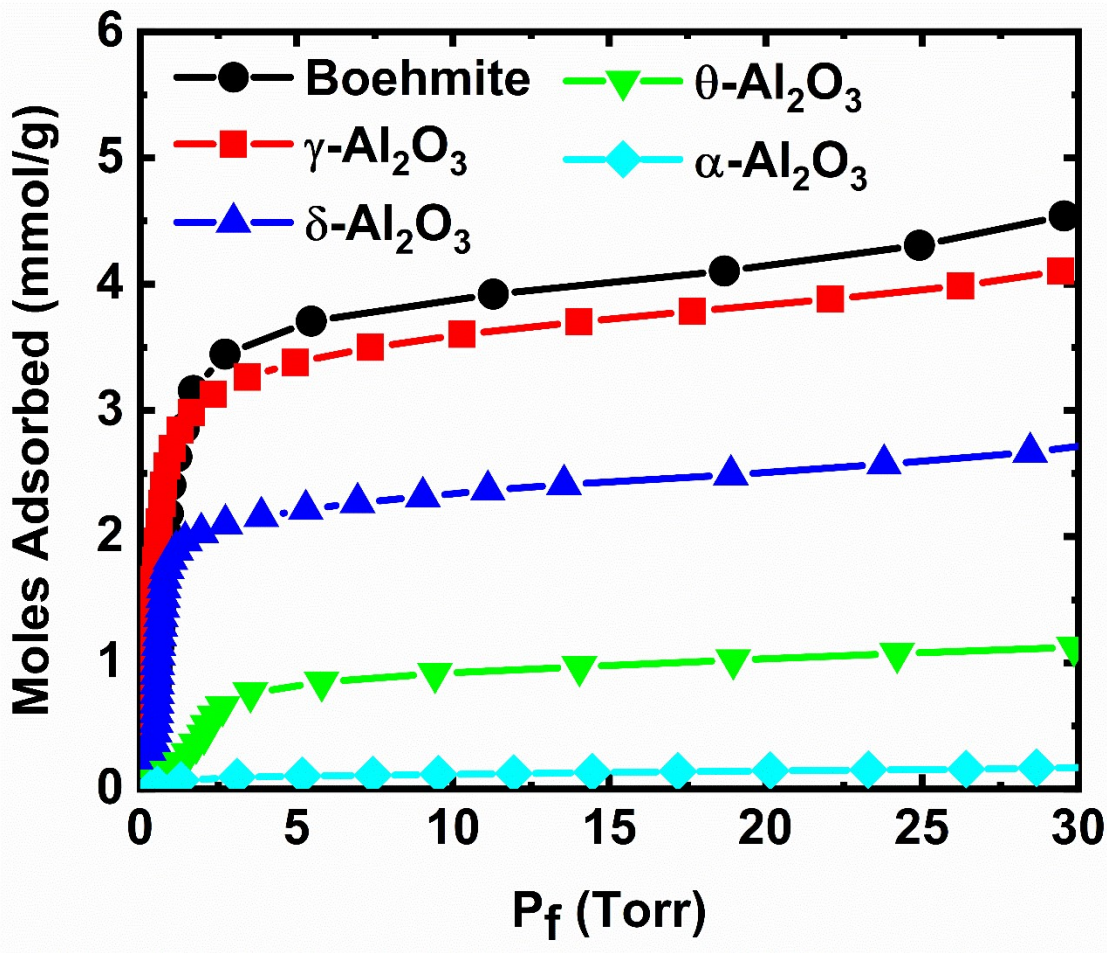

Figure S8. Adsorption isotherms from the calibration of monolayer coverage for ethanol on the aluminas

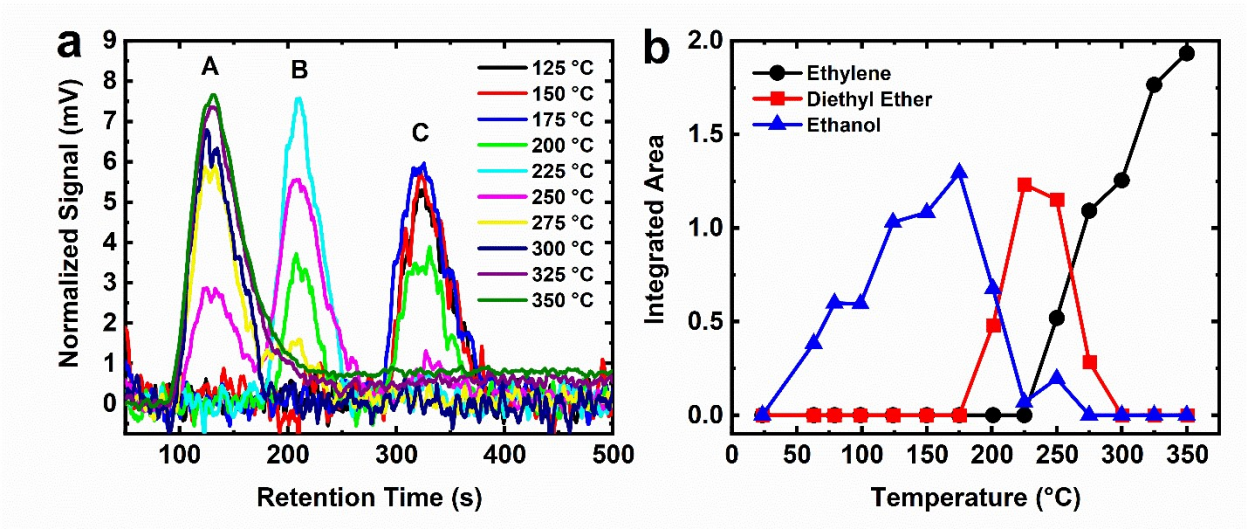

Figure S9. (a) TPD of monolayer coverage ethanol on the surface of δ-alumina. The observed peaks are labeled as A – ethylene, B – diethyl ether, and C – ethanol. (b) Numerically integrated peak areas obtained from the TPD as a function of temperature.

The TPD results displayed Figure S9 from ethanol adsorbed on the surface of δ-alumina clearly show that the temperature at which diethyl ether and ethylene form is consistent with the results reported previously for γ-alumina. At low temperatures, the gas phase signal from dissociated ethanol on δ-alumina is reduced appreciably in comparison to that from γ-alumina. This means there is a greater number of the surface sites on δ-alumina where ethanol is more tightly bound at low temperatures (e.g., chemisorbed ethoxide) than there are on γ-alumina. The ^{27}Al NMR results indicate that δ-alumina has a greater concentration of Al_V sites relative to the γ-phase but, perhaps during the calcination additional under-coordinated sites which are dehydroxylated also form. As the dissociated ethanol signal plateaus near 175 °C, diethyl ether is observed. Ethylene formation is detected at temperatures greater than 225°C which is consistent with γ-alumina, suggesting similar mechanisms for dehydration from an intermediate state. Although the surface of the δ-phase may contain more Al^{3+} reactive sites than the γ-phase, the reduced surface area appears to limit the total ethylene production at 350 °C.

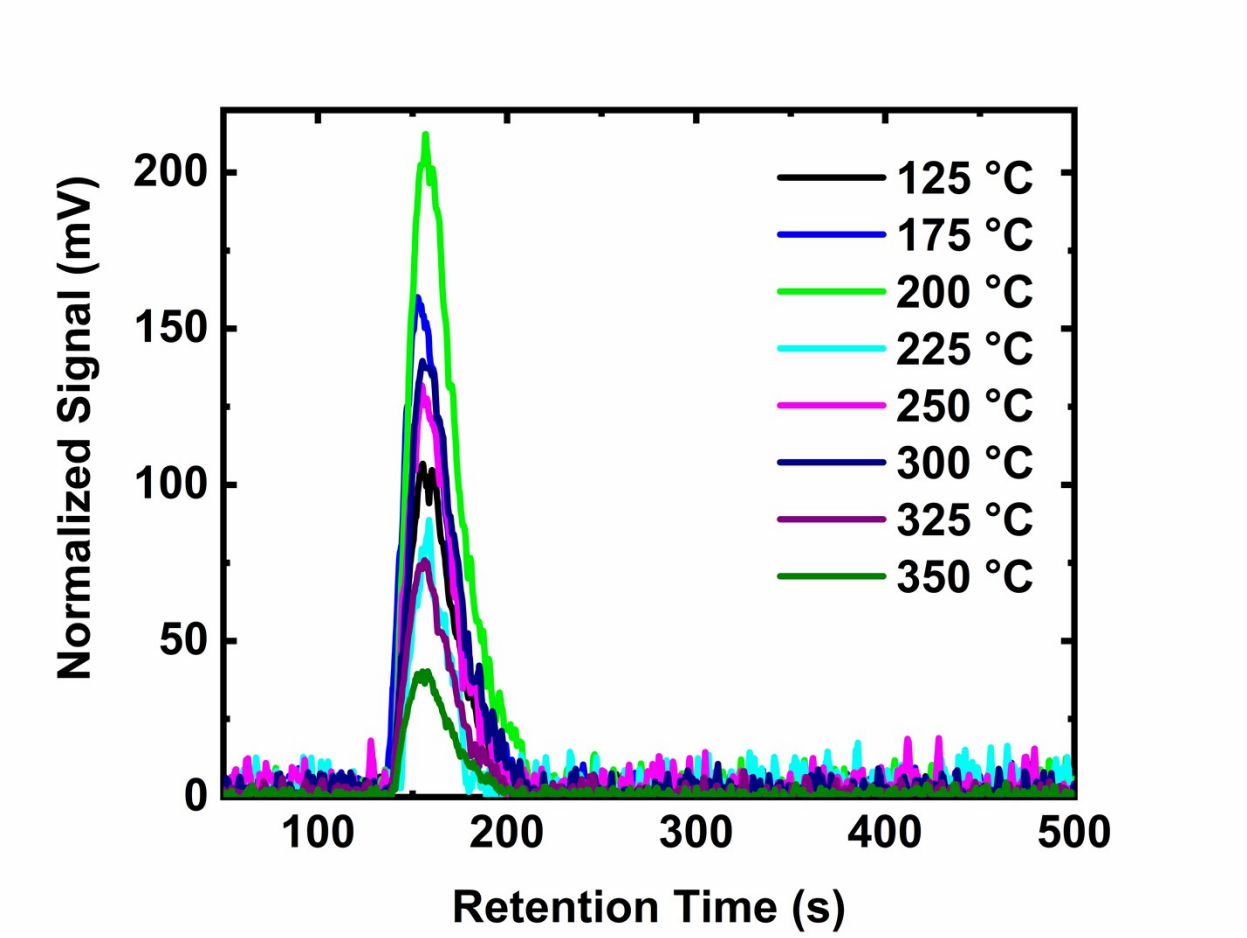

Figure S10. TPD from monolayer coverage ethanol on the surface of α-alumina

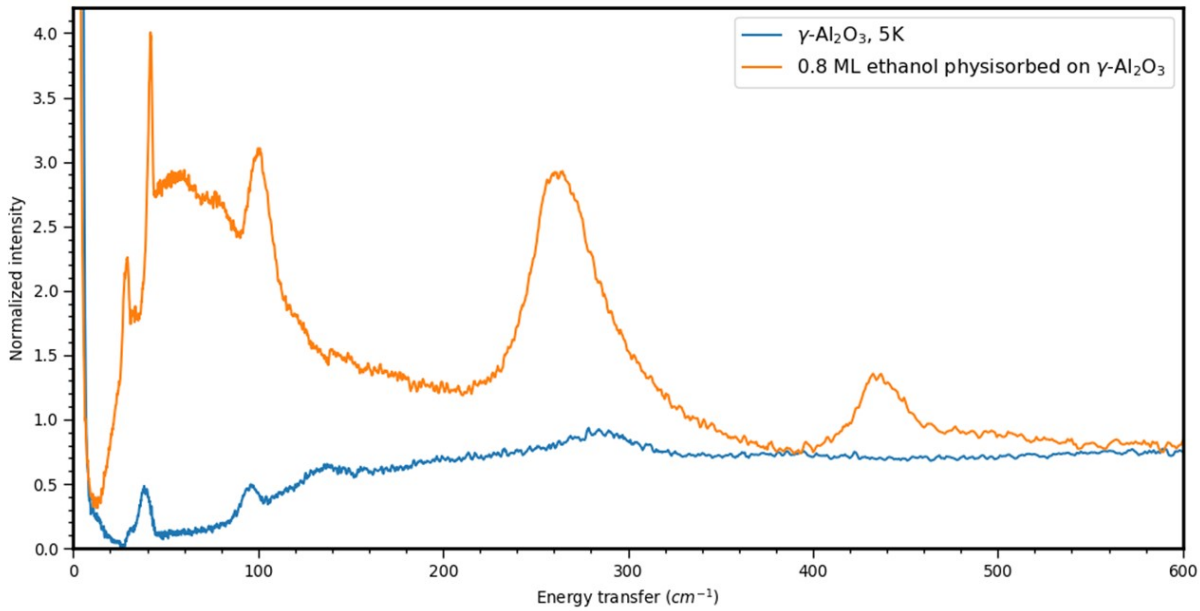

Figure S11. INS spectra of γ-alumina (blue) and 0.8 ML ethanol adsorbed on γ-alumina (orange) at 5 K in the low energy transfer regime (< 600 cm^{-1})