Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

Precise Identification and Characterization of Catalytically Active Sites on the Surface of γ-Alumina**

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Author Contributions

All authors participated in the planning of experiments, data collection and analysis, and writing of the manuscript.

Materials and methods

Rhombus-platelet γ-alumina used was synthesized from aluminum isopropoxide via a hydrolysis method (ref. 11 in the main text). More specifically, approximately 10 g of aluminum isopropoxide was added to ∼50 mL of water with vigorous stirring at 80 °C for 1 h. The mixture was transferred to the 125 mL Teflon liner of a Parr reactor and placed into an oven and kept at 200 °C for 24 h. After cooling to room temperature, the powder was collected by filtration, washed with distilled water, and dried at 100 °C. The as-synthesized boehmite powder was then calcined at 800 °C for 2 h to convert it to rhombus-platelet γ-alumina with surface area of approximately 70 m^2/g.

Commercial SBA-200 γ-alumina with surface area ~ 200 m^2/g was used without additional pretreatment.

Rod-like and platelet γ-alumina (with surface area ~70 m^2/g) were synthesized according to the previous method at the pH ~ 4 (ref. 24 in the main text).

Samples with anchored sodium ions were prepared as follows: desired amount of 99.995 % purity sodium nitrate was dissolved in the minimal amount of de-ionized water approximately equivalent to the pore volume alumina. Then it was added sequentially with a micropipette to alumina powder and vigorously mixed after each addition. The materials were dried at 80 ºC in flowing nitrogen and then calcined at 650 ºC in flowing dry air.

γ-Al_2O_3 was loaded with 5 wt % of Pt by wet impregnation (incipient wetness) using $[Pt(NH_3)_4](NO_3)_2$ in water. To form Pt nanoparticles, further calcination-reduction treatments were done at 350 °C for 2 h under O_2/He and H_2 flows, accordingly.

TPD experiments: 50 mg of alumina was treated at 400 ºC under 20% O_2/He flow (60 ml/min). The sample was cooled down to room temperature in helium flow and ethanol adsorption was carried out for 30 min with 2.0% ethanol/He gas mixture (60 ml/min), followed by a He purge for 30 min in order to remove weakly-bound ethanol molecules. After stabilization of the FID signal of an Agilent 7820A gas chromatograph (GC), TPD was carried out in flowing He (60 ml/min) with a heating rate of 10 °C/min.

The *in-situ* transmission IR experiments were conducted in a home-built cell housed in the sample compartment of a Bruker Vertex 80 spectrometer, equipped with an MCT detector and operated at 4 cm^{-1} resolution. The powder sample was pressed onto a tungsten mesh which, in turn, was mounted onto a copper heating assembly attached to a ceramic feedthrough. The sample could be resistively heated, and the sample temperature was monitored by a thermocouple spot welded onto the top center of the W grid. The cold finger on the glass bulb containing CO (99.995%) and N_2 (99.995%) was cooled with liquid nitrogen to eliminate any potential contamination originating from carbonyls and moisture. Prior to spectrum collection, a background with the activated (annealed, reduced or oxidized) sample in the IR beam was collected. Each spectrum reported is obtained by averaging 256 scans.

Microscopy analysis was performed with a FEI Titan 80-300 microscope operated at 300 kV. The instrument is equipped with a CEOS GmbH double-hexapole aberration corrector for the probe-forming lens, which allows for imaging with 0.1 nm resolution in scanning transmission electron microscopy mode (STEM). HAADF-STEM images were acquired with a high angle annular dark field (HAADF) detector with inner collection angle set to 52 mrad.

^{27}Al MAS NMR measurements were performed at room temperature on a Bruker 850 MHz NMR spectrometer, operating at a magnetic field of 19.975 T. The corresponding ^{27}Al Larmor frequency is 221.4125 MHz. A single pulse sequence comprised of a $\pi/9$ pulse width of 0.3 μs, a recycle delay of 2 s, and an acquisition time of 30 ms was employed to collect the free induction decays (FID). To enhance the intensity of the observed spectral features over the noise, 4,096 repetitions were employed for each FID. Each collected FID was subsequently Fourier Transformed to the frequency domain where both zero and first order phase corrections were applied. The broad spectrometer background signal was collected with a sample containing no Al species under the same conditions and subsequently subtracted from each Al_2O_3 spectra. The data were simulated for best fit and the intensities of each coordination environment from the simulations were taken together to provide the fractional abundance. Total intensity was normalized to the carefully measured mass of each sample used for the NMR experiment, which was typically ~ 15 mg. All NMR data were acquired at a sample spinning rate of 18.7 kHz (± 5 Hz) and externally referenced to 1.0 M aqueous $Al(NO_3)_3$ (0 ppm). If indicated, samples were thermally treated ex-situ at the temperature specified using a ramp rate of 5°C/min for x hours in dry N_2. The samples were then sealed into a tube (with valves to isolate it from the ambient air) under the drying environment, transferred to a glovebox without exposure to air, and packed inside 3.2 mm pencil-type NMR rotors. The rotors were subsequently sealed and placed in vials until transported to the NMR probe which was purged with dry N_2 and vacuumed.

X–ray diffraction (XRD) patterns were collected on a Rigaku Mini Flex II bench top X–ray diffractometer using a Cu–Kα radiation of 0.154056 nm (30 kV and 15 mA). Experiments were conducted on a powder sample holder in a 2θ range of 10–80°, with a step size of 0.02°/s. All measurements were performed under ambient conditions.

Ethanol catalytic experiments were performed in the flow-through reactor. 200 mg catalyst powder was pre-treated in the reactor in the flowing air at 350 ºC for 1 hour prior to starting the reaction. Ethanol was injected with a syringe pump with 240 sccm He and 0.01151 ml/min of ethanol liquid, corresponding to ~1.94% ethanol in He. Products were quantified with gas chromatography.

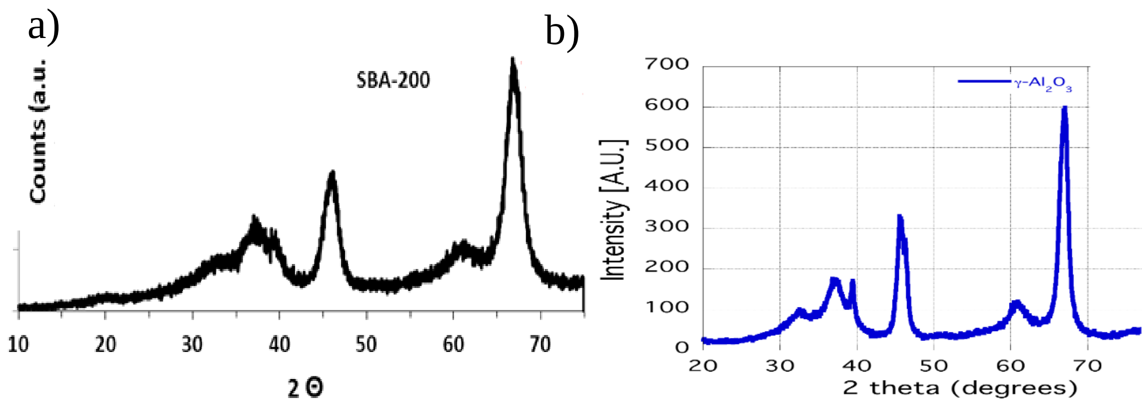
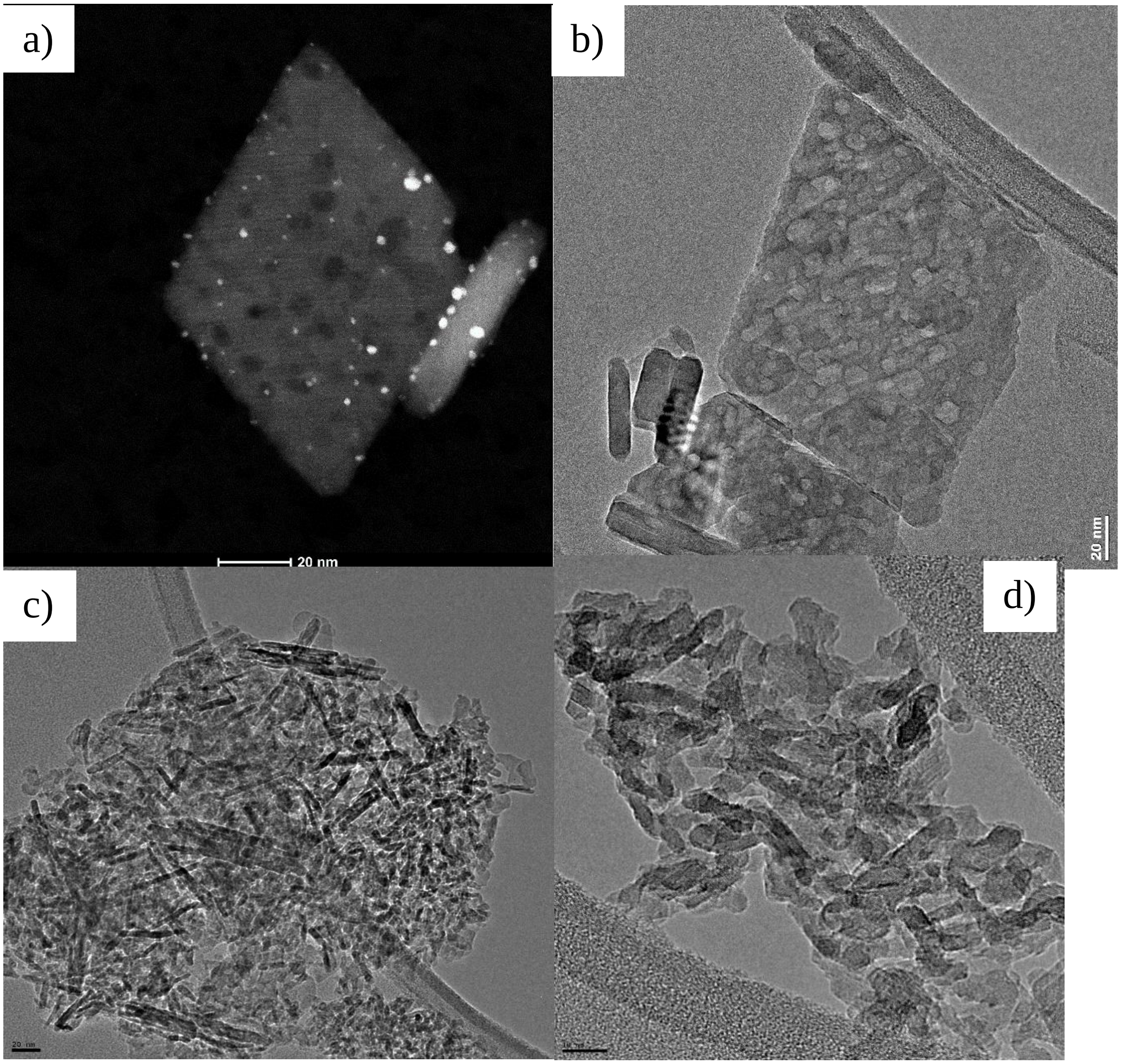


Fig. S1. XRD patterns of SBA-200 (a) and rhombus-platelet γ-alumina (b). SBA-200 has wider peaks due to smaller crystallite size (surface area 200 m^2/g). Rhombus-platelet alumina (surface area 70 m^2/g) has narrower peaks due to its larger crystallite size and more defined crystals (see additional electron microscopy images below for visualization).


a)
20 nm
b)
20 nm
c)
20 nm
d)

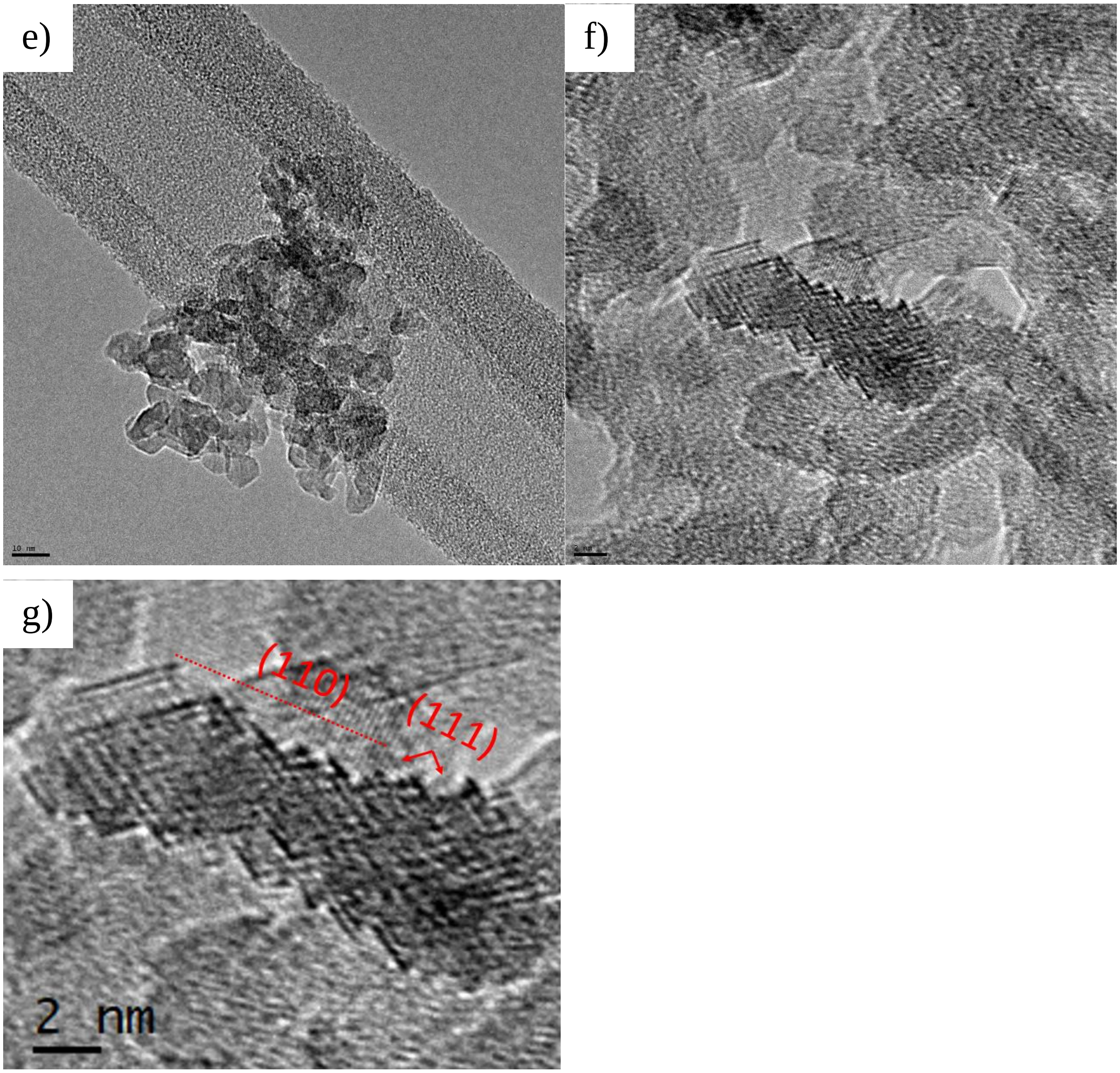


Fig. S2. a) HAADF-STEM of Pt on rhombus-platelet γ-alumina sample: it can be seen that Pt nanoparticles reside predominantly on (110) surface. (111) surface has significantly fewer Pt particles. b) typical HRTEM image of rhombus-platelet γ-alumina sample. c)-d) typical HRTEM images of SBA-200 γ-alumina sample. Abundant nanosized platelets can be easily seen as well as a significant fraction of less well-defined nanocrystal shapes. e) HRTEM image of SBA-200 γ-alumina sample showing less defined nanocrystals. f) nanocrystal of SBA-200 with macroscopically defined (110) surface. g) magnified nanocrystal from f) showing that (110) facet is reconstructed into (111) and (100) ridges analogous to Fig. 3 a)-c) in the Main text.

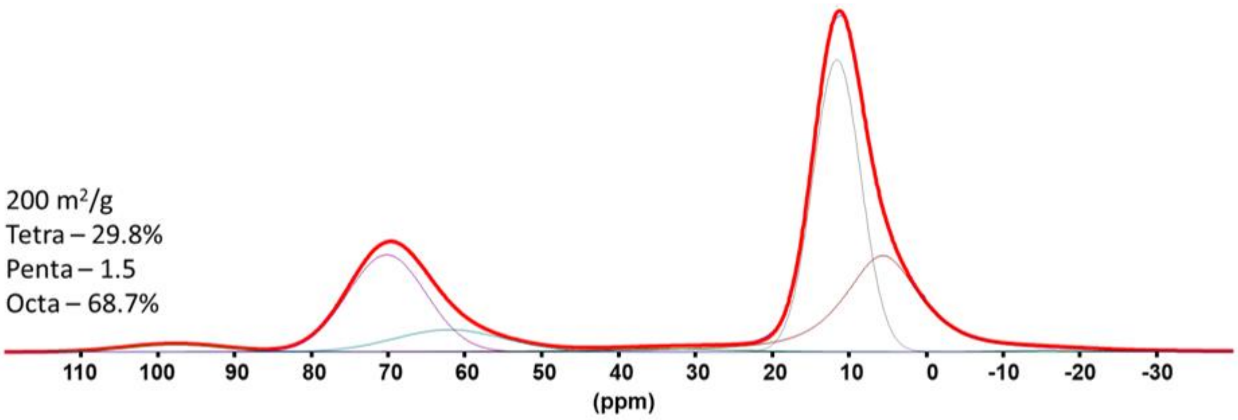


Fig. S3 High-field solid-state ^{27}Al NMR of fresh SBA-200 γ-alumina at 850 MHz. Decomposed features are not intended to be representative of specific Al species, but are used as a guide to determine the abundance of each Al site, shown for reference only.

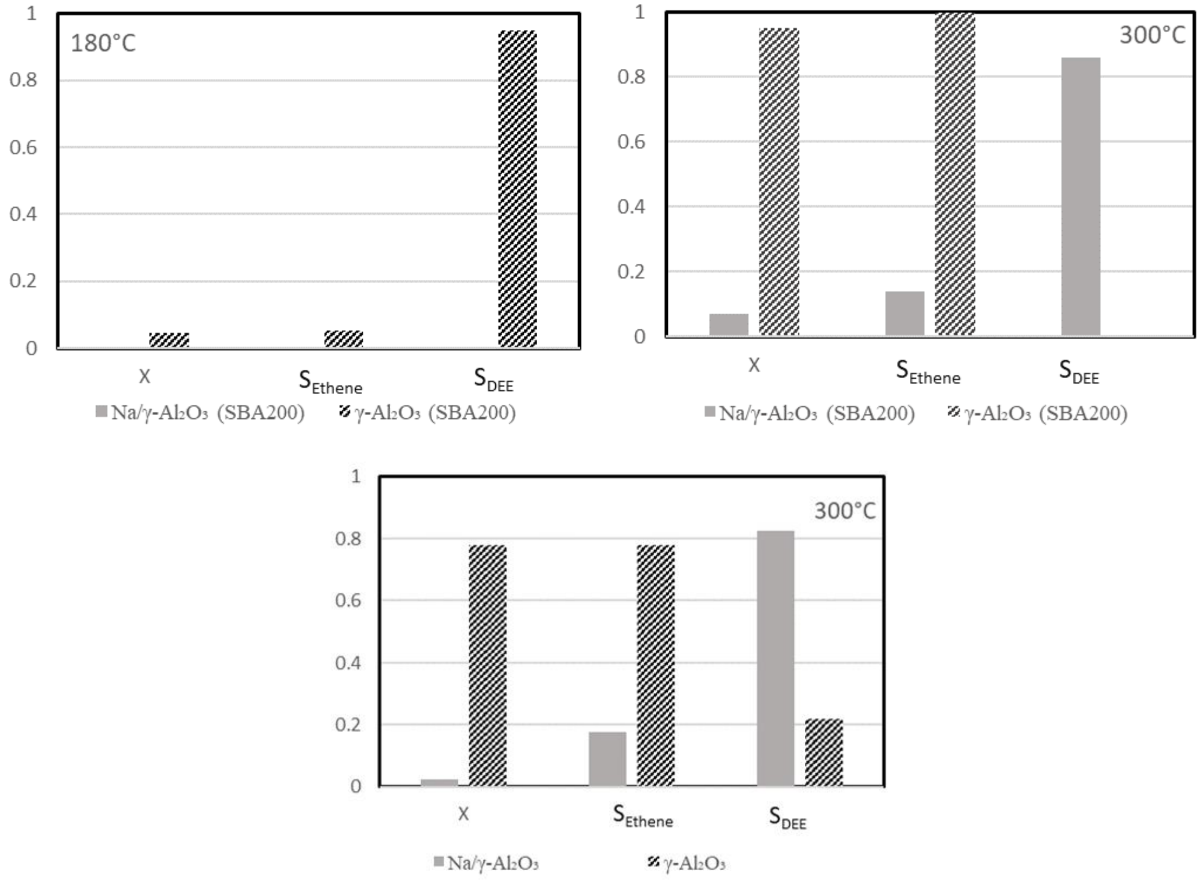


Fig. S4. Conversions and selectivities of SBA-200 alumina with and without Na in ethanol dehydration at 180 ºC and 300 ºC (Top) and the same for SBA90 (bottom). X=conversion. S=selectivity. Ethene=Ethylene. DEE=diethyl ether.

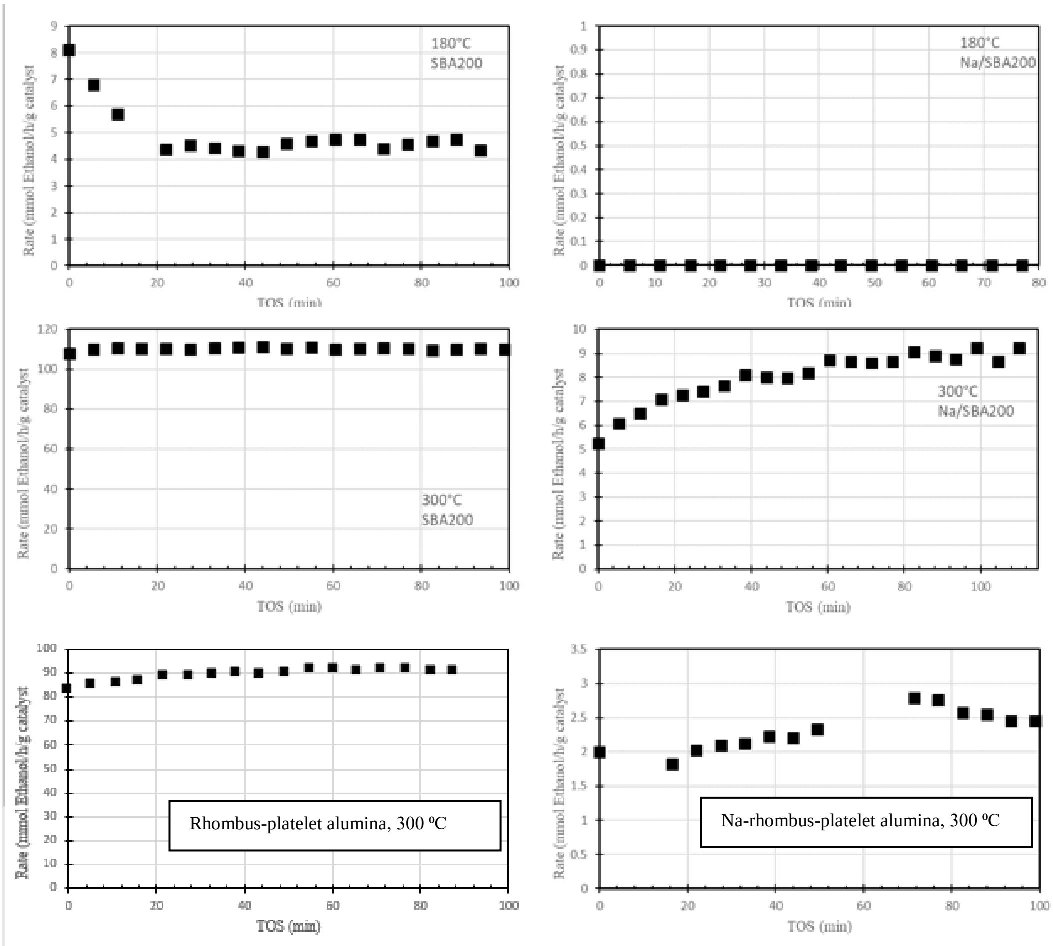


Fig. S5. Ethanol dehydration time-on-stream behavior of aluminas (rhombus-platelet and SBA-200) with and without sodium at 180 ºC and 300 ºC. TOS=Time-on-stream. Rate is expressed as mmol/h/$g_{catalyst}$

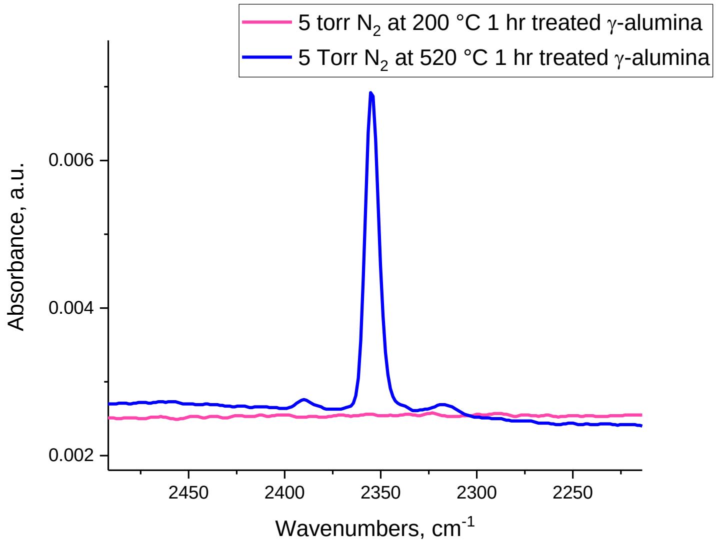


Fig. S6. FTIR during N_2 adsorption (5 Torr) on 600ºC heated (1 hr, 10^{-7} Torr) γ-alumina (spectra taken at 298 K) (rhombus-platelet alumina was used).

Table 1. Relative intensities of -OH and N-N IR bands of rhombus-platelet γ-alumina at 298 K after thermal treatment at each temperature and exposure to 5 Torrs of N_2 at each temperature. The in-situ studies were performed on one tablet (see Fig. 1 in the Main text).

Temperature, ºC	Relative intensity of 3,770 cm^{-1} band, %	Relative intensity of 2,355 cm^{-1} band, %
275	100	0
375	100	0
420	80	21
520	46	50
700	0	100

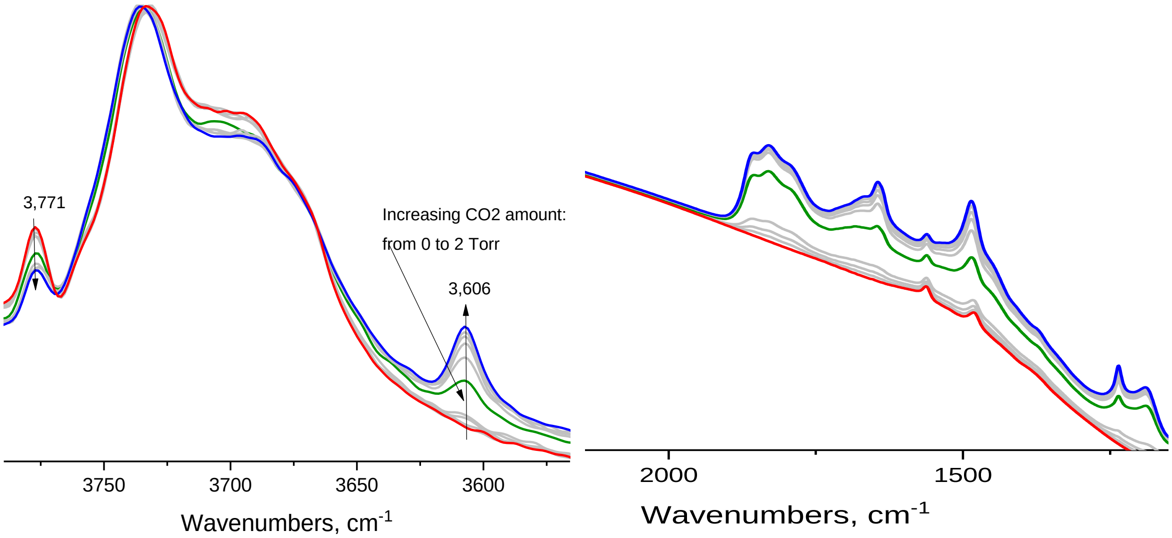


Fig. S7. The OH and CO regions during in-situ FTIR during CO_2 adsorption (2 Torr) on the γ-alumina sample pre-heated at 500ºC for 1 hr under 10^{-7} vacuum.

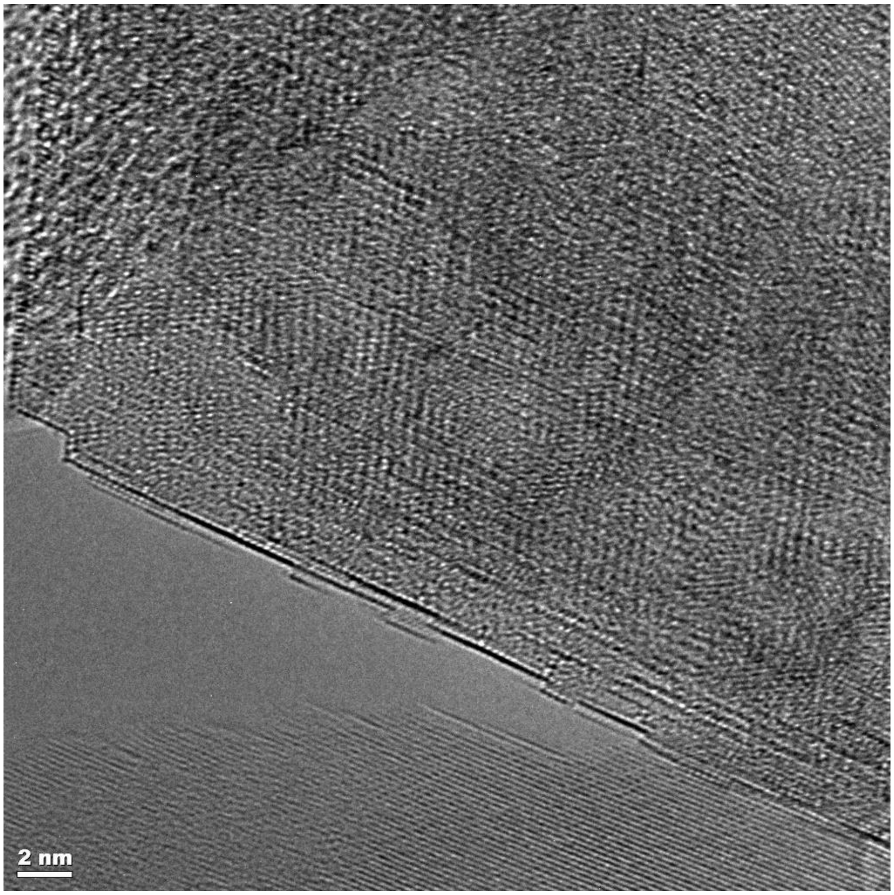


Fig. S8. Another view of macroscopically defined (111) γ-Al_2O_3 surface in HRTEM.

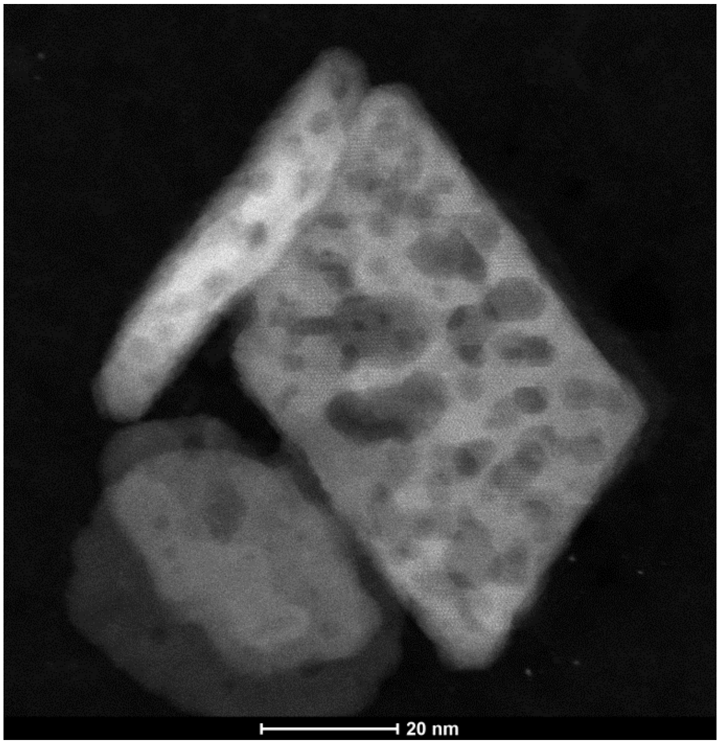


Fig. S9. HRTEM images of rhombus-platelet γ-Al_2O_3 sample showing not only well-defined uniform crystals but also some less well-defined crystals (lower left corner) with irrational surfaces co-existing with well-defined crystals (upper and upper right corner).

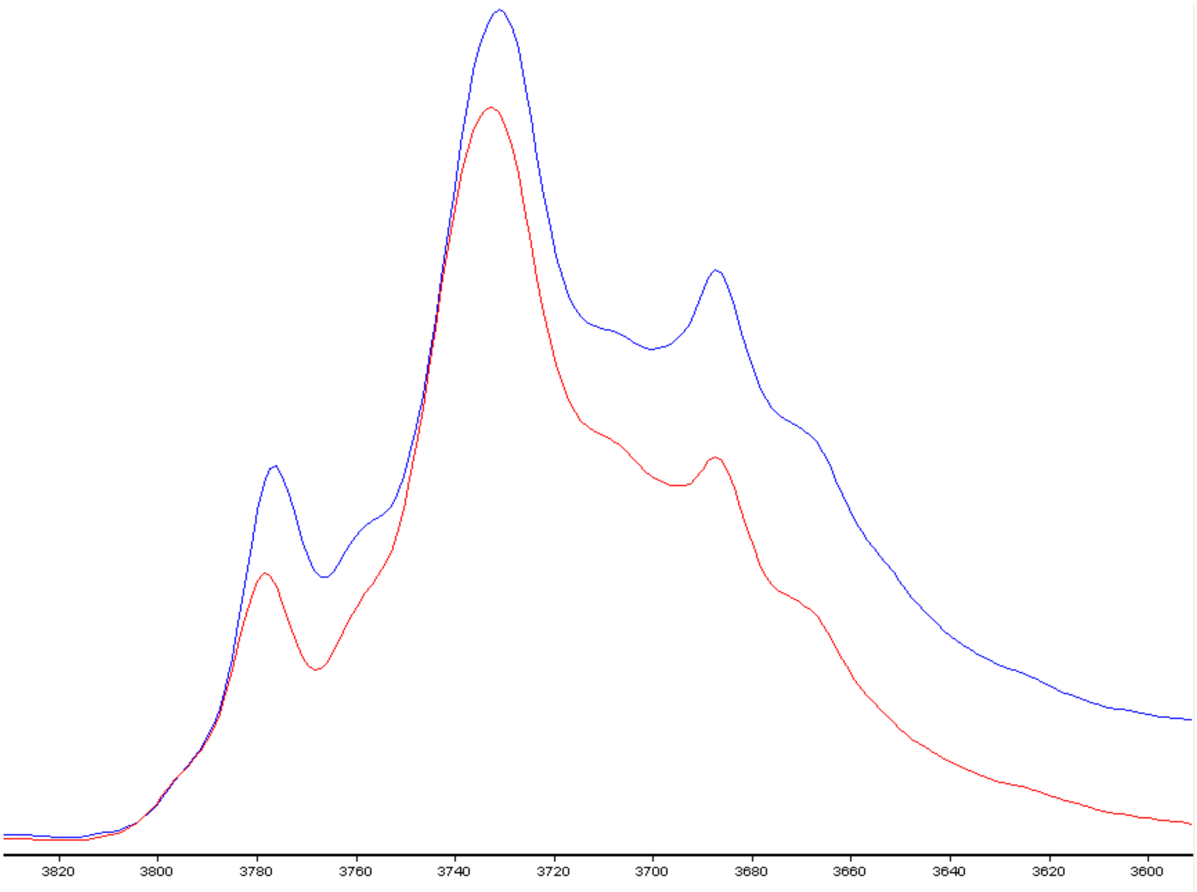


Fig. S10. FTIR in the OH stretching region of rod-like γ-alumina sample heated under vacuum at 500 ºC (for 15 min, blue spectrum) and 700 ºC (for 15 minutes, red spectrum). 3772 cm^{-1} band goes down, and shifts towards 3778 cm^{-1}, analogous to rhombus-platelet and SBA-200 samples (Figs. 1 and 2 in the main text). 3790 cm^{-1} band does not decrease and thus, does not dehydroxylate.

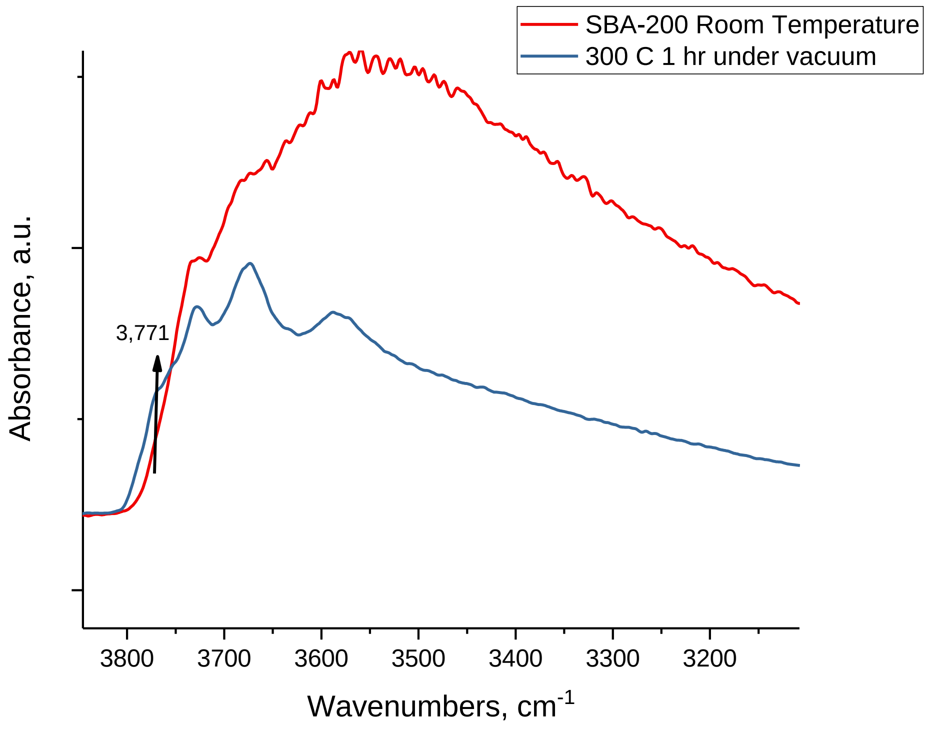
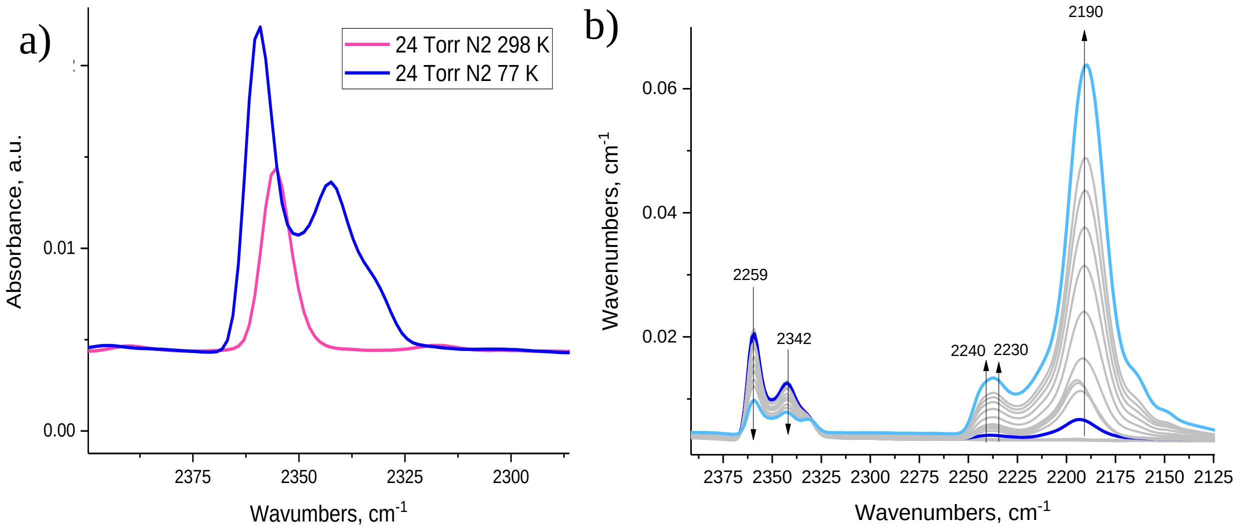


Fig. S11. FTIR spectrum of SBA-200 loaded from air at RT and under 10^{-7} Torr vacuum and then heated at 300ºC for 1 hr prior to cooling back to 298 K.



Figs. S12. a) FTIR after 24 Torr N_2 adsorption at 77 K (blue curve); comparison with 24 Torr N_2 adsorption at 298 K (pink curve) . b) FTIR during subsequent CO adsorption on N_2-saturated alumina sample at 77 K.

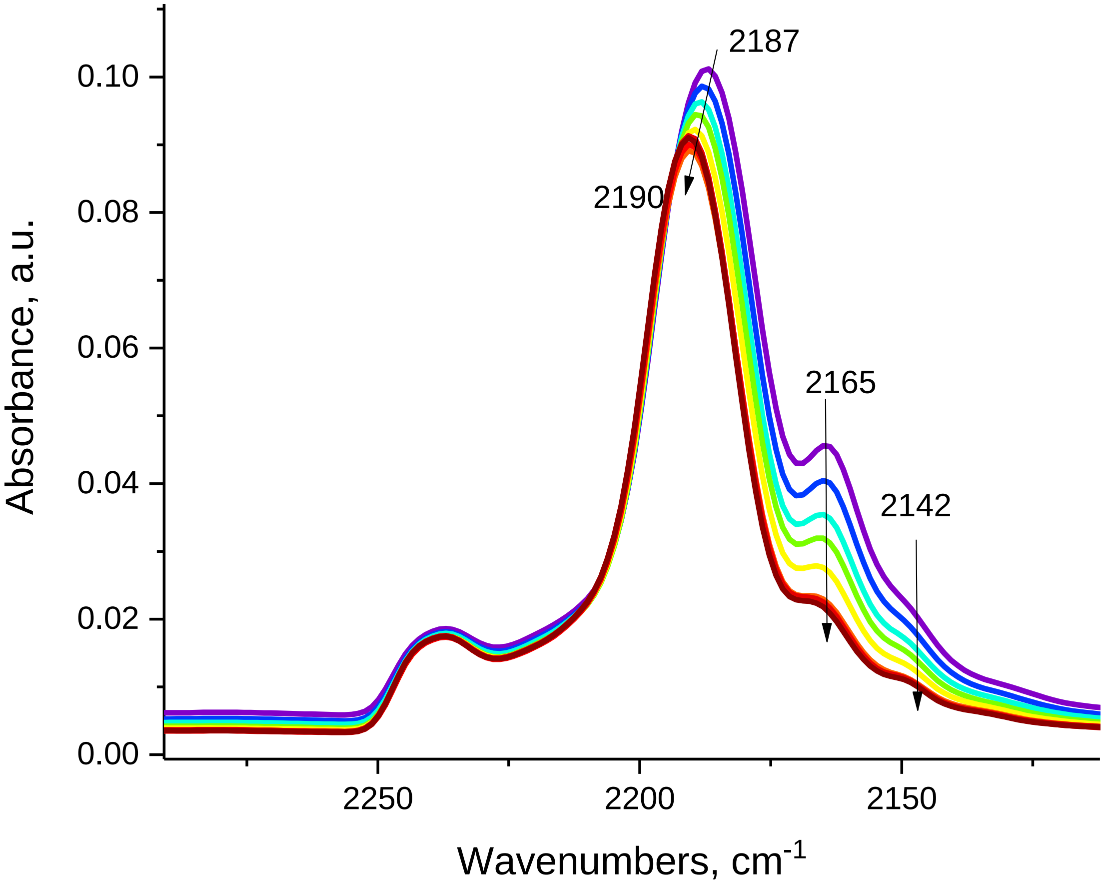


Fig. S13. Vacuum on CO covered alumina sample at 77 K.

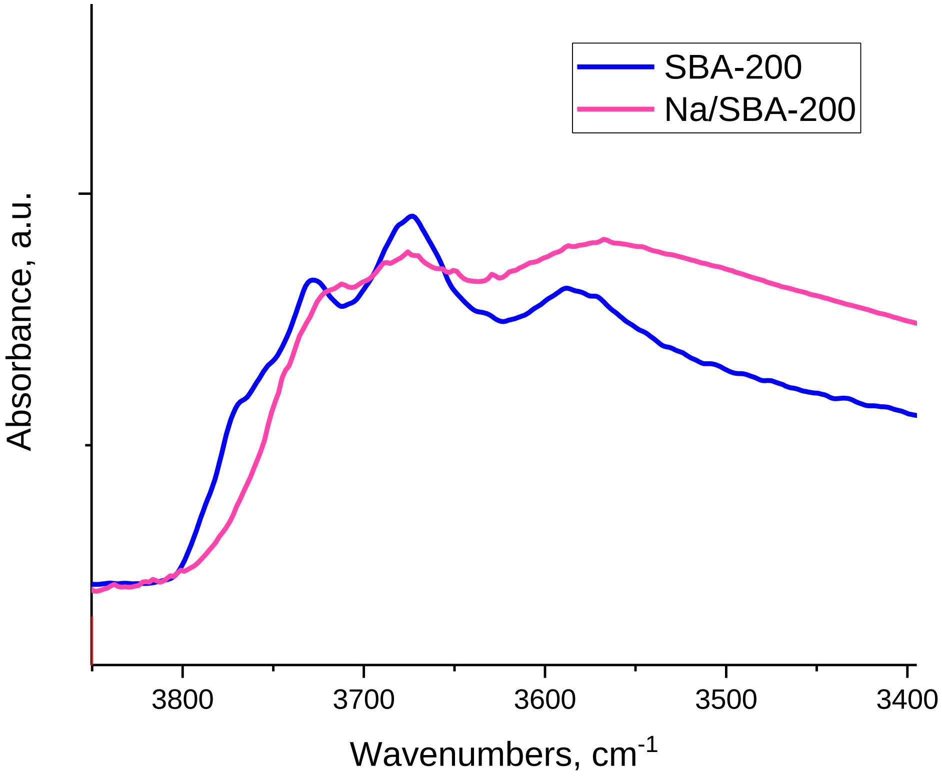


Fig. S14. Comparison of the -OH stretching region of SBA-200 sample (pre-treated at 350 ºC) and Na/SBA-200 (pre-treated at 350 ºC). Note that the spectra were collected on two different tablets.

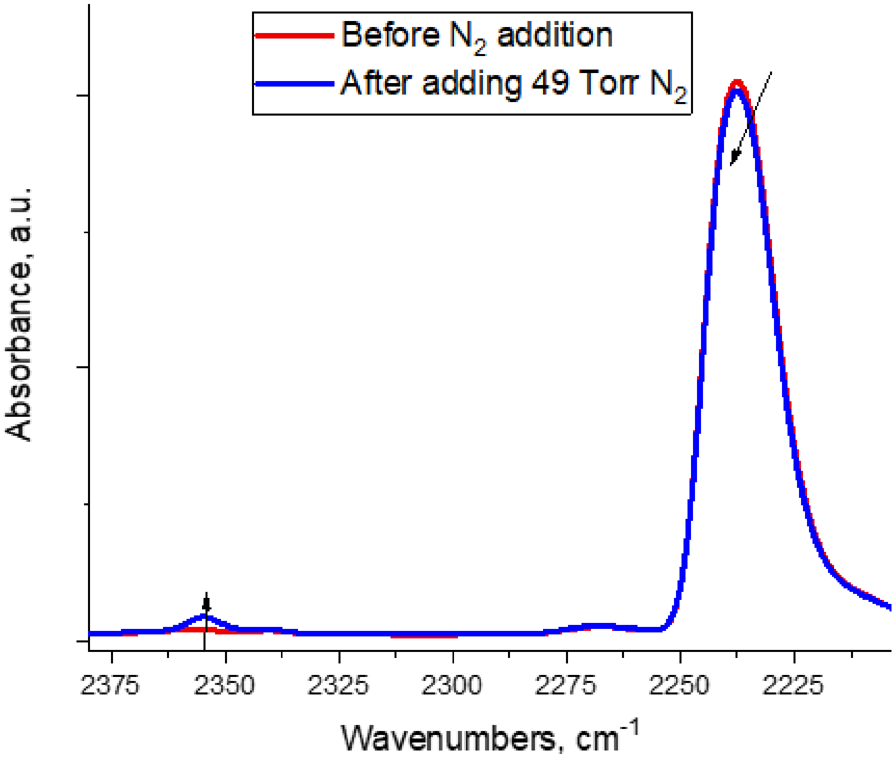


Fig. S15. in-situ FTIR during addition of 49 Torr N_2 to $O_5Al(VI)$-CO complex formed in Fig. 4b at room temperature.

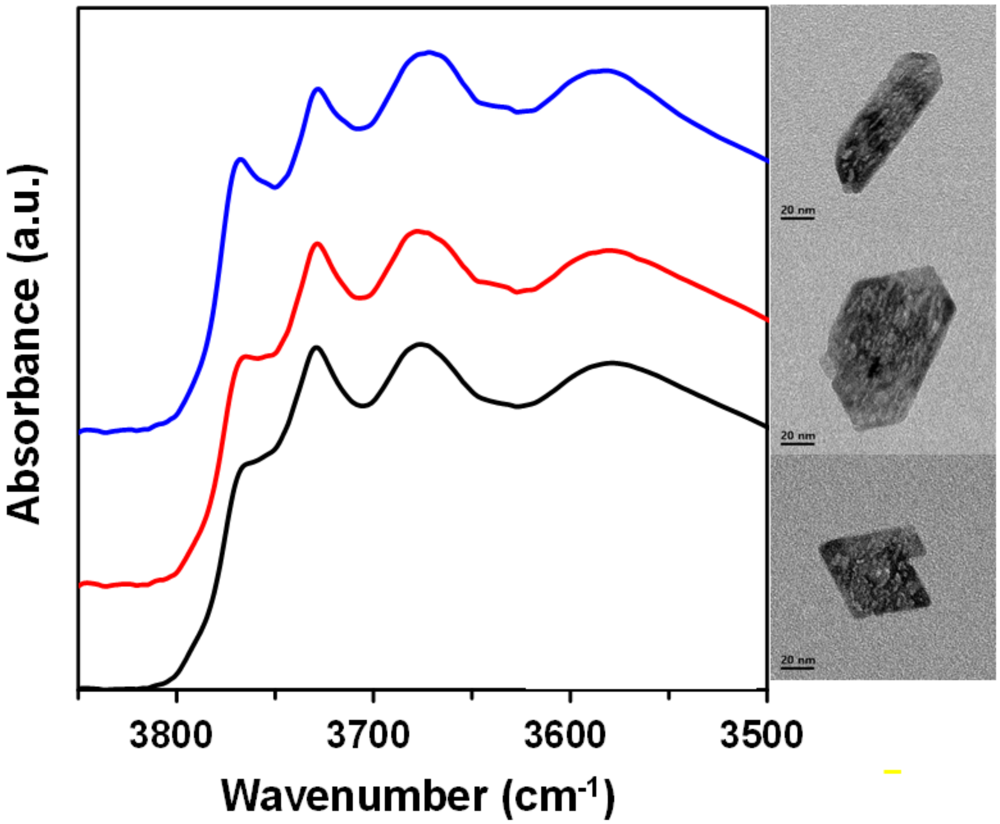


Fig. S16. FTIR spectra of the -OH region of platelet (black), rhombus-platelet (red) and rod-like (blue) gamma-alumina samples with the corresponding HRTEM images on the right for each sample. Spectra were normalized by the intensity of ~3,725 cm^{-1} band.

Ethanol TPD

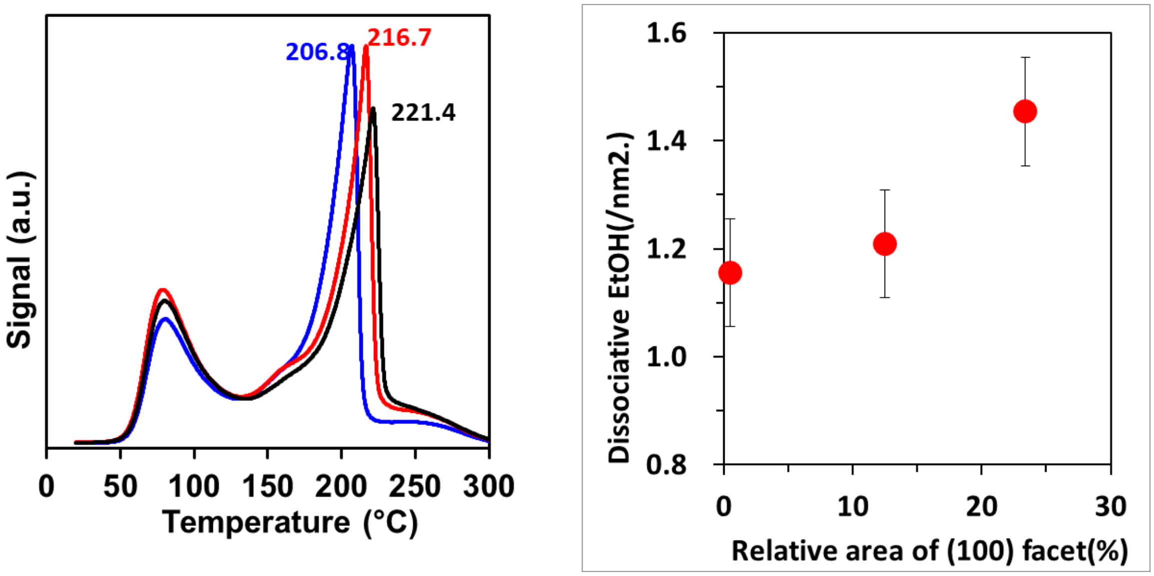


Fig. S17. TPD results for rhombus-platelet, platelet and rod-like gamma-alumina samples. The peak around ~210 ⁰C in TPD corresponds to desorbed ethylene molecules. The graph on the right correlates the relative ratio of (100) facet with the surface-normalized amount of reacted ethanol.

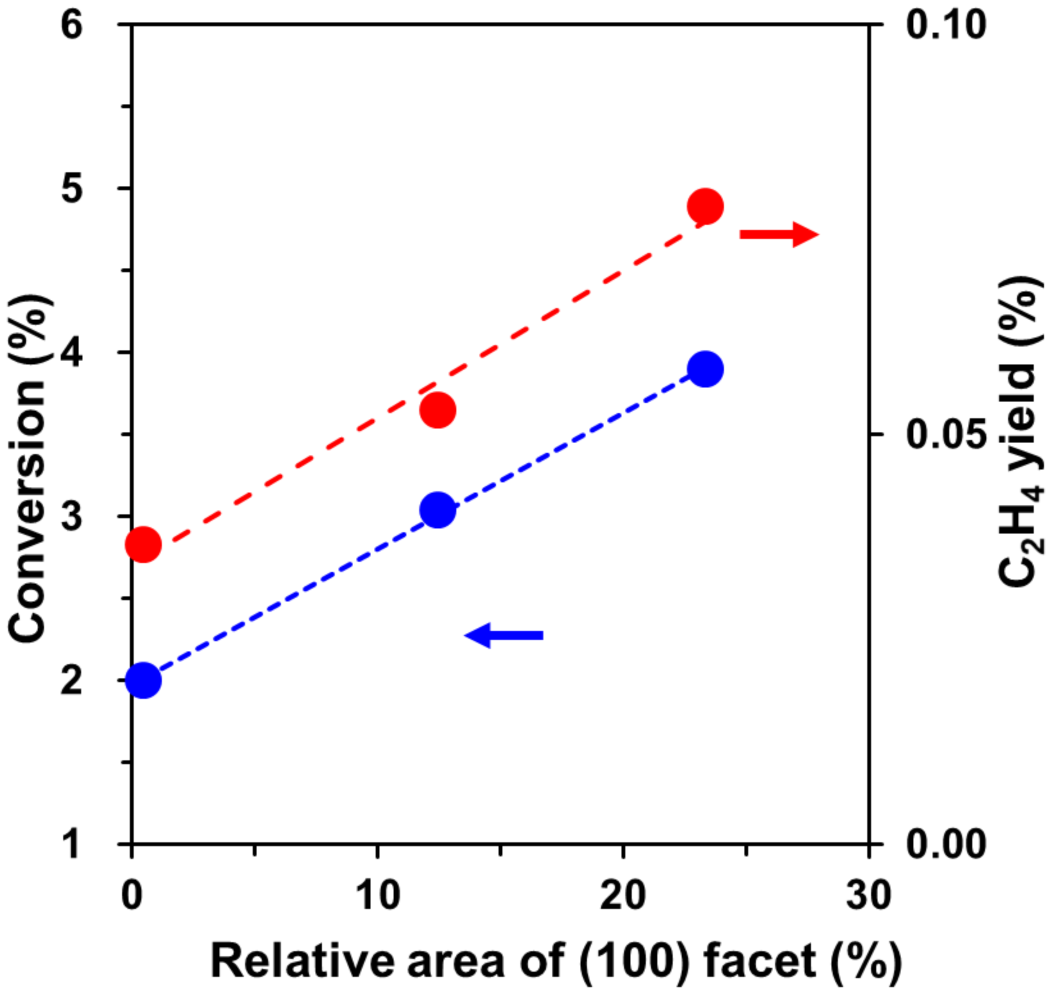


Fig. S18. Ethanol dehydration catalytic results (conversion and ethylene yield) with the corresponding relative fraction of macroscopically defined (100) facet. Reaction conditions: 2% ethanol in He (total flow rate = 120 ml/min), 10 mg gamma-alumina, T = 180 ºC.