

On the Nature of Extra-Framework Aluminum Species and Improved Catalytic Properties in Steamed Zeolites

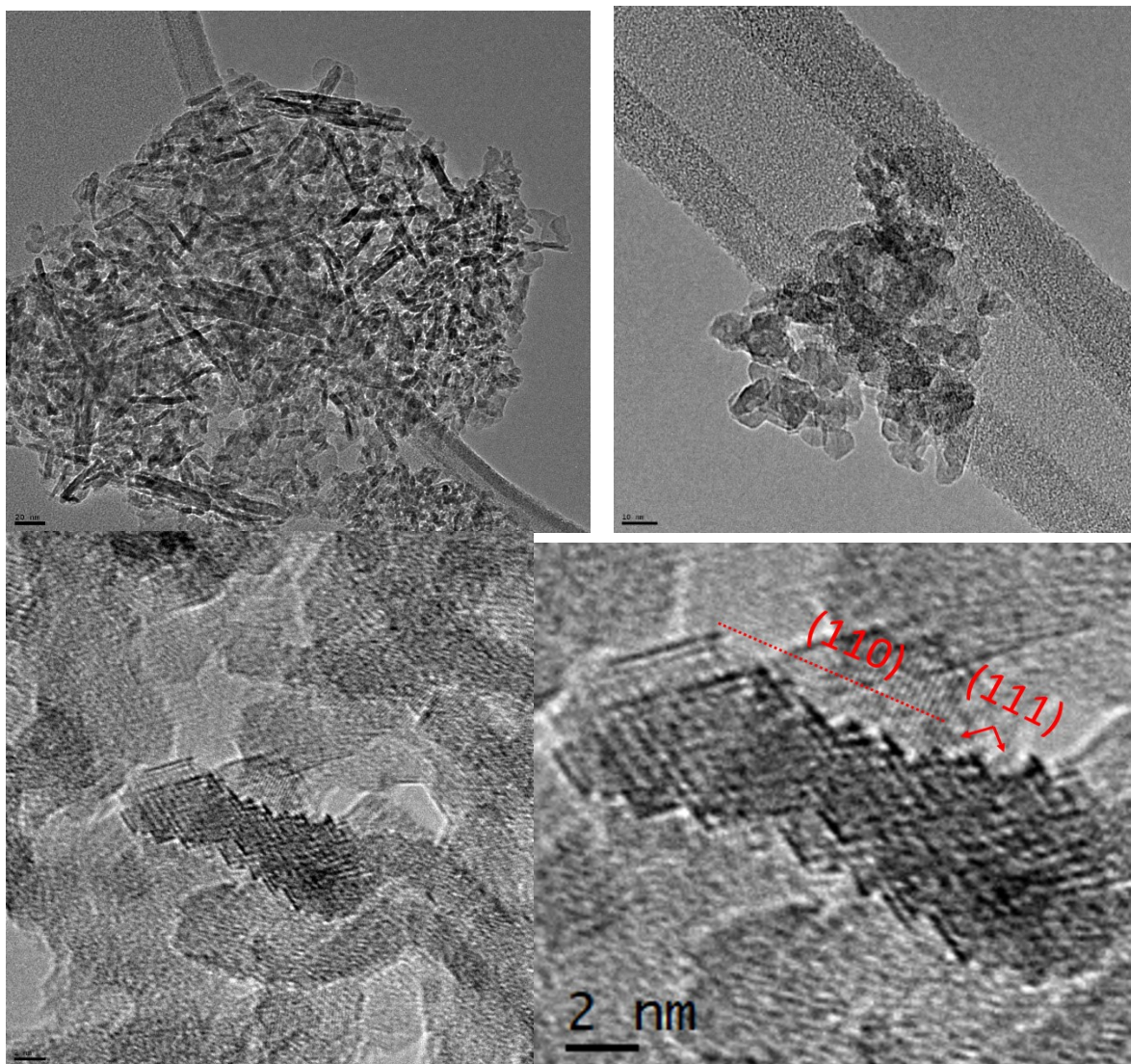


Figure S1. typical HRTEM images of high surface area ($\sim 200 \text{ m}^2/\text{g}$) SBA-200 γ -alumina sample. It consists of abundant platelets can be easily seen (image 1) as well less common less well-defined nanocrystal shapes (image 2). Image 3 shows nanocrystal of SBA-200 with macroscopically defined (110) surface: image 4 shows magnified nanocrystal showing that (110) facet is reconstructed into nano (111) and (100) ridges, completely analogous to all gamma-alumina surfaces.

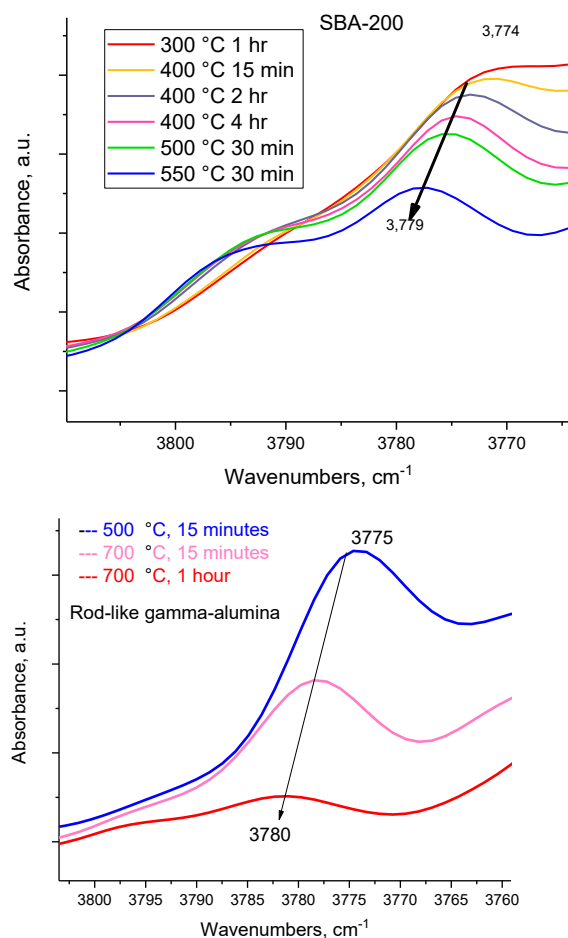


Figure S4. FTIR of the OH region of SBA-200 and rod-like gamma-alumina samples during thermal treatments. Spectra were recorded at room temperature after specified thermal treatments.

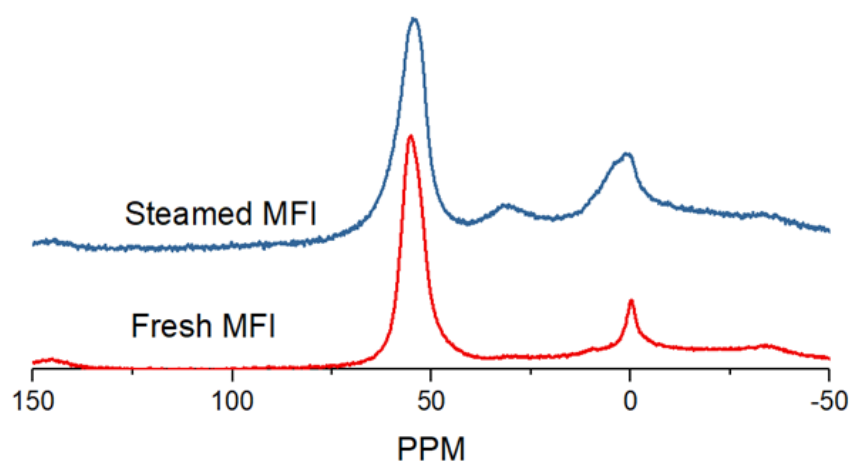


Figure S5. Solid-state ^{27}Al NMR of fresh and steamed MFI samples. The band ~ 33 ppm corresponds to penta-coordinated Al.

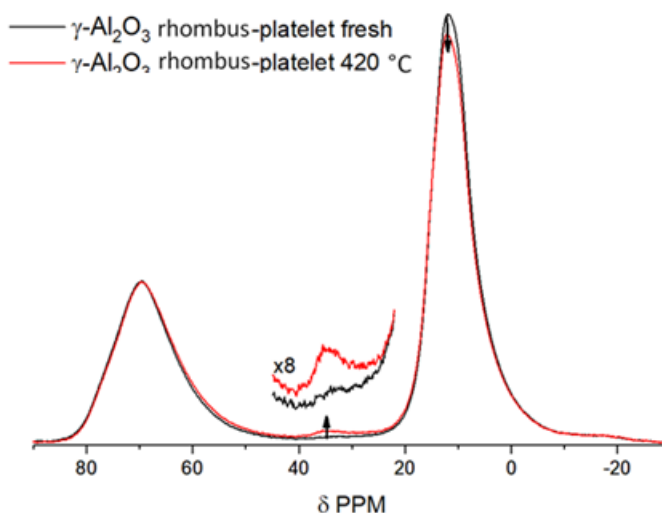


Figure S6. Solid-state ^{27}Al NMR fresh and dehydroxylated rhombus-platelet gamma-alumina sample ($\text{SA} \sim 70 \text{ m}^2/\text{g}$). Only tetra, penta and octa-Al sites are present. Upon dehydroxylation, surface octahedral $\text{O}_5\text{Al(VI)-OH}$ sites dehydroxylate [12] and form penta-sites. Their small abundance is due to the fact that majority of Al remains in the bulk (tetra and octa-Al sites), and only a smaller fraction of Al sites resides on the surface. As the Alumina nano-particle size decreases, more and more Al surface atoms (in terms of relative surface/bulk ratio) get exposed as evidenced from Figure S5 and discussion in the main text. Reprinted with permission from *Angew. Chem. Int. Ed.* 2021, 60, 17522–17530. Copyright Wiley-VCH GmbH 2021.

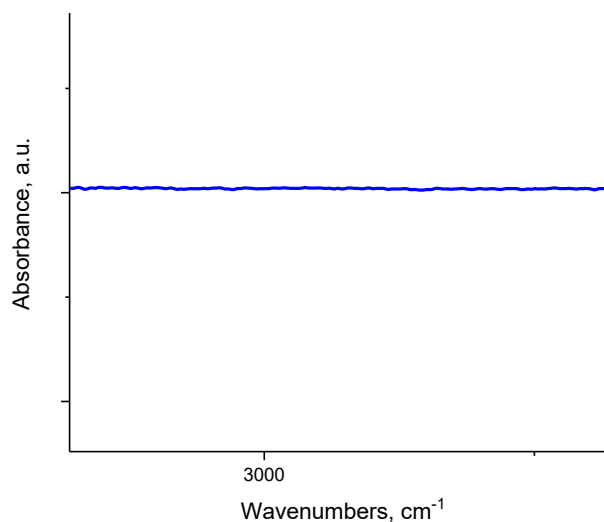


Figure S7. FTIR spectra showing the C-H stretching region of gamma-alumina that was not treated at high temperature (the sample was heated at $300 \text{ }^\circ\text{C}$ under vacuum for 15 minutes, this treatment is not enough to dehydroxylate $\text{O}_5\text{Al(VI)-OH}$ sites) before and after methane pulse at $200 \text{ }^\circ\text{C}$.

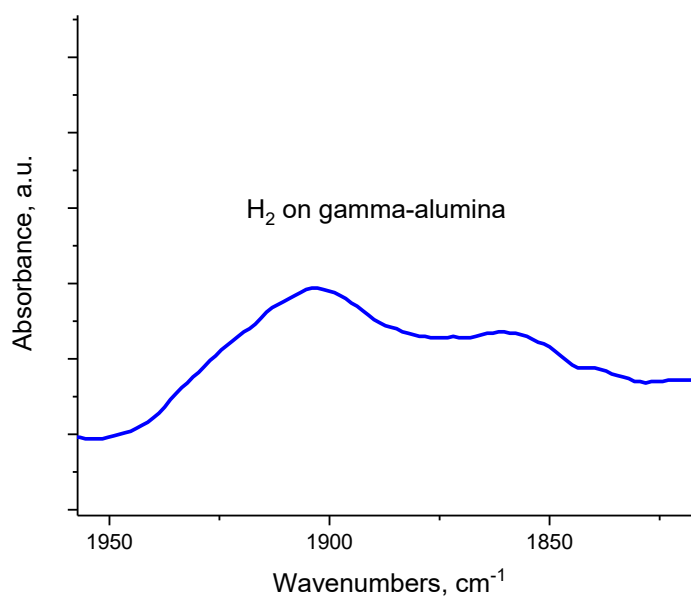


Figure S8. FTIR spectra in the Al-H stretching region after H₂ treatment of gamma-alumina (treated at 500 °C).

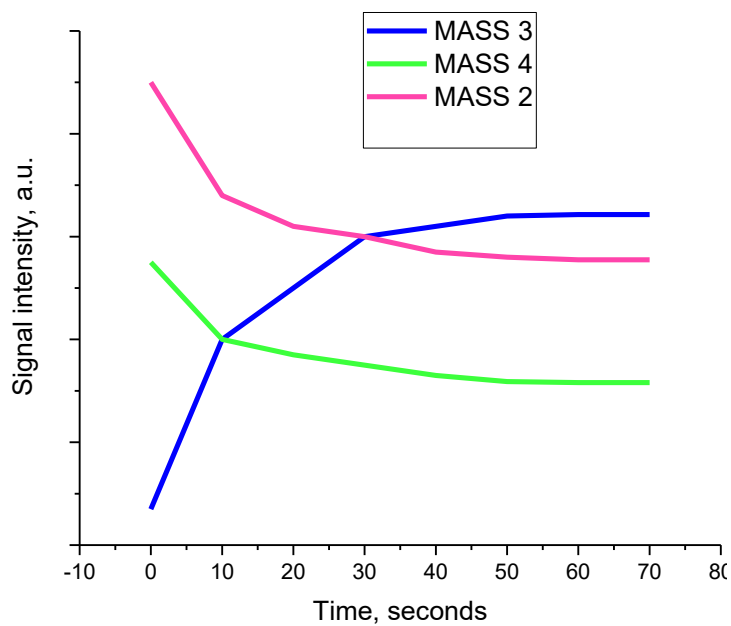


Figure S9. H₂+D₂ reaction monitored with mass-spec in static FTIR system at temperature 100 °C. A mixture of H₂+D₂ was pre-mixed in ~ 1.6-1.7 volume ratio and introduced into the infra-red cell with rhombus-platelet gamma-alumina sample (dehydroxylated at 500 °C). Mass 3 corresponds to product of the reaction HD. Mass 2 corresponds to H₂. Mass 4 corresponds to D₂.