

Supporting Information for

Frustrated Lewis Pairs on Pentacoordinated Al³⁺-Enriched Al₂O₃ Promote

Heterolytic Hydrogen Activation and Hydrogenation

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Experimental Section; Figure S1 to S14; Table S1.

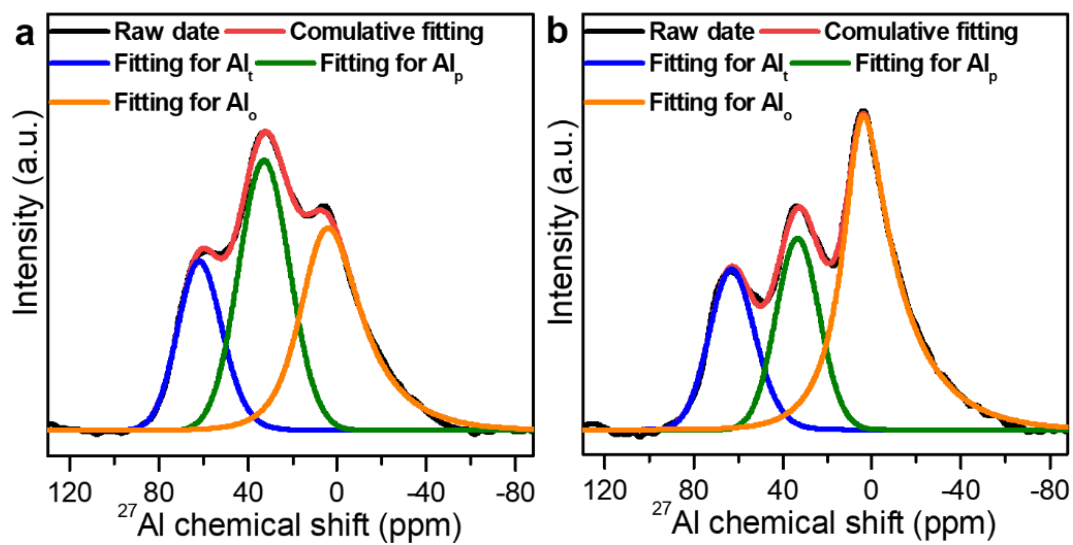


Figure S1. Fitting of solid state ^{27}Al MAS-NMR spectra of $\text{d-Al}_2\text{O}_3$ (a) and NH_3 treated $\text{d-Al}_2\text{O}_3$ (b).

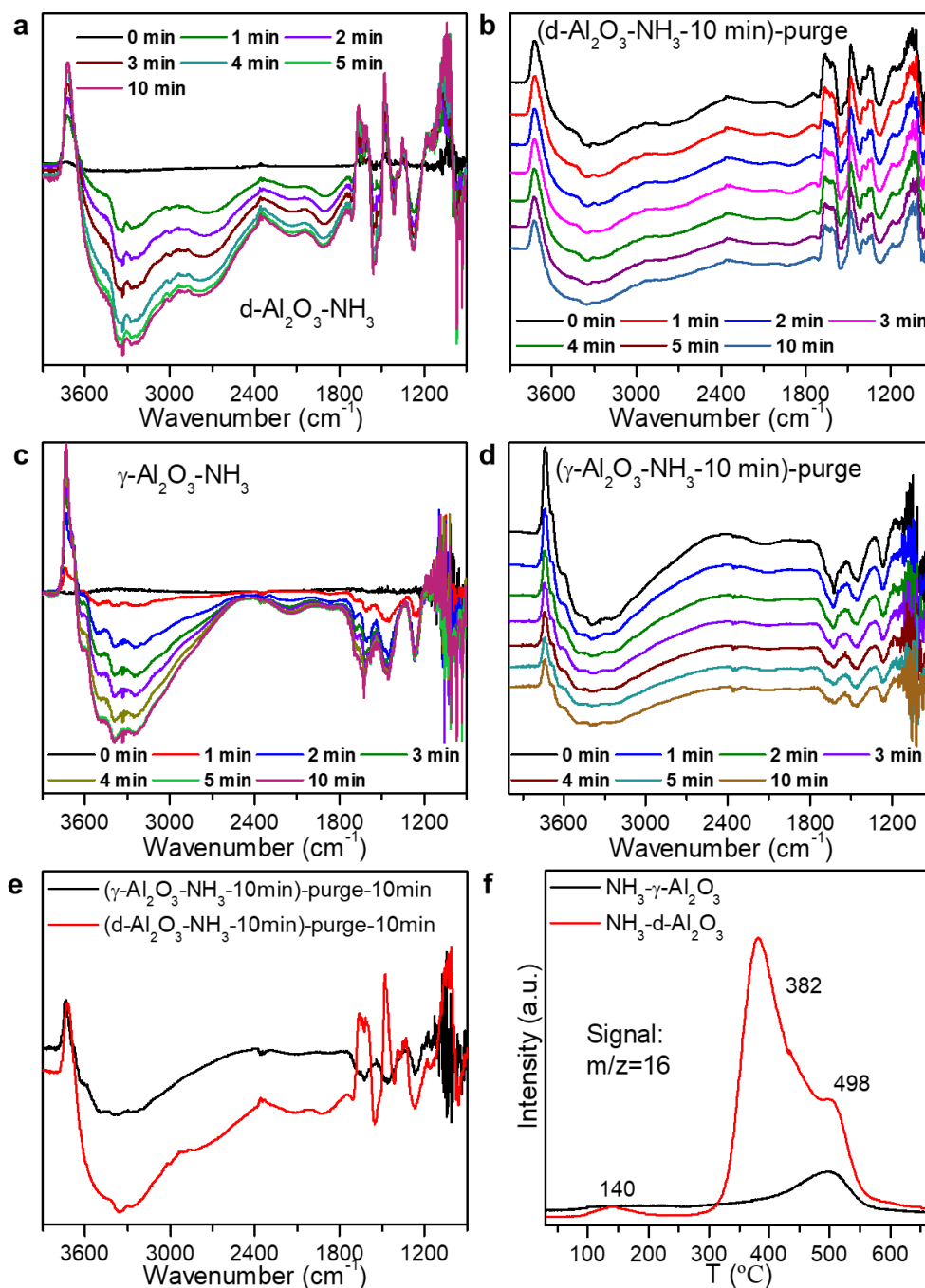


Figure S2. (a) *In-situ* NH₃-FTIR of d-Al₂O₃ treated with NH₃. (b) *In-situ* NH₃-FTIR of d-Al₂O₃ treated with NH₃ for 10 min and then purged with N₂. (c) *In-situ* NH₃-FTIR of γ-Al₂O₃ treated with NH₃. (d) *In-situ* NH₃-FTIR of γ-Al₂O₃ treated with NH₃ for 10 min and then purged with N₂. (e) *In-situ* NH₃-FTIR of d-Al₂O₃ and γ-Al₂O₃ treated with NH₃ for 10 min and then purged with N₂ for another 10 min. (f) NH₃-TPD-MS of d-Al₂O₃ and γ-Al₂O₃.

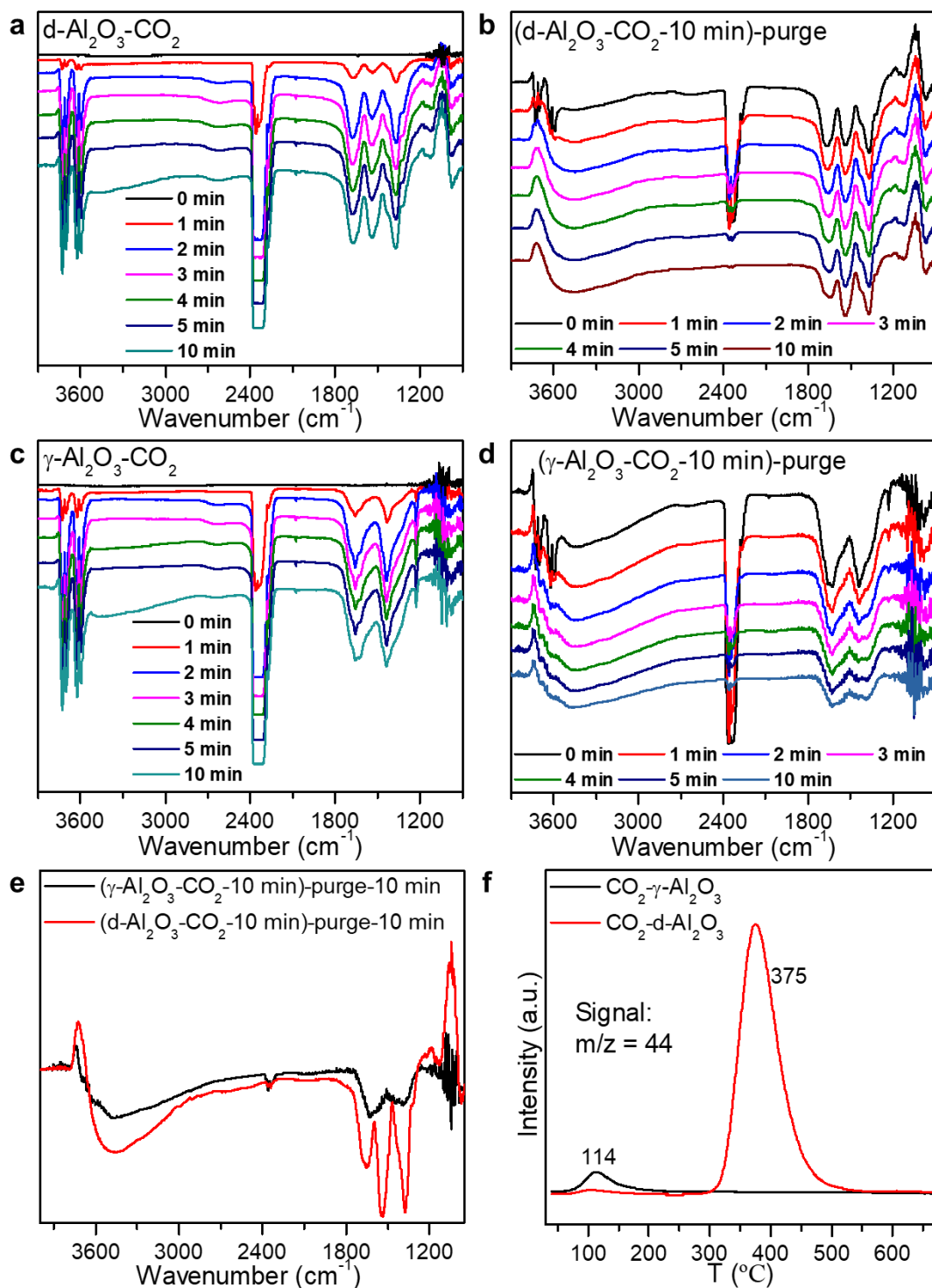


Figure S3. (a) *In-situ* CO₂-FTIR of d-Al₂O₃ treated with CO₂. (b) *In-situ* CO₂-FTIR of d-Al₂O₃ treated with CO₂ for 10 min and then purged with N₂. (c) *In-situ* CO₂-FTIR of γ-Al₂O₃ treated with CO₂. (d) *In-situ* CO₂-FTIR of γ-Al₂O₃ treated with CO₂ for 10 min and then purged with N₂. (e) *In-situ* CO₂-FTIR of d-Al₂O₃ and γ-Al₂O₃ treated with CO₂ for 10 min and then purged with N₂ for another 10 min. (f) CO₂-TPD-MS of d-Al₂O₃ and γ-Al₂O₃.

Al₂O₃. *In-situ* CO₂-FTIR of d-Al₂O₃ is different from γ -Al₂O₃, which varies in adsorption intensity and absorption peak position. Compared to commercial γ -Al₂O₃, there are only a few bicarbonate species (1656-1628, 1436 and 1228 cm⁻¹) derived from the reaction of CO₂ and -OH on the surface of d-Al₂O₃, while a large number of monodentate coordinated carbonate species (1538 and 1370 cm⁻¹) derived from the reaction of CO₂ and surface exposure O atom, and bidentate coordinated carbonate species (1670 and 1320 cm⁻¹) derived from the reaction of CO₂ with both surface exposed O and Al atom. According to literature reports,¹⁻² d-Al₂O₃ is similar to γ -Al₂O₃ dehydroxylated at high temperature, containing less surface -OH and more exposed O and Al atom. That is, d-Al₂O₃ contains rich FLPs.

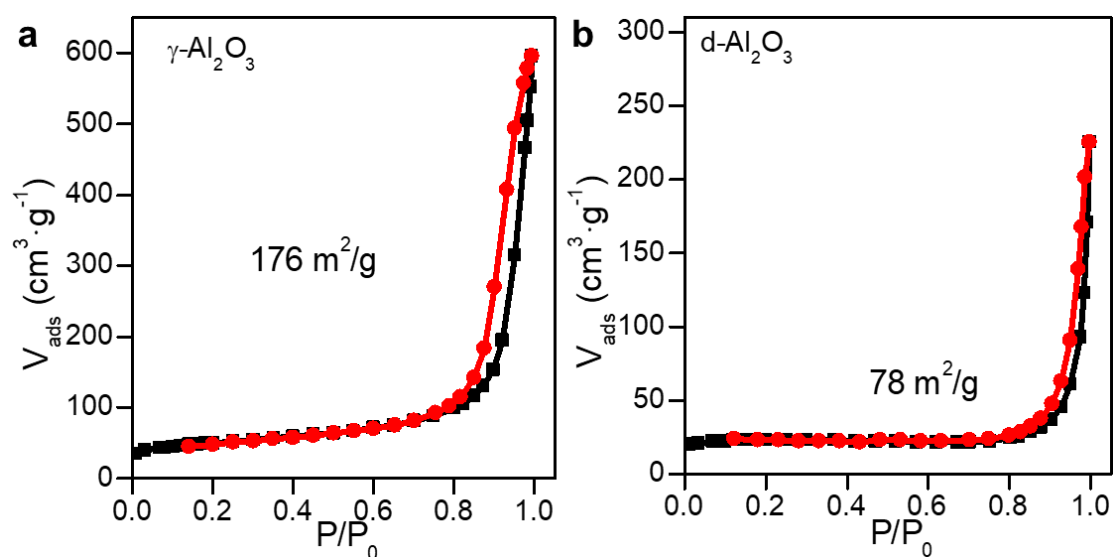


Figure S4. N₂ adsorption/desorption isotherm of γ -Al₂O₃ (a) and d-Al₂O₃ (b). The specific surface areas of γ -Al₂O₃ (176 m²/g) is higher than that of d-Al₂O₃ (78 m²/g).

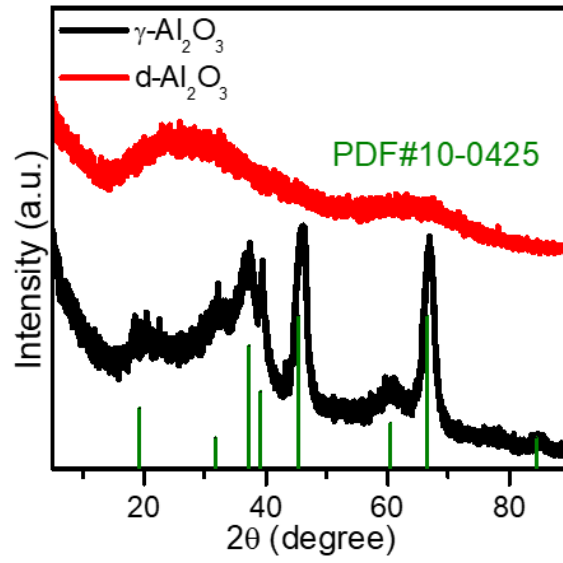


Figure S5. XRD of $\gamma\text{-Al}_2\text{O}_3$ and $\text{d-Al}_2\text{O}_3$.

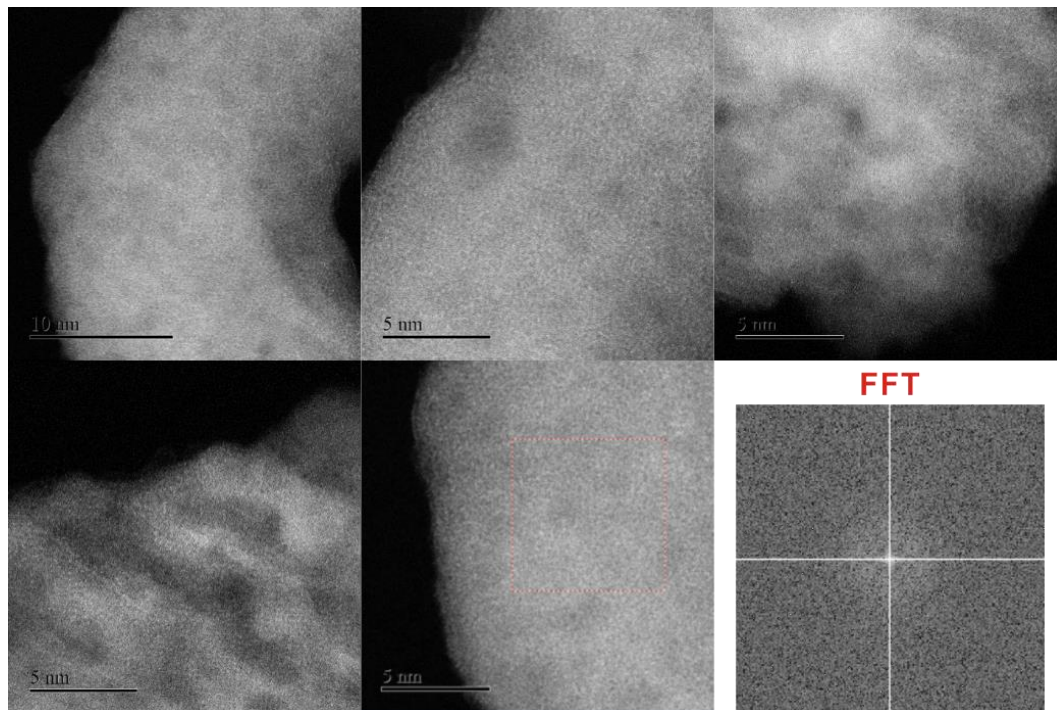


Figure S6. HAADF-STEM images and FFT measurements of $\text{d-Al}_2\text{O}_3$.

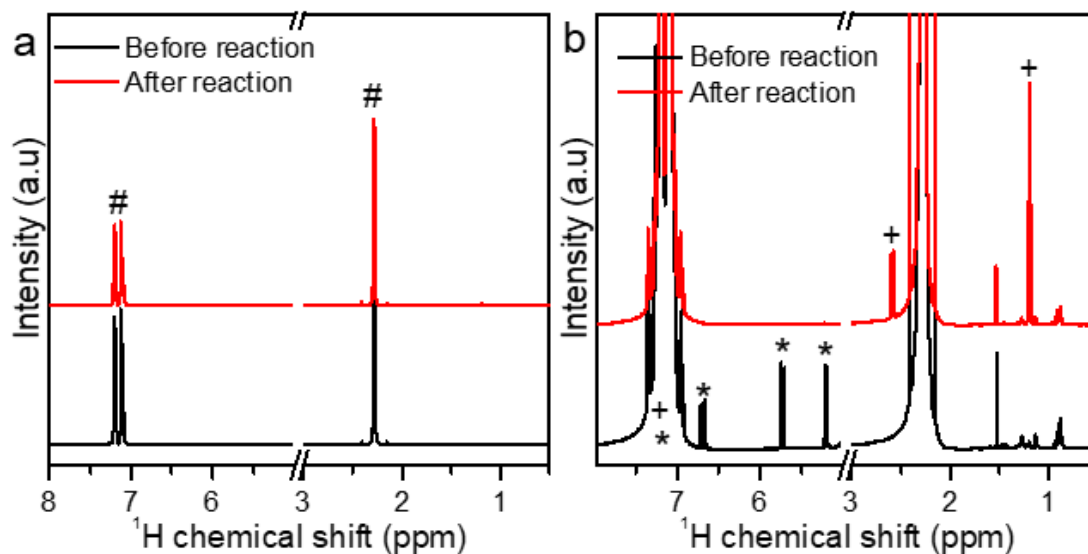


Figure S7. (a) ^1H NMR spectra of $\text{d-Al}_2\text{O}_3$ catalyzed styrene hydrogenation. (b) Magnified spectra. Before reaction (black trace), only toluene (marked as #) and styrene (marked as *) were present. After reaction (red trace), only toluene (marked as #) and ethylbenzene (marked as +) were present.

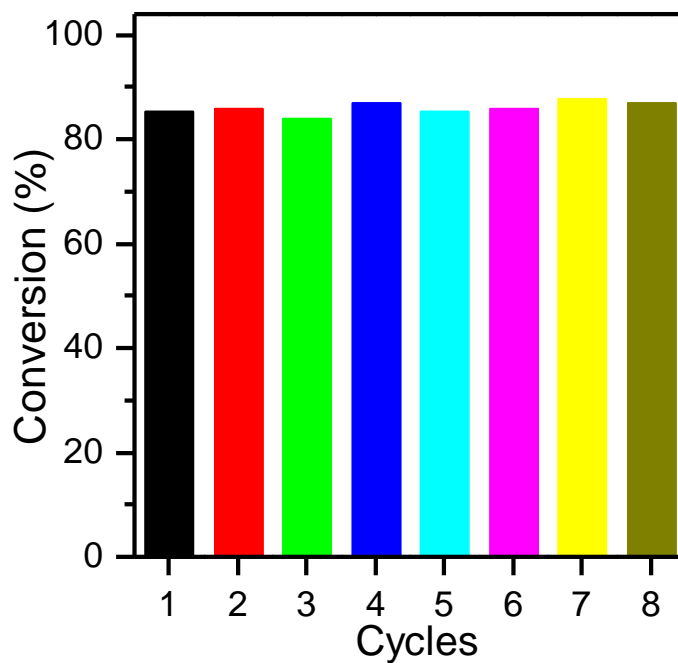


Figure S8. Catalytic performances of $\text{d-Al}_2\text{O}_3$ in styrene hydrogenation for 8 cycles. Reaction time: 150 min

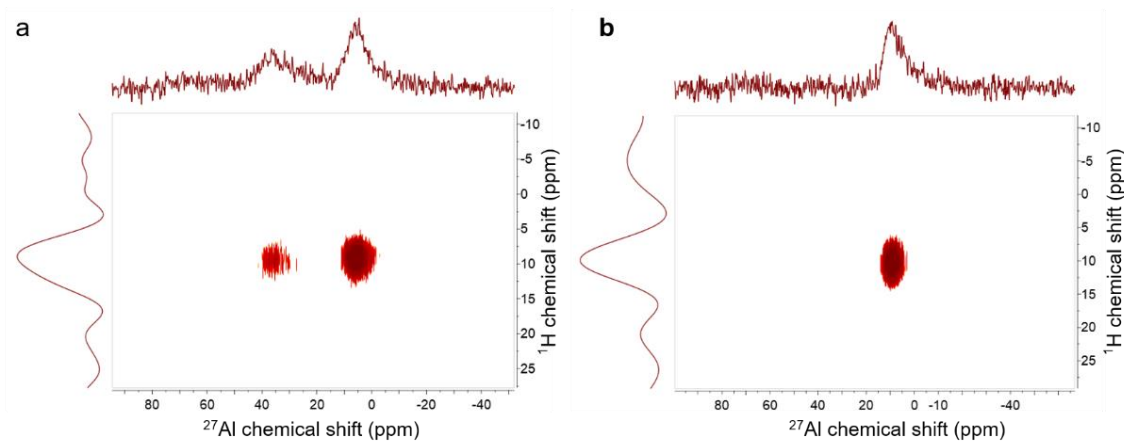


Figure S9. 2D solid state ^1H - ^{27}Al HETCOR experiment of H_2 treated $\text{d-Al}_2\text{O}_3$ (a) and $\gamma\text{-Al}_2\text{O}_3$ (b). Cross correlation peaks between Al_o and H species both on H_2 -treated $\text{d-Al}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$ proved the occurrence of H species were very adjacent to Al_o sites with a short CP contact time of $50\ \mu\text{s}$. Cross correlation peak between Al_p and H species on H_2 -treated $\text{d-Al}_2\text{O}_3$ proved the occurrence of H species were very adjacent to Al_p sites with a short CP contact time of $50\ \mu\text{s}$.

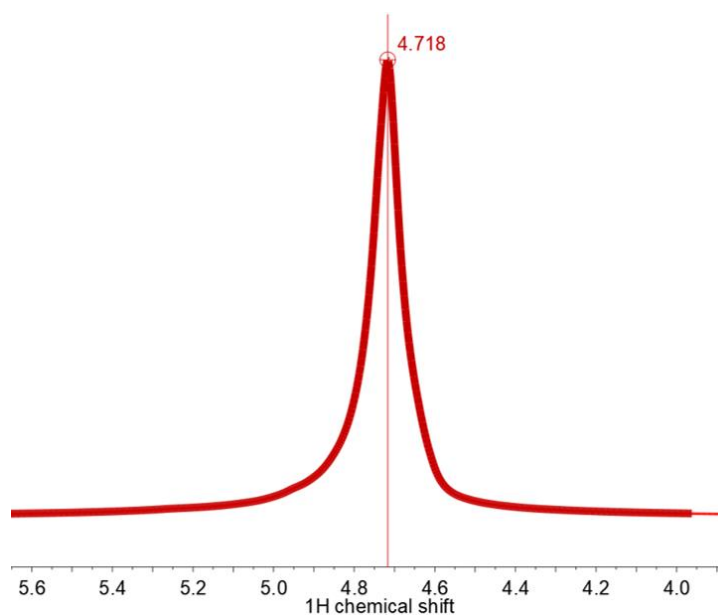


Figure S10. Solid state ^2H MAS-NMR spectra of D_2O .

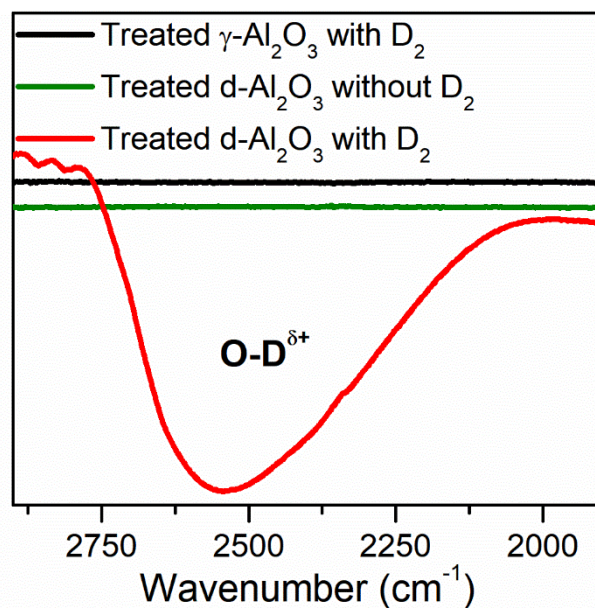


Figure S11. *In-situ* D_2 -FTIR of $\gamma\text{-Al}_2\text{O}_3$, $\text{d-Al}_2\text{O}_3$ treated without D_2 and $\text{d-Al}_2\text{O}_3$ treated with D_2 at 100°C .

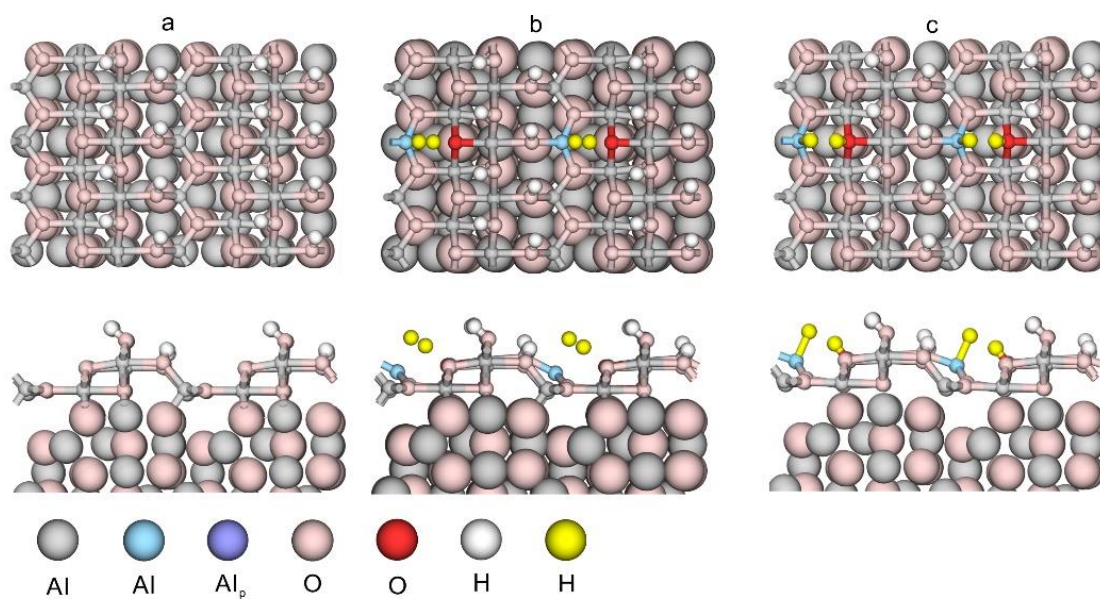


Figure S12. Top-view and side-view structures of (a) $\gamma\text{-Al}_2\text{O}_3$ with exposing (110) facet, transition state (b) and steady state (c) of heterolytic dissociation of H_2 on $\gamma\text{-Al}_2\text{O}_3$ with reconstructed surface Al site.

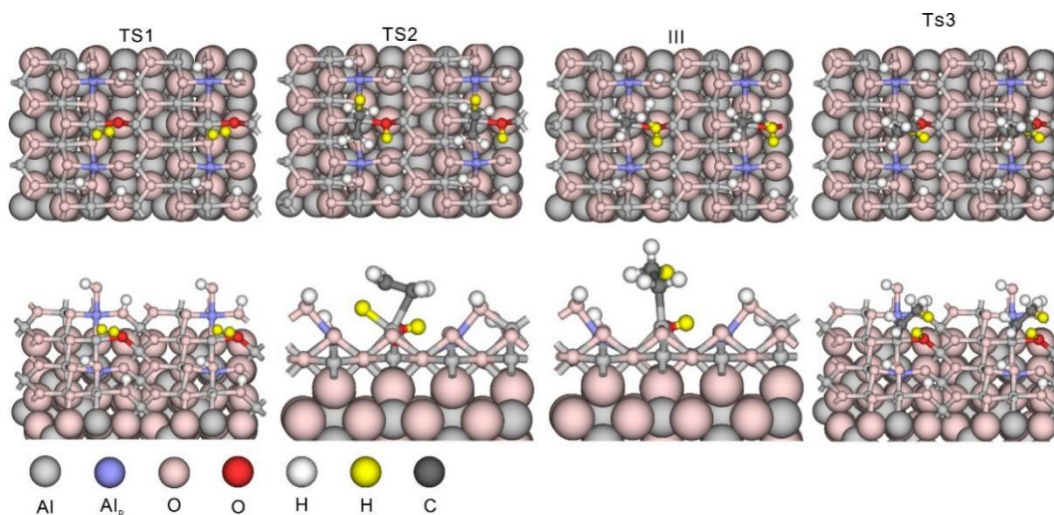


Figure S13. Top-view and side-view structures of the transition states (TS1) of heterolytically dissociation of H_2 on $\text{d-Al}_2\text{O}_3$, and transition states (TS2, TS3) and intermediate state (III) involved in C_2H_4 hydrogenation.

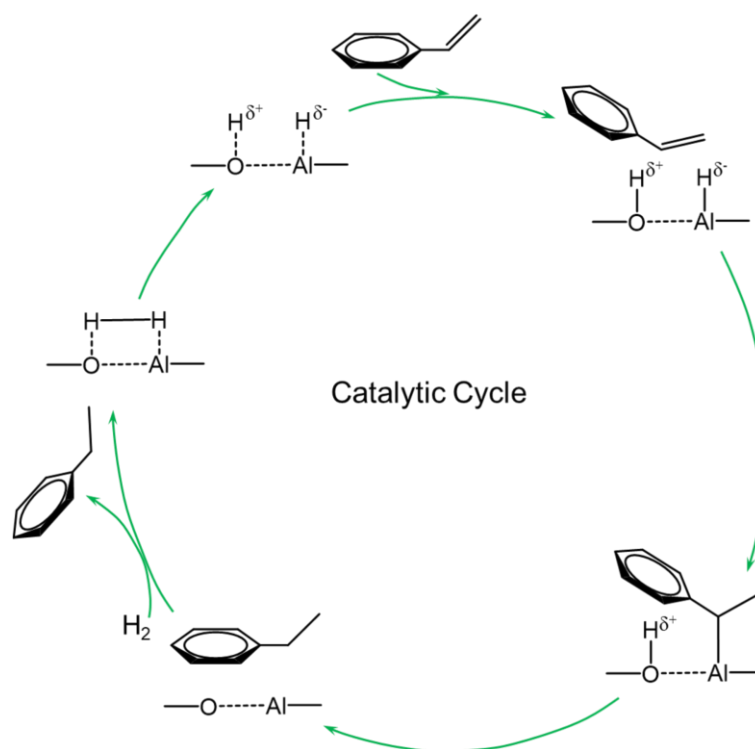


Figure S14. Pathways for the catalytic hydrogenation of styrene over FLPs on $\text{d-Al}_2\text{O}_3$ surface.

Table S1. ^{27}Al MAS NMR peak integration.

Sample	Al_t	Al_p	Al_o
d- Al_2O_3	21.6%	39.1%	39.3%
NH_3 -d- Al_2O_3	21.1%	23.8%	55.1%

References

- 1 Parkyns, N. D., *J. Phys. Chem.*, 1971, **75**, 526.
- 2 Szanyi, J.; Kwak, J. H., *Phys. Chem. Chem. Phys.*, 2014, **16**, 15117.