SUPPORTING INFORMATION

Atomic-Scale Changes of Silica-Supported Catalysts with Nanocrystalline or Amorphous Gallia Phases: Implications of Hydrogen Pretreatment for their Selectivity for Propane Dehydrogenation

Pedro Castro-Fernández,[a] Alexander I. Serykh,[b] Alexander V. Yakimov,[c] Igor P. Prosvirin,[d] Andrey V. Bukhtiyarov,[d] Paula M. Abdala,[,a] Christophe Copéret,[b] Alexey Fedorov,[*,a] Christoph R. Müller[*,a]*

[a] *Department of Mechanical and Process Engineering, ETH Zürich, CH-8092, Zürich, Switzerland*

[b] *Zelinsky Institute of Organic Chemistry, RAS, Moscow, 119991, Russia*

[c] *Department of Chemistry and Applied Biosciences, ETH Zürich, CH-8093, Zürich, Switzerland*

[d] *Boreskov Institute of Catalysis, SB RAS, 630090 Novosibirsk, Russia*

* Corresponding authors. E-mails: abdalap@ethz.ch; fedoroal@ethz.ch; muelchri@ethz.ch

Figures

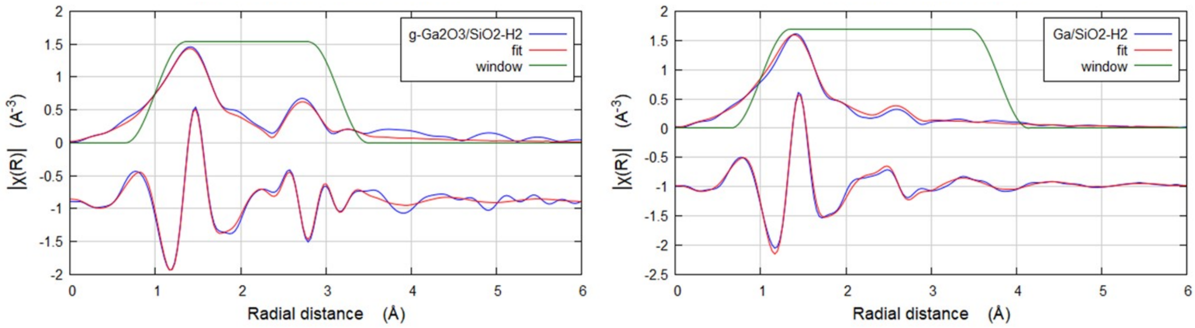

Figure S1. Results of EXAFS fittings for γ-Ga_2O_3/SiO_2-H_2 and Ga/SiO_2-H_2.

Fitting results for γ-Ga_2O_3/SiO_2 and Ga/SiO_2 have been published in our previous work.[1]

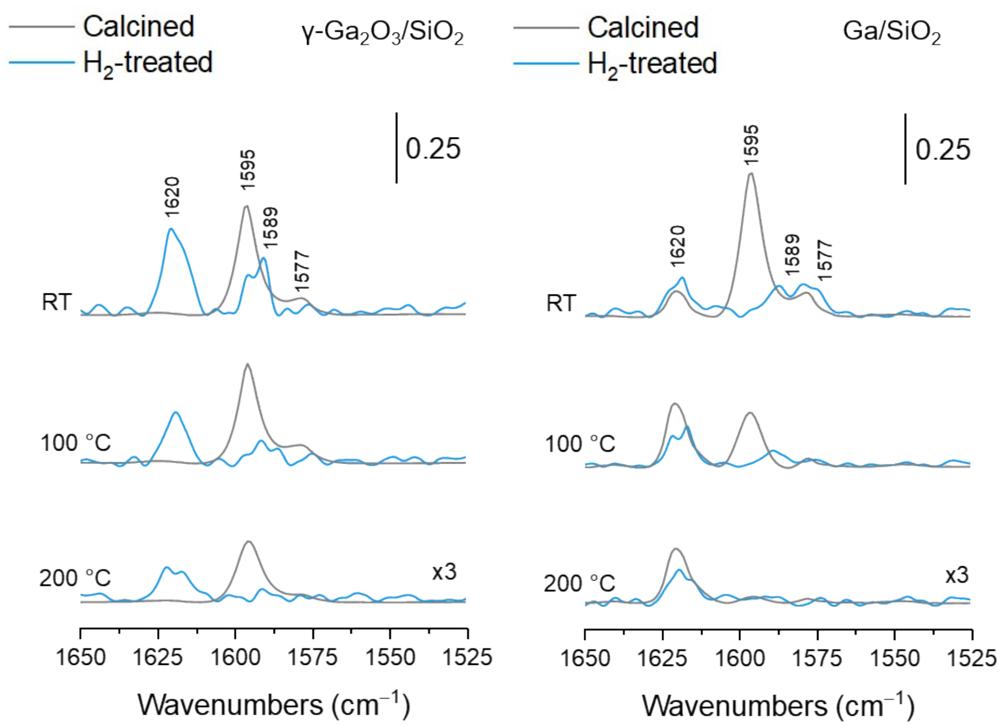

Figure S2. Py-FTIR results for calcined and H_2-treated materials evacuated under ca. 10^{-5} mbar at RT, 100 and 200 °C.

Py-FTIR results for γ-Ga_2O_3/SiO_2 and Ga/SiO_2 have been published in our previous work.[1]

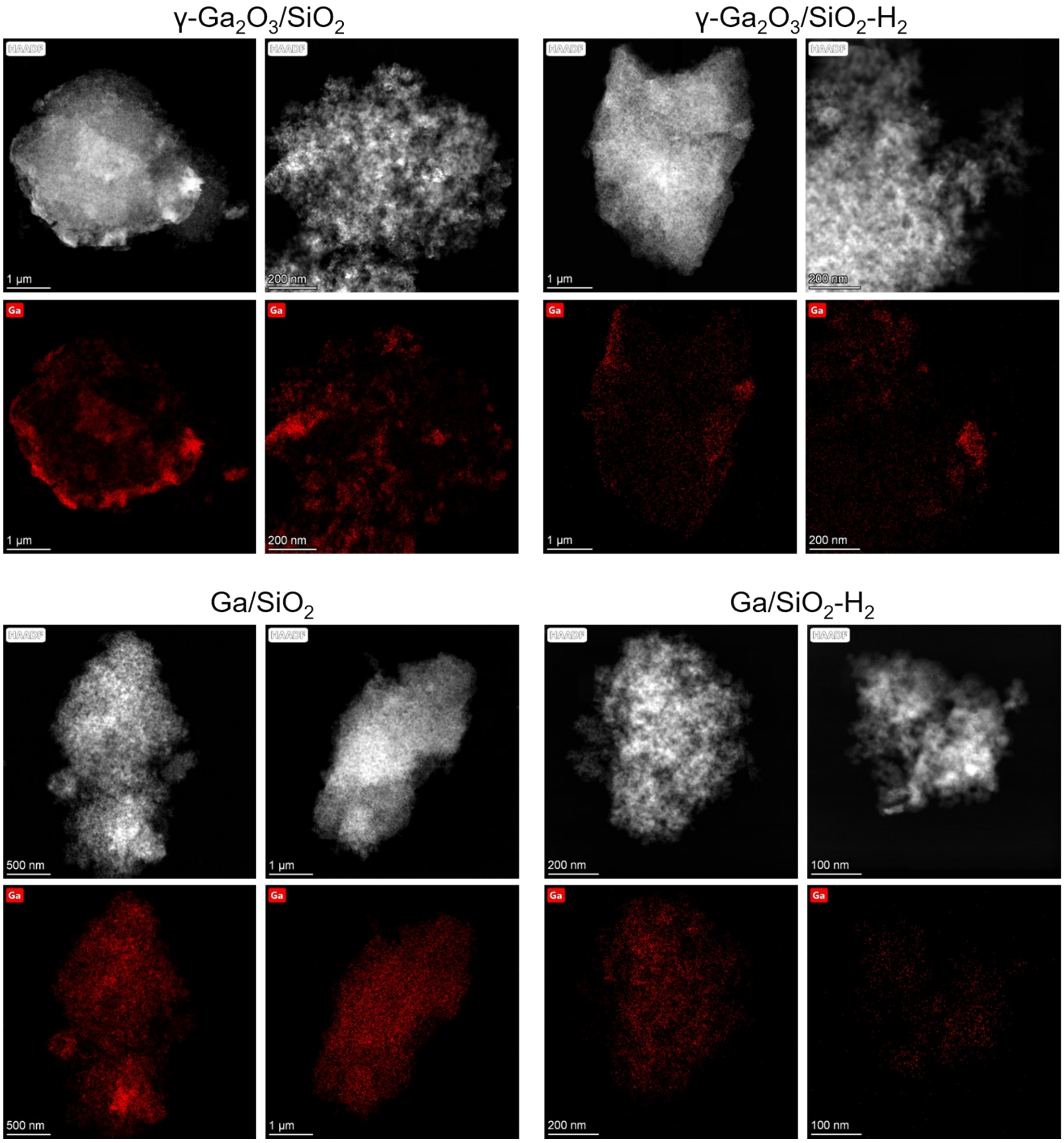

Figure S3. STEM-EDX images of calcined and H_2-treated catalysts.

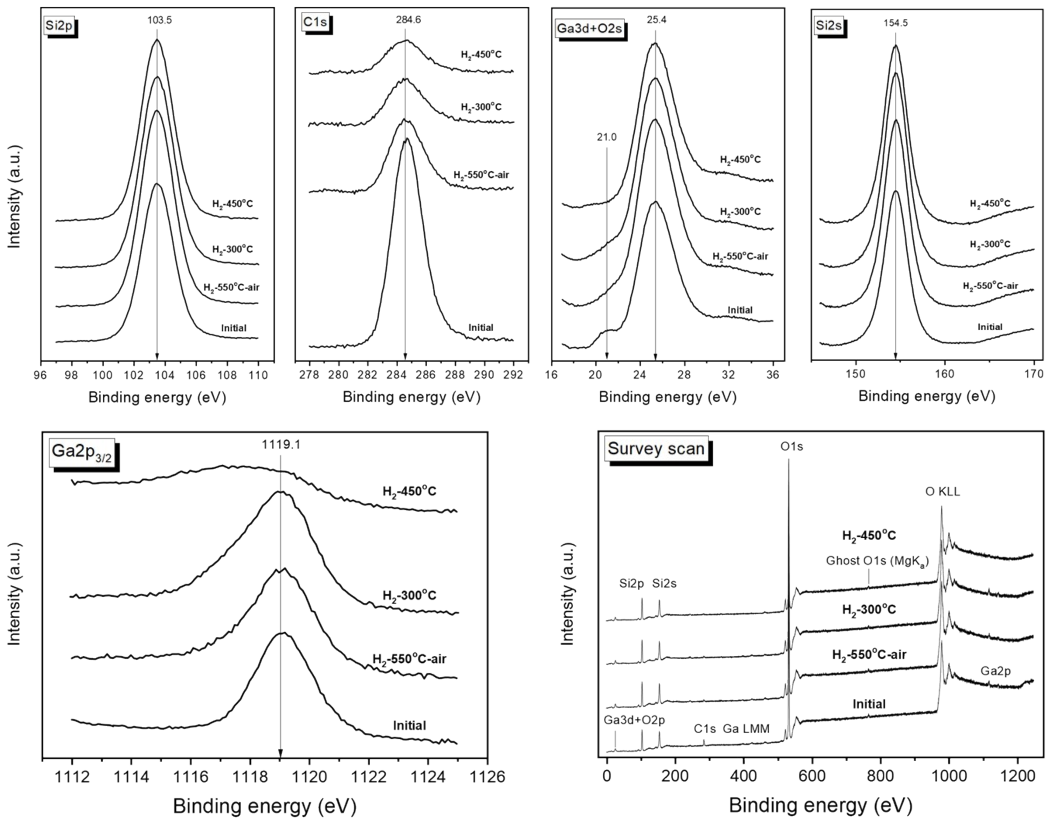

Figure S4. XPS Si2p, C1s, Ga3d, O2s, Si2s, Ga2p3/2 and survey spectra of γ-Ga_2O_3/SiO_2. XPS spectra were acquired on calcined materials (initial), after treating them in a reactor under H_2 flow at 550 °C (H_2-550 °C) followed by the exposure to air during material transfer, and reduced in situ at 300 °C and 450 °C in the pretreatment chamber of the XPS instrument (labelled H_2-300 °C and H_2-450 °C, respectively).

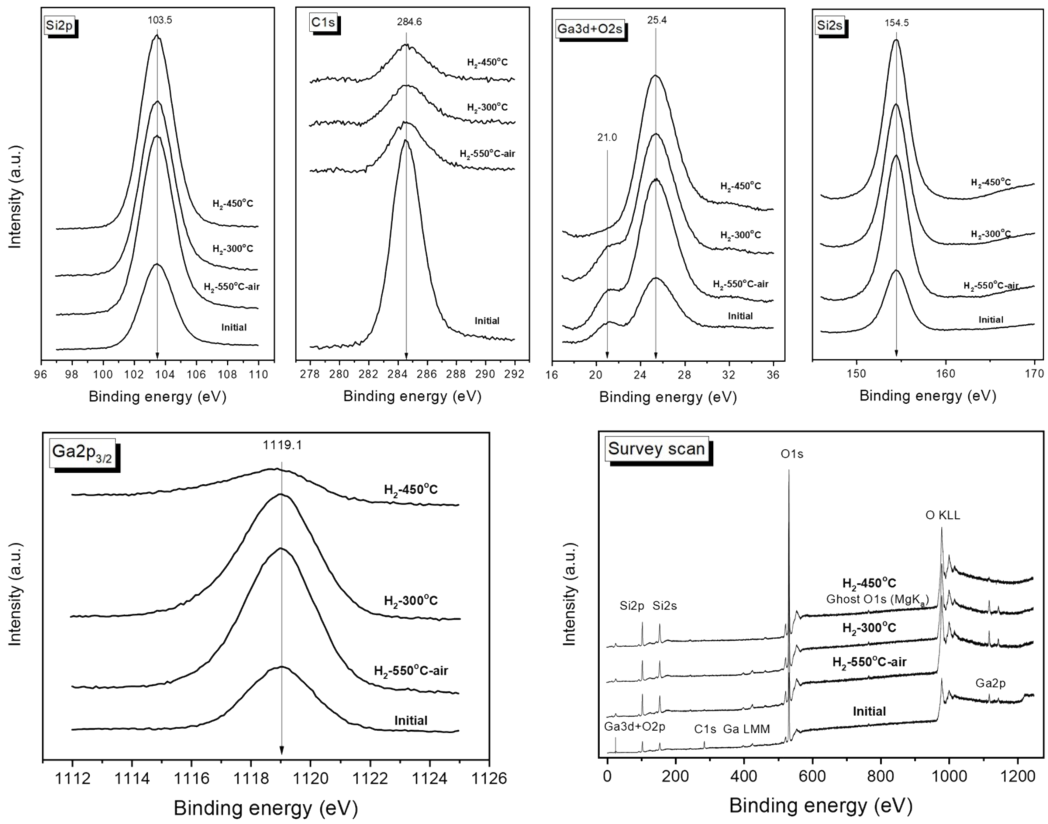

Figure S5. XPS Si2p, C1s, Ga3d, O2s, Si2s, Ga2p3/2 and survey spectra of Ga/SiO_2. XPS spectra were acquired on calcined materials (initial), after treating them in a reactor under H_2 flow at 550 °C (H_2-550 °C) followed by the exposure to air during material transfer, and reduced in situ at 300 °C and 450 °C in the pretreatment chamber of the XPS instrument (labelled H_2-300 °C and H_2-450 °C, respectively).

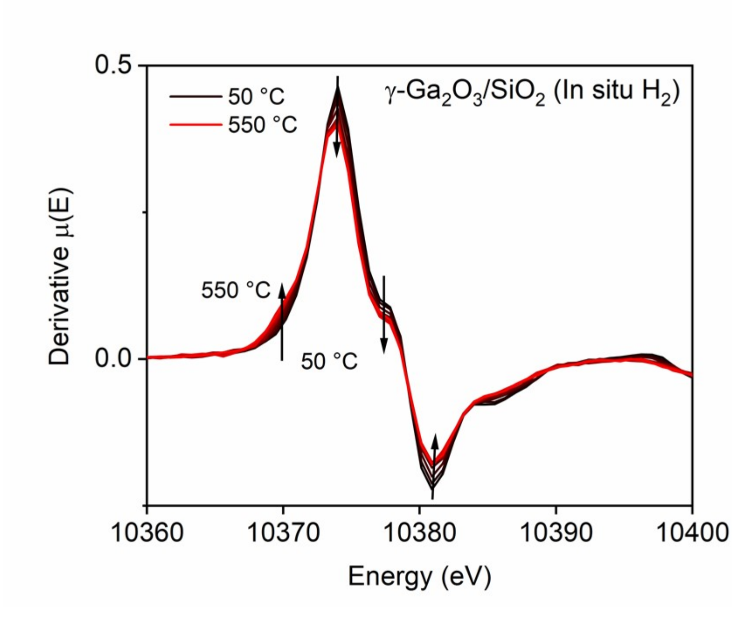

Figure S6. In situ Ga K-edge XANES derivative plot during H_2 treatment of γ-Ga_2O_3/SiO_2 (50-550 °C). Arrows indicate gradual changes in intensities at increasing temperatures.

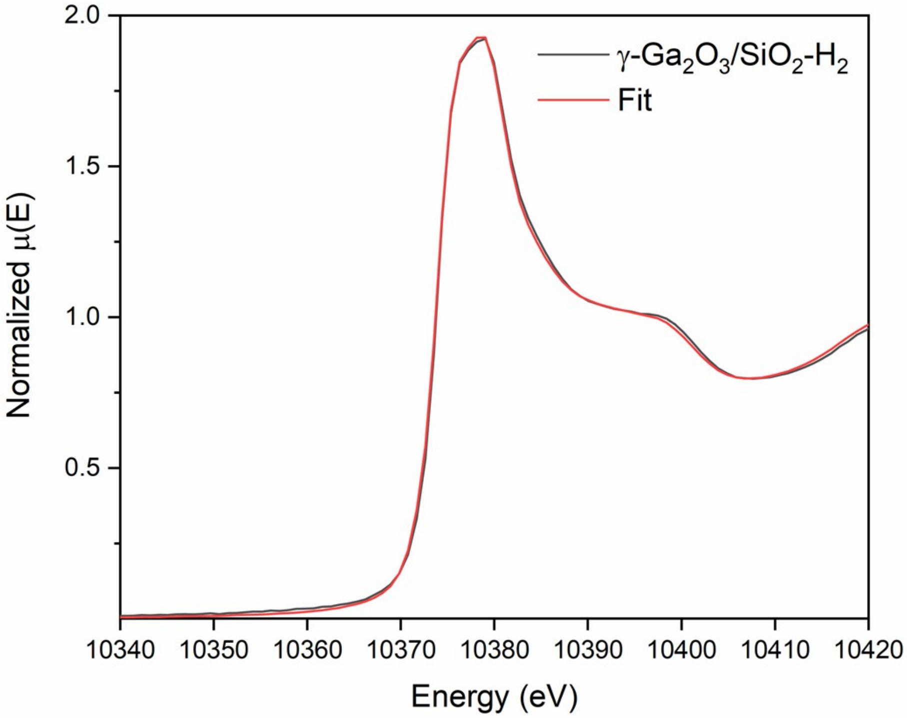

Figure S7. Linear combination fitting analysis results of Ga K-edge XANES from γ-Ga_2O_3/SiO_2-H_2 using γ-Ga_2O_3/SiO_2 and Ga/SiO_2 as components. Fitting results gave a 52% fraction of γ-Ga_2O_3/SiO_2 and 48% fraction of Ga/SiO_2-H_2 in γ-Ga_2O_3/SiO_2-H_2.

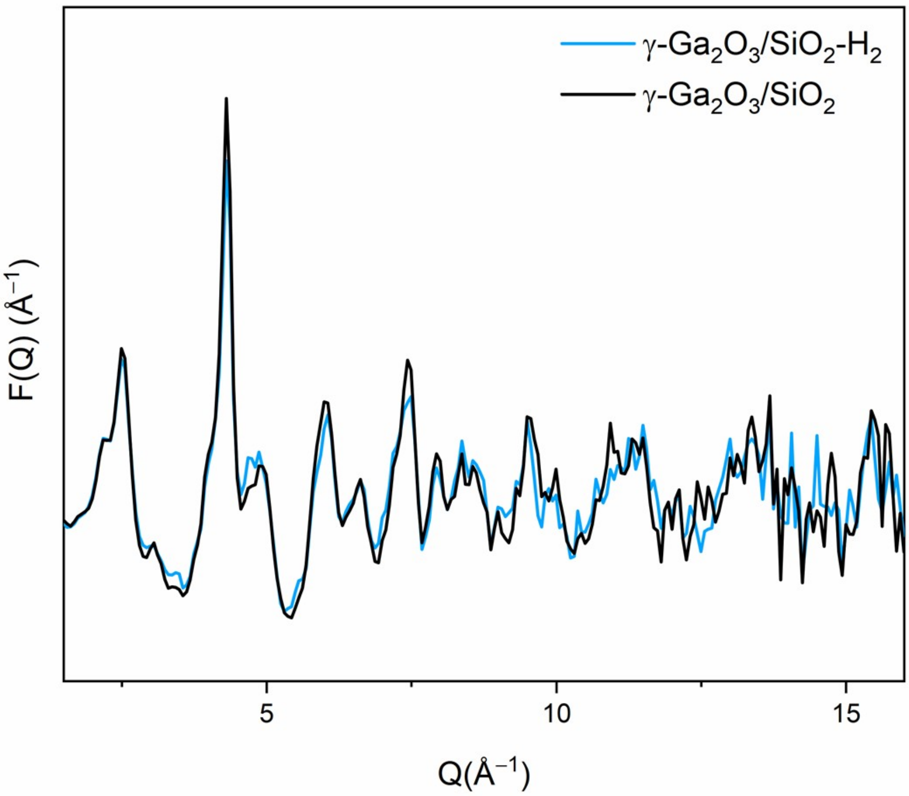

Figure S8. In situ reduced structure function plots for γ-Ga_2O_3/SiO_2-H_2 and γ-Ga_2O_3/SiO_2.

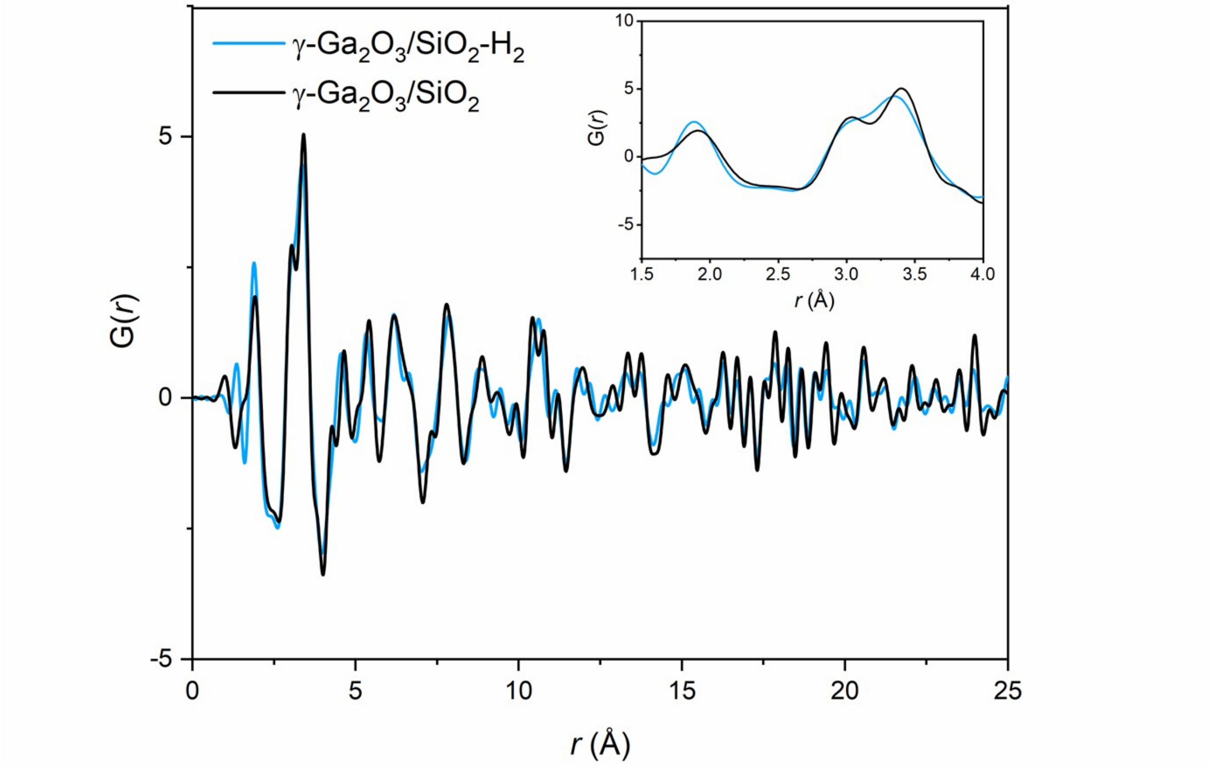

Figure S9. In situ pair distribution function plots comparing γ-Ga_2O_3/SiO_2-H_2 and γ-Ga_2O_3/SiO_2. The inset shows detail of the ca. 1.6-4 Å range, mainly influenced by the local structure.

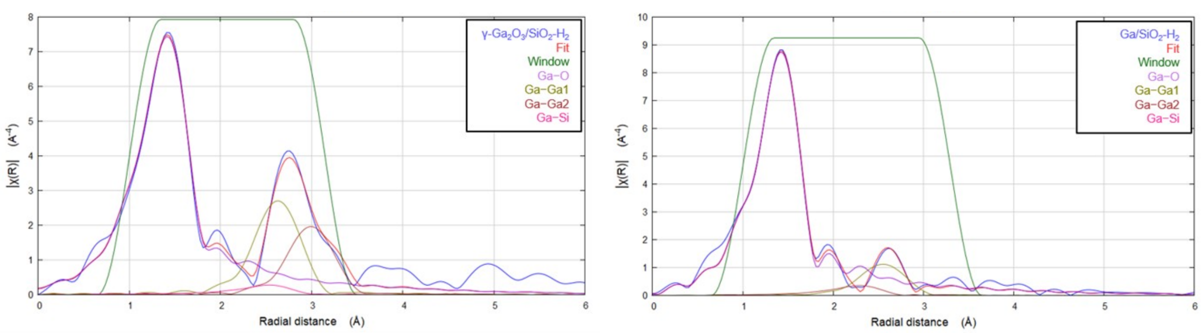

Figure S10. EXAFS fittings of γ-Ga_2O_3/SiO_2-H_2 (left) and Ga/SiO_2-H_2 (right) including Ga–O, Ga–Ga and Ga−Si paths.

Tables

Table S1. ^{15}N DNP SENS experimental parameters.

Material	Desorption T (°C)	E_{solv}[a]	DNP buildup time[b] (sec)	Measurement time (h)	Number of scans
γ-Ga_2O_3/SiO_2	150	109	7.7	9.9	11896
Ga/SiO_2		52	7.1	11.1	13368

[a] measured from the comparison between 1H NMR signals of TCE in the spectra with MW ON and OFF
[b] T_1 relaxation times measured from saturation-recovery experiments with MW ON

Table S2. Results of EXAFS fittings including Ga−Si paths.

Material	Path	CN	Distance (Å)	σ² (Å²)	R-factor
γ-Ga_2O_3/SiO_2-H_2	Ga–O	5.2(2)	1.87(1)	0.011*	0.002
	Ga–Ga	3.4(7)	2.99(1)	0.012*	
	Ga–Ga	2.7(7)	3.36(1)	0.012*	
	Ga–Si	1.0(7)	3.06(7)	0.012*	
Ga/SiO_2-H_2	Ga–O	4.7(1)	1.86(1)	0.008*	0.003
	Ga–Si	0.5(1)	2.80(7)	0.013*	
	Ga–Ga	1.3(3)	2.91(2)	0.013*	

Table S3. Results of EXAFS fittings obtained when varying both the σ² factors and CN.

Material	Path	CN	Distance (Å)	σ² (Å²)	R-factor
γ-Ga_2O_3/SiO_2-H_2	Ga–O	5.5(5)	1.87(1)	0.011(1)	0.004
	Ga–Ga_1	3(3)	2.99(3)	0.012(7)	
	Ga–Ga_2	3(3)	3.37(3)	0.012(7)	
Ga/SiO_2-H_2	Ga–O	4.7(3)	1.86(1)	0.008(1)	0.004
	Ga–Ga	1.1(5)	2.92(1)	0.011(3)	

Table S4. Results of EXAFS fittings obtained when varying the σ^2 factors while fixing CN (to the values obtained for the calcined state).

Material	Path	CN	Distance (Å)	σ^2 (Å^2)	R-factor
γ-Ga_2O_3/SiO_2-H_2	Ga–O	5.4*	1.87(1)	0.011(1)	0.004
	Ga–Ga_1	2*	2.99(3)	0.011(1)	
	Ga–Ga_2	3*	3.37(3)	0.011(1)	
Ga/SiO_2-H_2	Ga–O	5.7*	1.85(1)	0.010(1)	0.012
	Ga–Ga	2.0*	2.92(2)	0.015(2)	

References

1 P. Castro-Fernández, D. Mance, C. Liu, I. B. Moroz, P. M. Abdala, E. A. Pidko, C. Copéret, A. Fedorov, C. R. Müller, *ACS Catal.*, 2021, **11**, 907–924.