Supporting Information

Reversible Transformation of Sub-nanometer Ga-based Clusters to Isolated $^{[4]}Ga_{(4Si)}$ Sites Creates Active Centers for Propane Dehydrogenation

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FIGURES

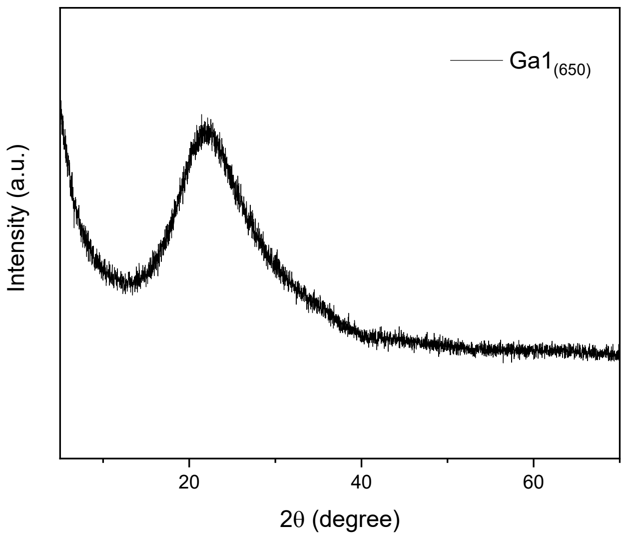


Figure S1. XRD pattern of Ga1$_{(650)}$.

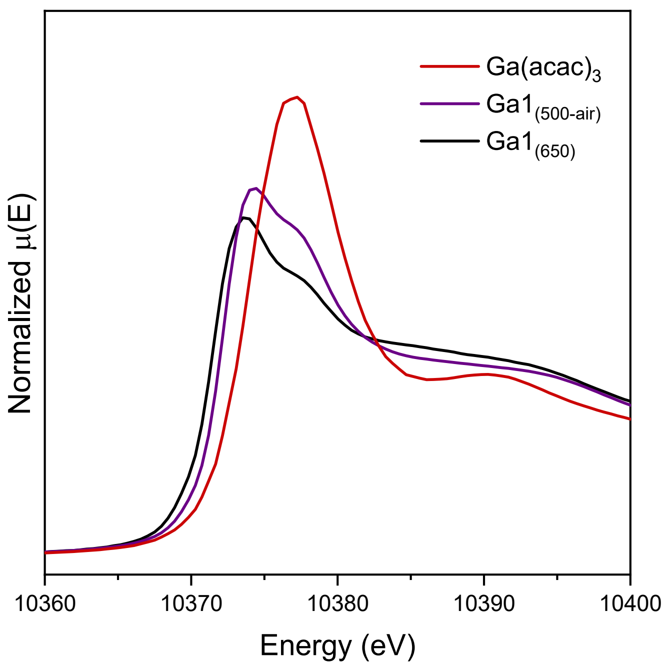


Figure S2. XANES comparison of Ga1$_{(500\text{-air})}$, Ga1$_{(650)}$ and the reference material Ga(acac)$_3$.

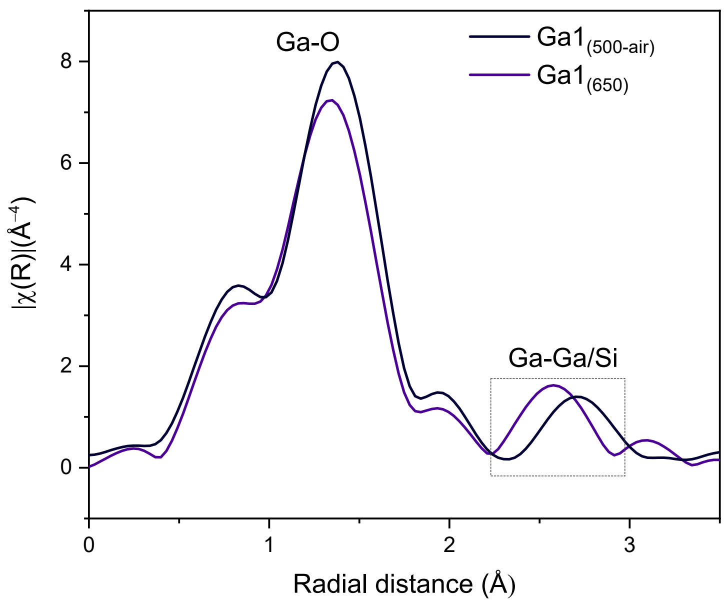


Figure S3. Ga K-edge Fourier transformed EXAFS functions (non-phase corrected) of $Ga1_{(500\text{-air})}$ and $Ga1_{(650)}$ collected at 50 °C.

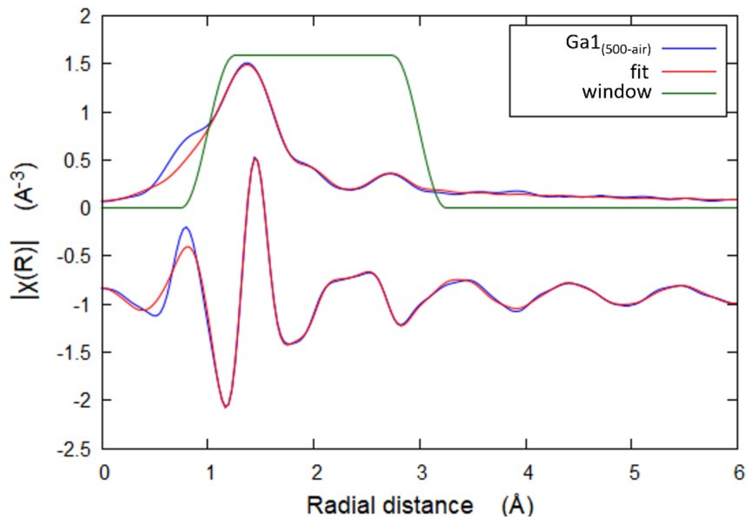


Figure S4. EXAFS fittings of $Ga1_{(500\text{-air})}$ at Ga K-edge: magnitude (top) and imaginary (bottom) parts of the FT in R space.

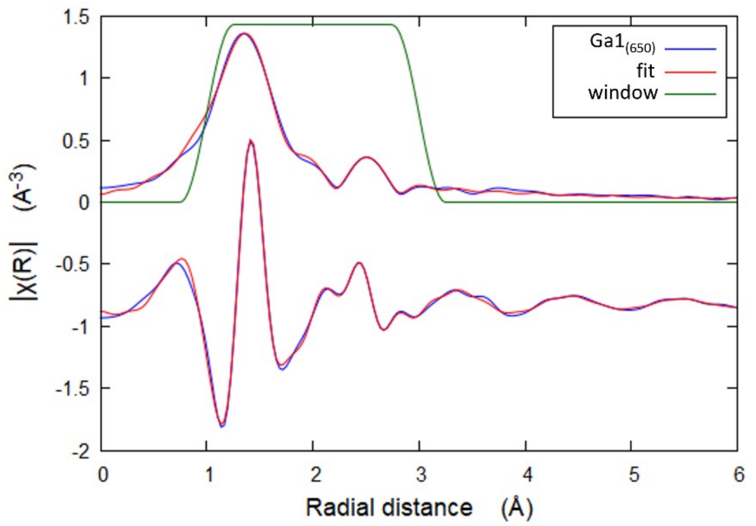


Figure S5. EXAFS fittings of $Ga1_{(650)}$ at Ga K-edge: magnitude (top) and imaginary (bottom) parts of the FT in R space.

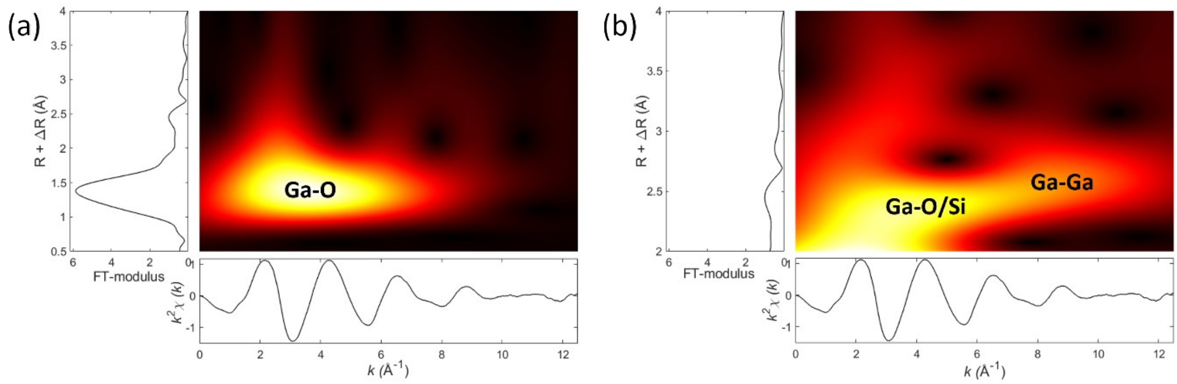


Figure S6. Wavelet transform (WT) analysis of EXAFS data for $Ga1_{(500\text{-}air)}$ in the R range: (a) 0.5-4 Å and (b) 2-4 Å.

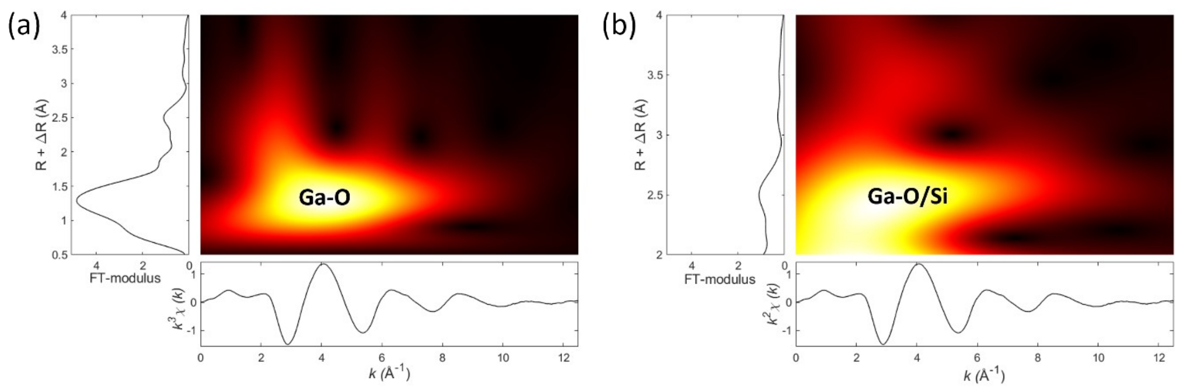


Figure S7. Wavelet transform (WT) analysis of EXAFS data for $Ga1_{(650)}$ in the R range: (a) 0.5-4 Å and (b) 2-4 Å.

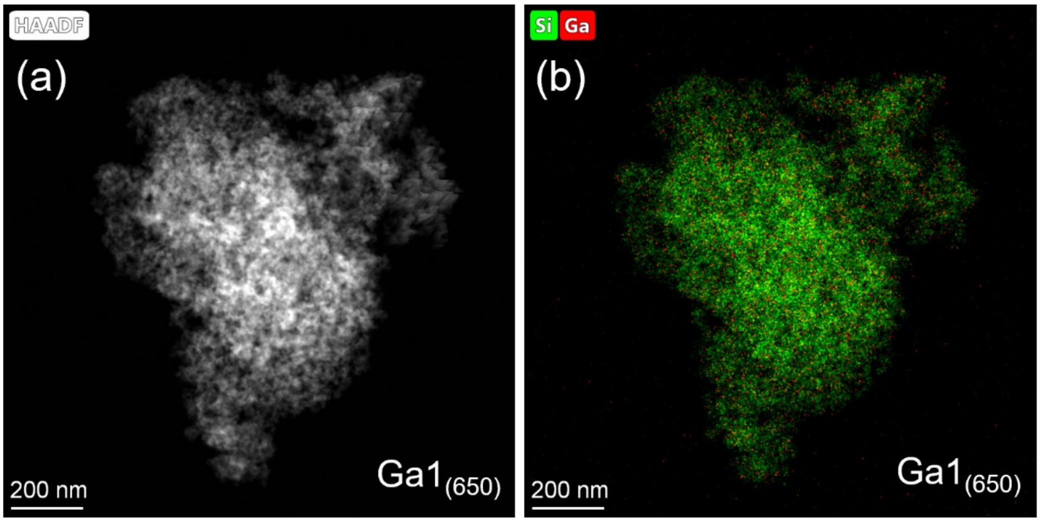
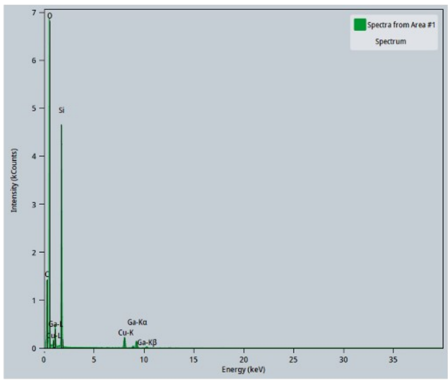


Figure S8. (a) ADF-STEM image and (b) EXD mapping of Ga1$_{(650\text{-air})}$.

(a)

Ga1$_{(650)}$		
Element	at %	wt %
O	67.4	52.5
Si	31.2	42.6
Ga	1.4	4.9

(b)



(c)

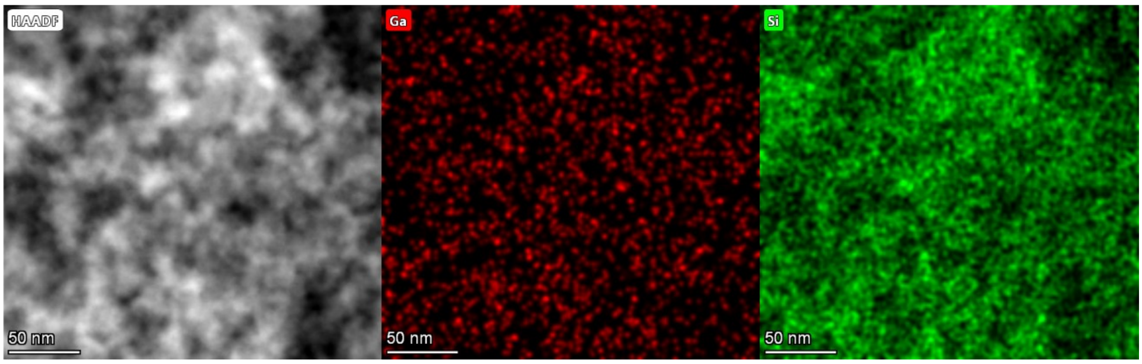


Figure S9. (a) Atomic and weight percentage of Ga content, (b) EDX spectrum and (c) ADF-STEM image and EDX mappings of a selected area of Ga1$_{(650\text{-air})}$.

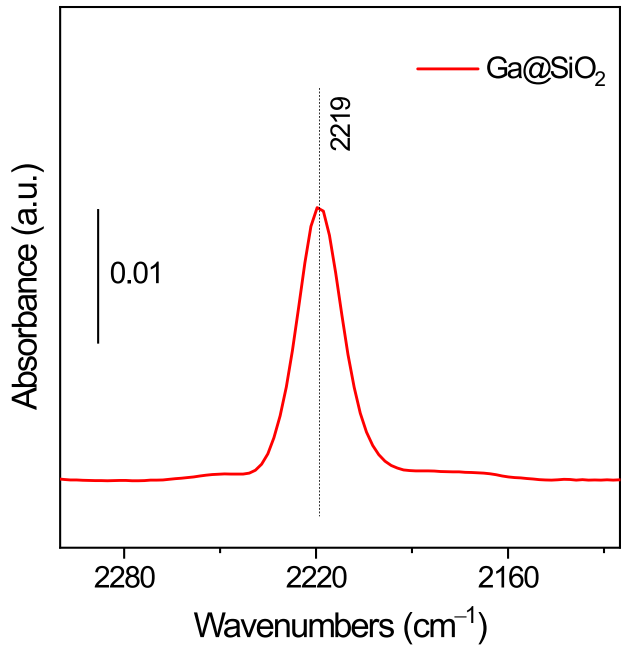


Figure S10. FTIR spectra of SOMC-prepared Ga@SiO_2 after evacuation at 650 °C and CO adsorption at a pressure of 20 Torr at room temperature.

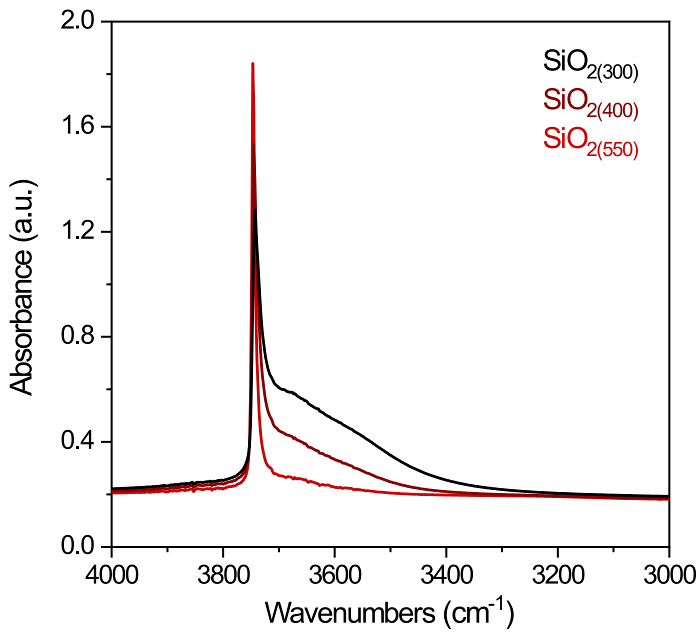


Figure S11. FTIR spectra of SiO_2 in the hydroxyl region outgassed at 300, 400 or 550 °C.

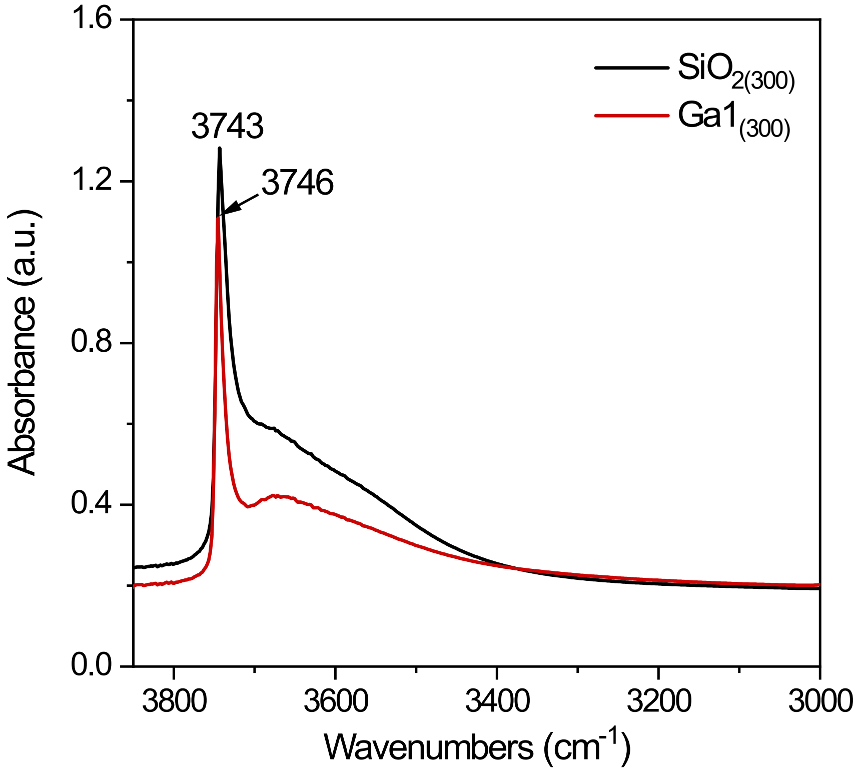


Figure S12. FTIR comparison of the hydroxyl region of SiO_2 and $Ga1_{(500\text{-air})}$ after evacuation at 300 °C.

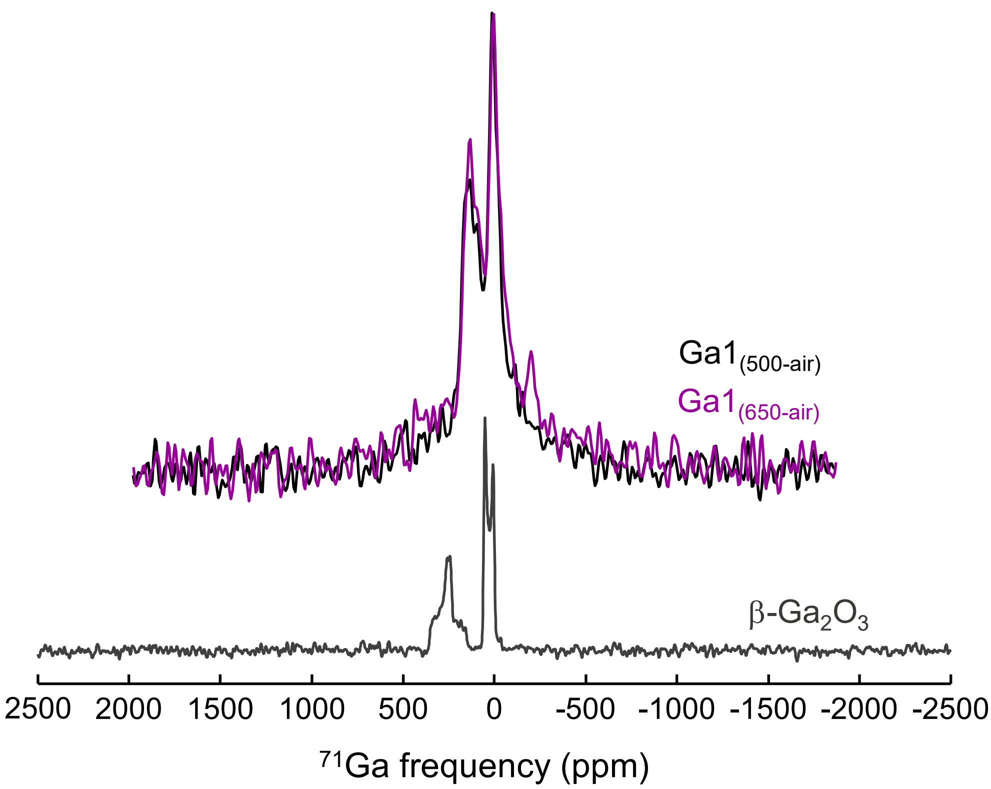


Figure S13. Comparison of the ^{71}Ga MAS NMR spectra (obtained at 20.0 T with a spinning rate of 64 kHz) of $Ga1_{(500\text{-air})}$ and $Ga1_{(650\text{-air})}$ alongside the reference β-Ga_2O_3.

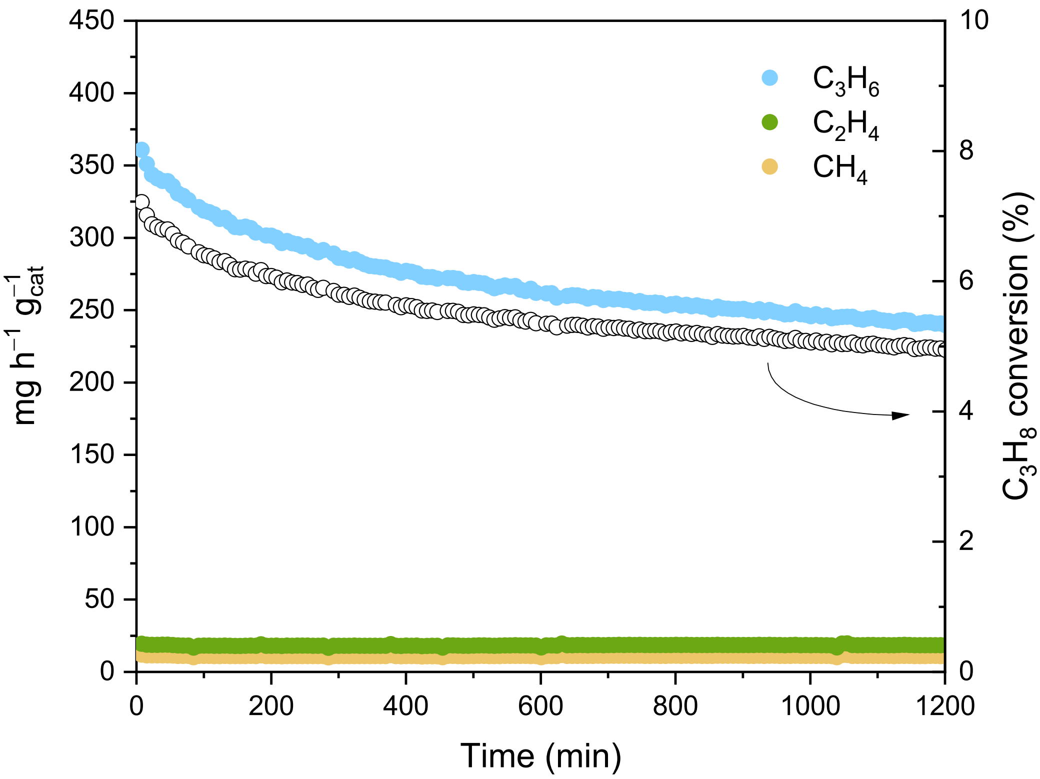


Figure S14. Propane conversion and product formation rate (mg h^{-1} g_{cat}^{-1}) of C_3H_6 (blue), C_2H_4 (green) and CH_4 (yellow) on $Ga1_{(650)}$ over 20 h TOS.

Reaction conditions: 10% of C_3H_8 in N_2, WHSV = 8.5 h^{-1}, T = 550 °C.

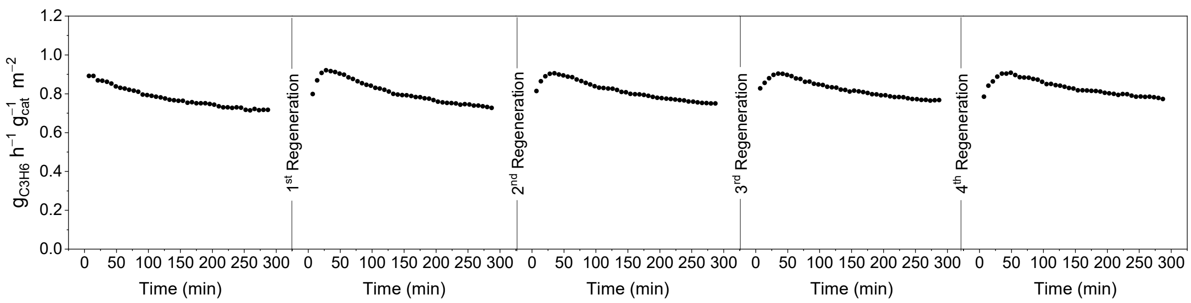


Figure S15. Normalized propene formation rate (g_{C3H6} h^{-1} g_{Ga}^{-1} m^{-2}) on $Ga1_{(650)}$ over 25 h (5 × 5 h) TOS including four regeneration cycles (synthetic air, 550 °C, 1 h) performed after every 5 h.

Reaction conditions: 10% of C_3H_8 in N_2, WHSV = 8.5 h^{-1}, T = 550 °C. We assumed that the regeneration cycles did not change the surface area of $Ga1_{(650)}$.