Electronic Supplementary Material (ESI) for Green Chemistry.

Ga/ZSM-5 Catalyst Improves Hydrocarbon Yields and Increases Alkene Selectivity during Catalytic Fast Pyrolysis of Biomass with Co-fed Hydrogen

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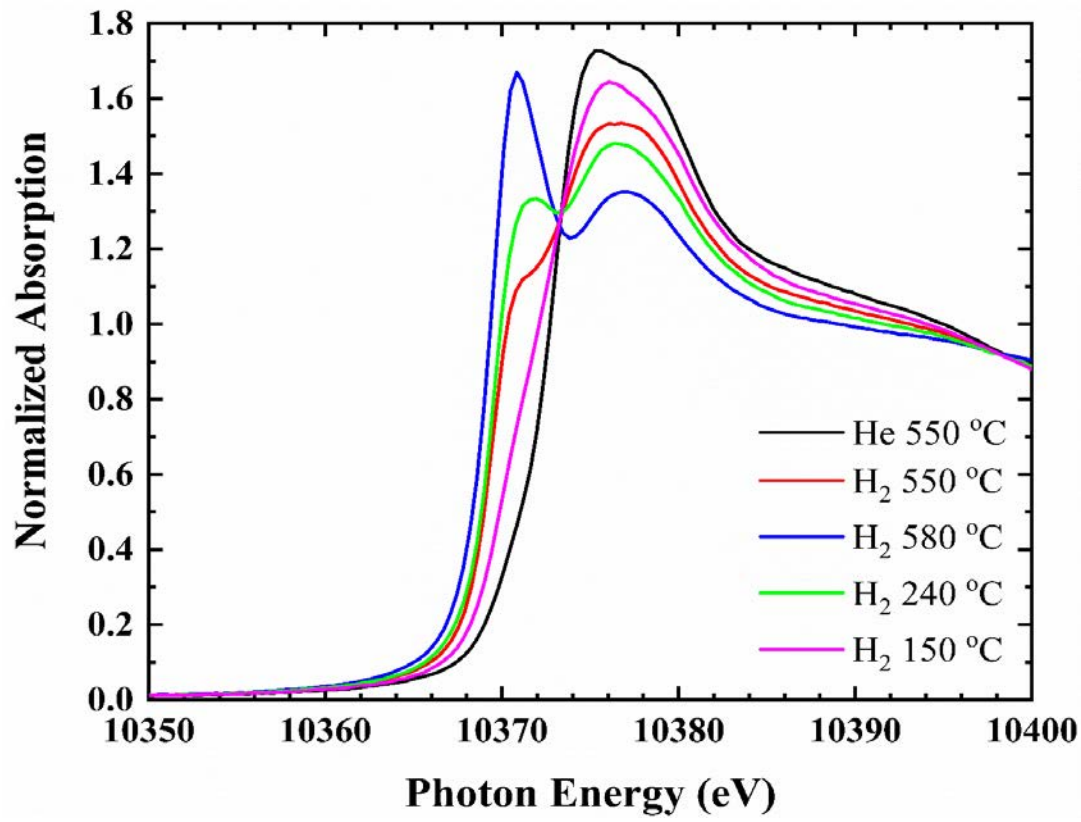

Fig. S1 K edge XANES of 5wt% Ga/ZSM-5 heated in flowing hydrogen and He from RT to 580 and 550 °C, respectively.

Table S1 XANES K edge energies for 5wt% Ga/ZSM-5 measured at different temperatures in H_2 or He

Treatment Conditions	**Edge Energy (keV)**
550 °C He	10.3730
550 °C H_2	10.3695
580 °C H_2	10.3695
240 °C H_2	10.3695
150 °C H_2	10.3730

Table S2 Acid site densities for the parent ZSM-5 and Ga/ZSM-5 catalysts with SAR 30.

	Total acidity, mmol/g	Brønsted acidity, mmol/g	Lewis acidity, mmol/g
ZSM-5 (SAR30)	0.71	0.50	0.21
0.5% Ga/ZSM-5	0.69	0.44	0.25
1% Ga/ZSM-5	0.76	0.47	0.29
5% Ga/ZSM-5	0.74	0.42	0.32

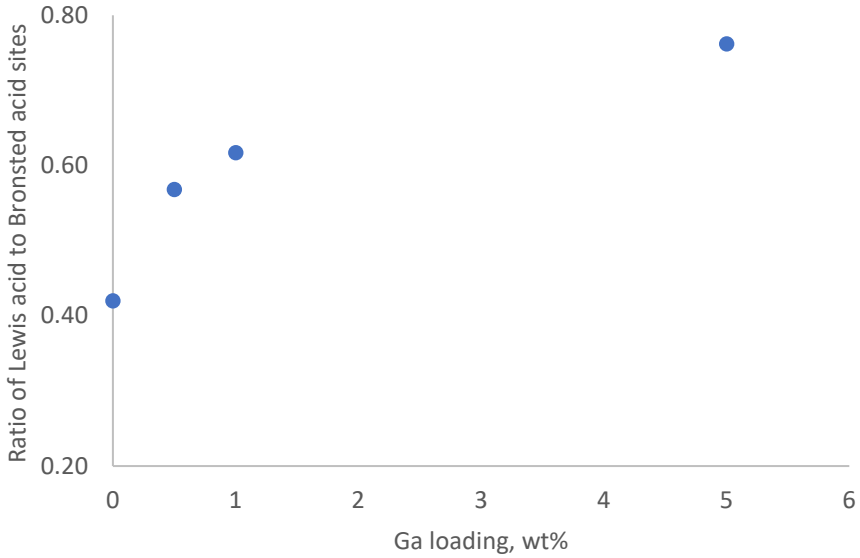

Fig. S2 The impact of Ga loading on the Lewis acid-to-Brønsted acid ratio.

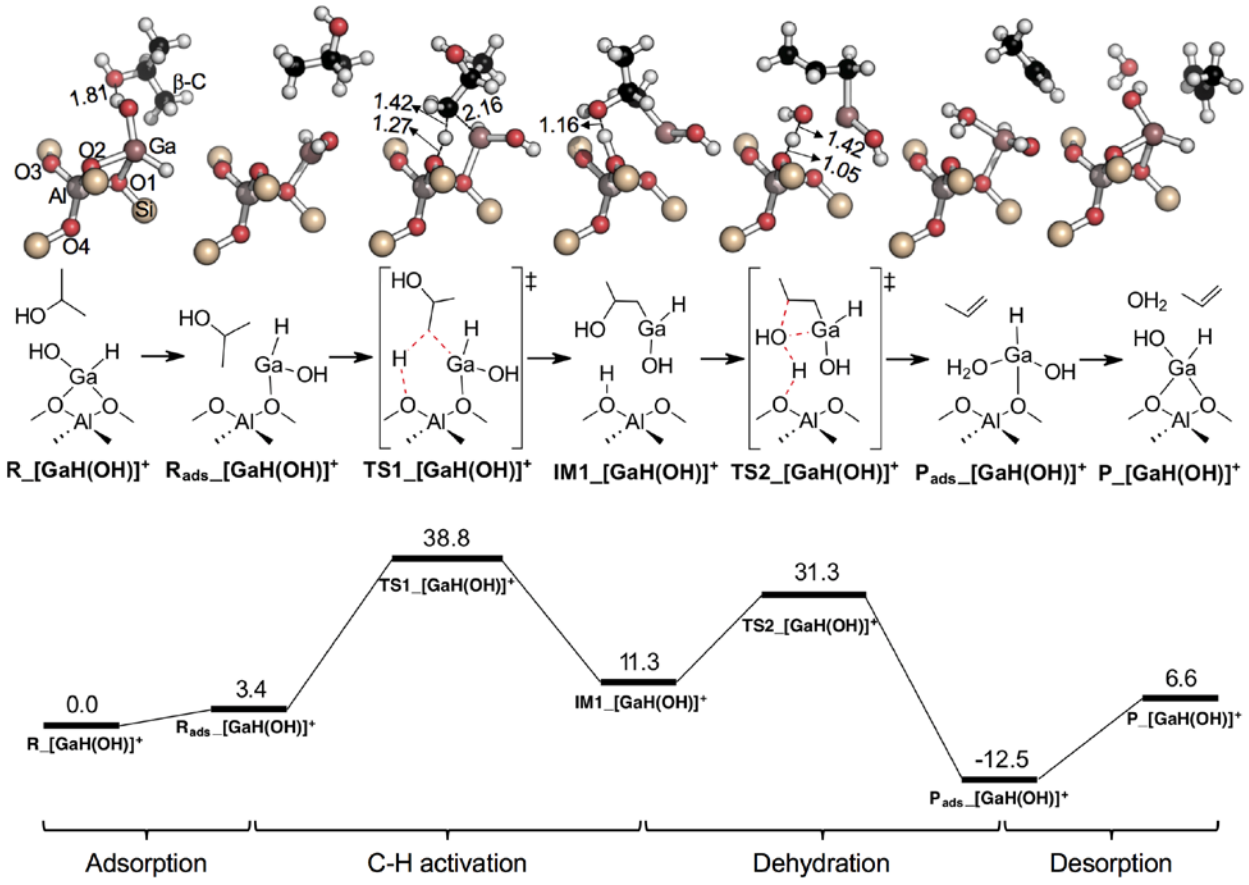

Fig. S3 Reaction mechanism of isopropanol dehydration on $[GaH(OH)]^+$ with corresponding free energy surface. For clear representation of reactions, only the key part in QM region is shown. All energy values are in kcal/mol.

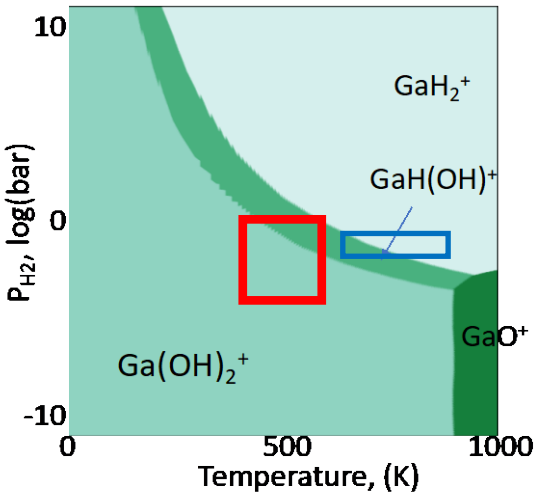

Fig. S4 Phase diagram of Ga species at a H_2O partial pressure of 10^{-6} bar. The blue and red squares indicate the range of temperatures and H_2 partial pressures in our biomass (blue) and isopropanol (red) upgrading experiments, respectively.

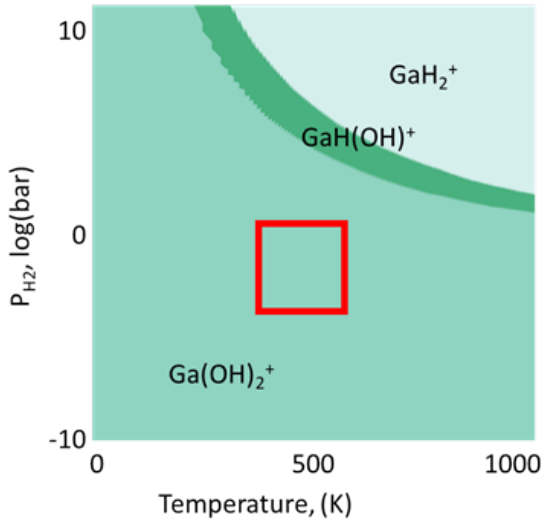

Fig. S5 Phase diagram of Ga species at a H_2O partial pressure of 0.01 bar. The red square indicates the range of temperatures and H_2 partial pressures in our isopropanol upgrading experiments.

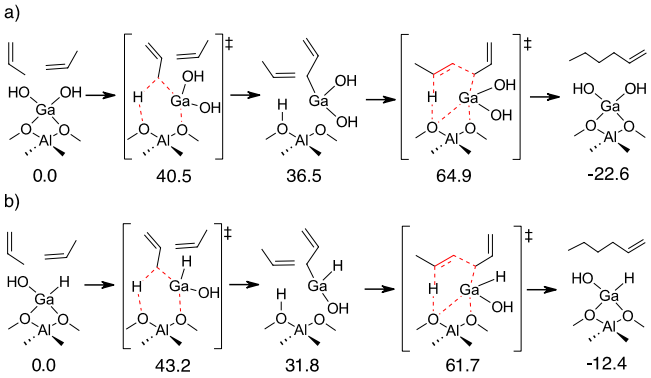

Fig. S6 Reaction mechanisms of propene oligomerization into hexene on a) $[Ga(OH)_2]^+$, and b) $[GaH(OH)]^+$, with relative Gibbs free energies of each reaction state. The calculations were conducted using the ONIOM (M06-2X/6-311G(d,p):PM6) model at 250 °C. All the Gibbs free energy values are in kcal mol^{-1}.