Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Surface-functionalized mesoporous gallosilicate catalysts for the efficient and sustainable upgrading of glycerol to solketal

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Table S1 – amount (expressed in mmol) of TEOS and RTES (R = Me, Pr or Ph) used in the synthesis of non-functionalized and alkyl-functionalized solids

Material	**n_{TEOS} (mmol)**	**n_{RTES} (mmol)**
Ga-P(F)-0	57.6	-
Ga-P(F)-5-Me	56.4	2.94
Ga-P(F)-10-Me	53.4	5.88
Ga-P(F)-15-Me	50.5	8.82
Ga-P(F)-5-Pr	56.4	2.94
Ga-P(F)-5-Ph	56.4	2.91

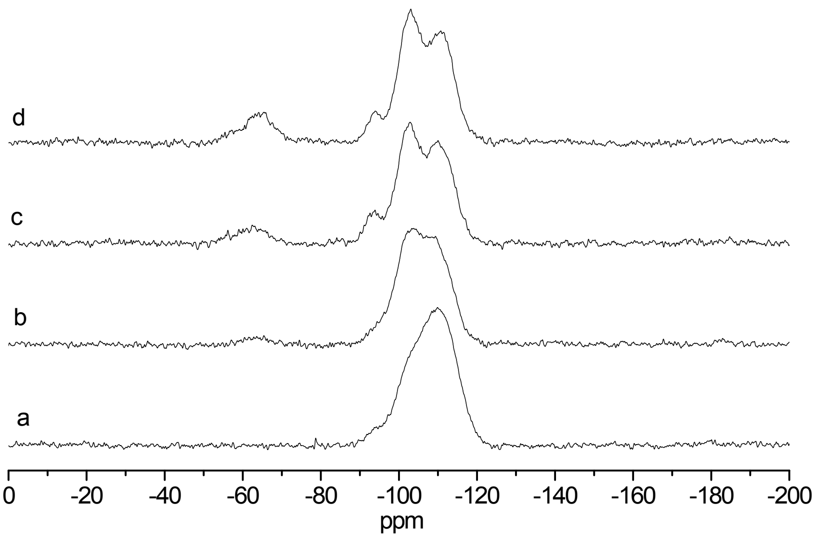


Figure S1: Solid-state ^{29}Si DE-MAS NMR spectra of (a) Ga-F-0 (b) Ga-F-5-Me (c) Ga-F-10-Me (d) Ga-F-15-Me after calcination at 250°C for 8h

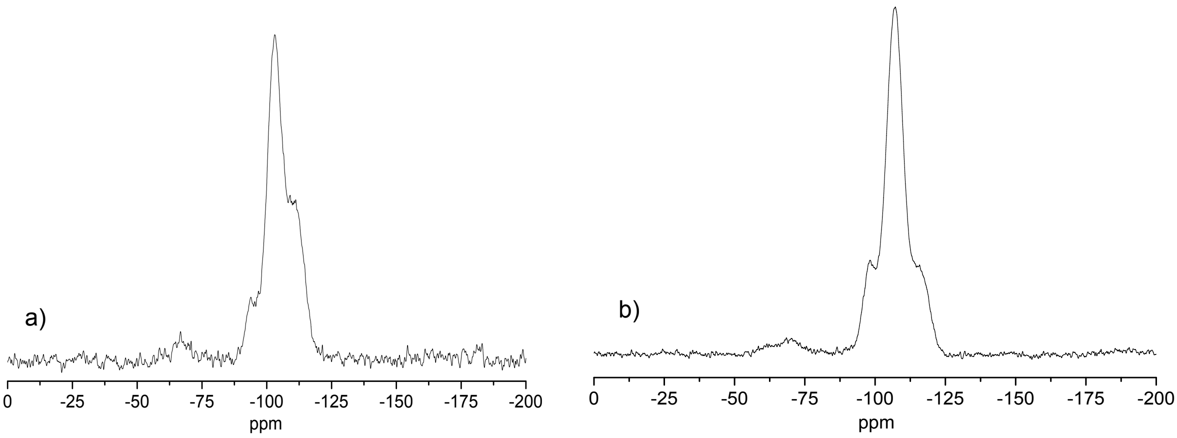


Figure S2: Solid-state ^{29}Si MAS NMR spectra of Ga-P-5-Pr, (a) before calcination (direct excitation experiment) and (b) after calcination at 250°C for 8h (cross-polarization experiment)

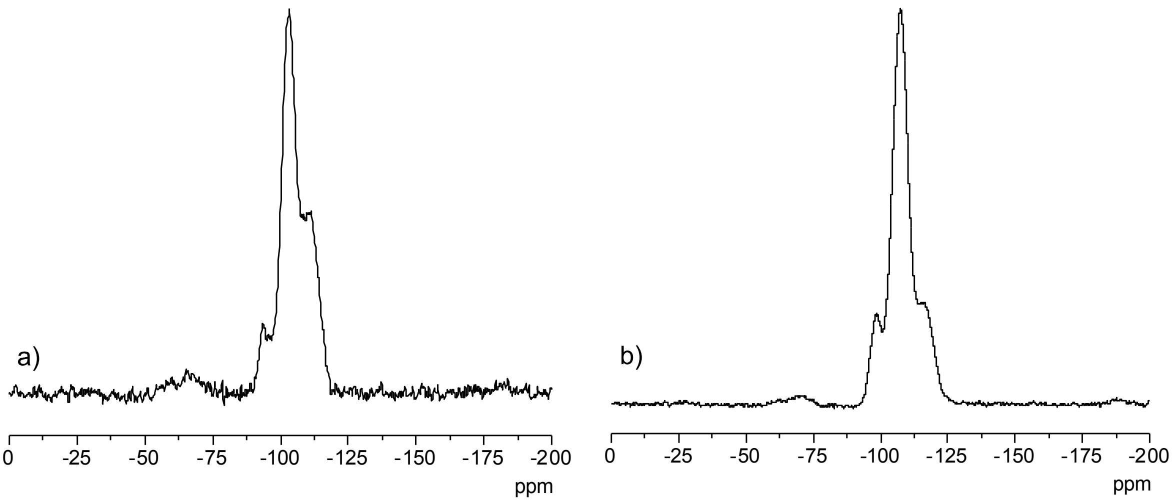


Figure S3: Solid-state ^{29}Si MAS NMR spectra of Ga-F-5-Pr, (a) before calcination (DE) and (b) after calcination at 250°C for 8h (CP)

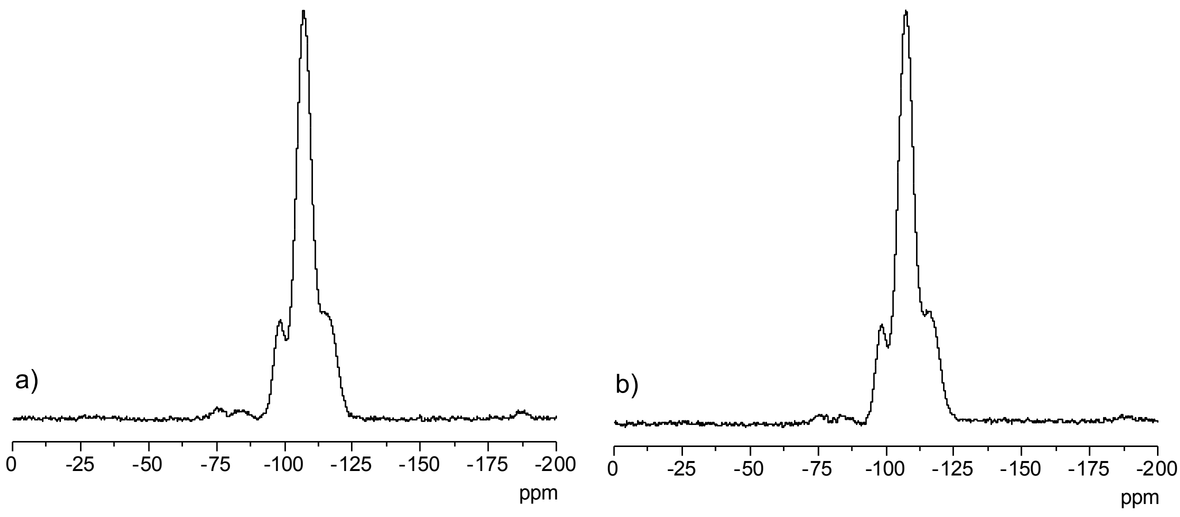


Figure S4: Solid-state ^{29}Si MAS NMR spectra of (a) Ga-P-5-Ph and (b) Ga-F-5-Ph after calcination at 250°C for 8h (CP)

Table S2: Amount of gallium and percentage of functionalization of Ga-silicate solids

Material	% Funct.[(1)]	Ga (mmol/g)[(2)]
Ga-P-0	-	2.0
Ga-P-5-Me	4	1.9
Ga-P-10-Me	8	1.8
Ga-P-15-Me	13	1.8
Ga-P-5-Pr	< 3	1.8
Ga-P-5-Ph	< 3	2.0
Ga-F-0	-	2.1
Ga-F-5-Me	3	1.8
Ga-F-10-Me	8	1.9
Ga-F-15-Me	14	1.9
Ga-F-5-Pr	< 3	2.0
Ga-F-5-Ph	< 3	2.0

[1] %Funct. = $100 * \left(\frac{T^i}{\sum_i T^i + Q^i}\right)$ [2]mmol of gallium per gram of catalyst determined by ICP-OES analysis

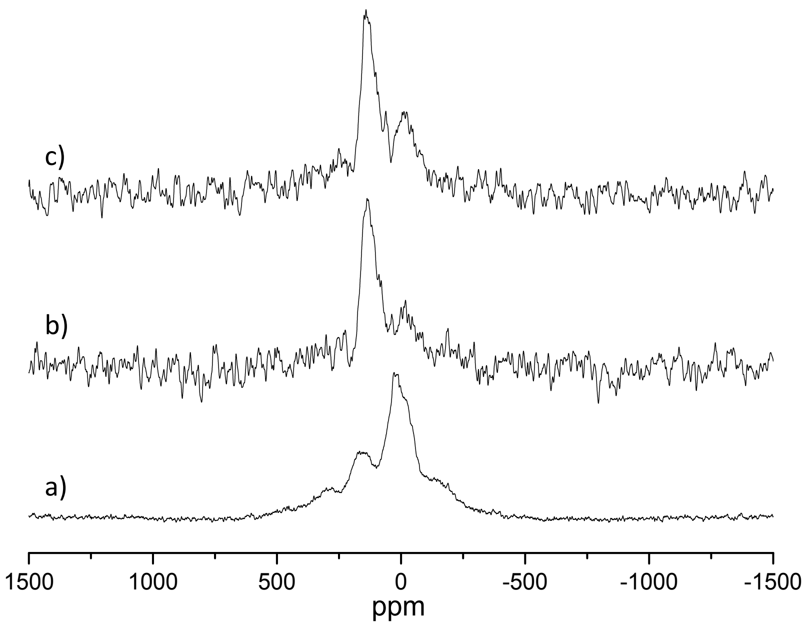


Figure S5: Solid State ^{71}Ga MAS NMR spectra of a) Ga_2O_3 b) Ga-P-0 and c) Ga-F-0. The spectra were recorded using a Hahn echo sequence (see experimental)

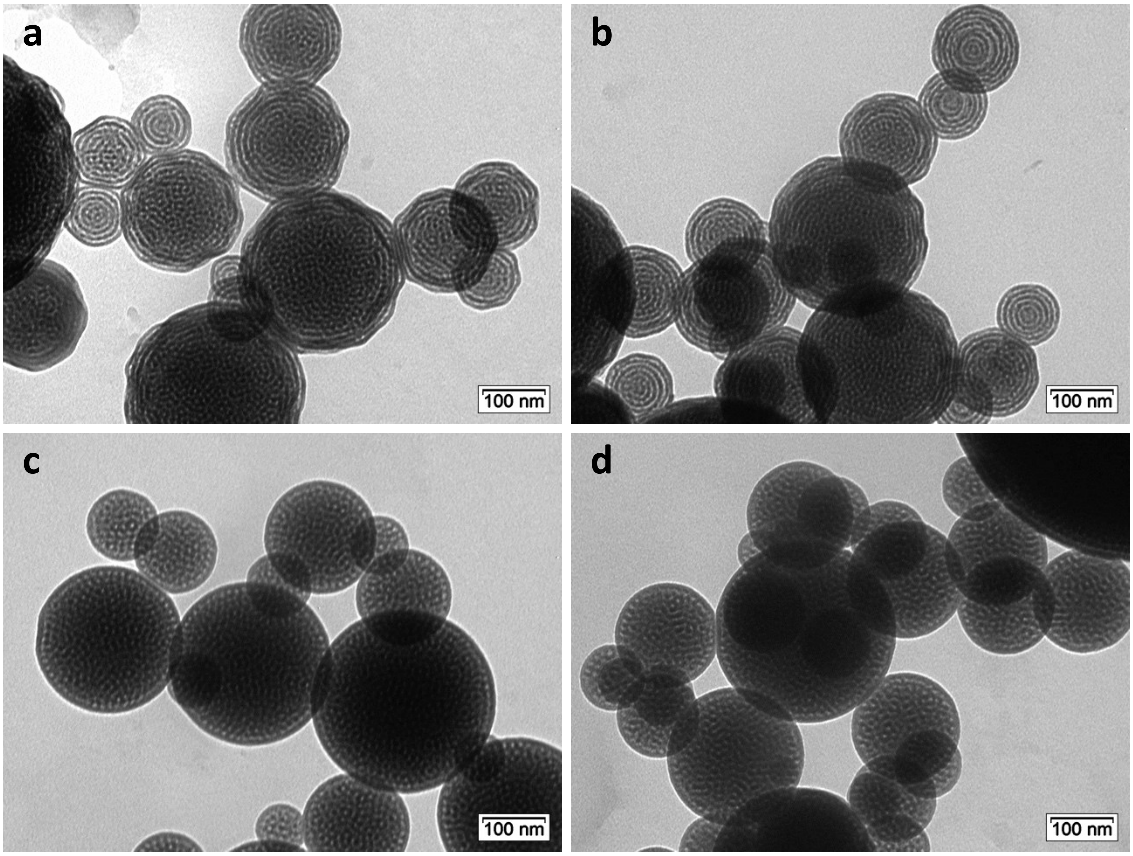


Figure S6: TEM micrographics of (a) Ga-P-5-Pr (b) Ga-P-5-Ph (c) Ga-F-5-Pr (d) Ga-F-5-Ph

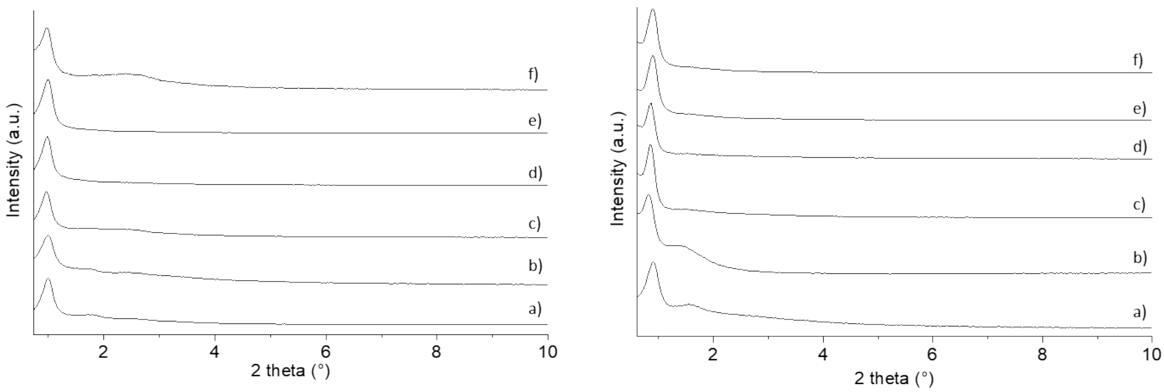


Figure S7: Powder XRD patterns of (a) Ga-P-0 (b) Ga-P-5-Me (c) Ga-P-10-Me (d) Ga-P-15-Me (e) Ga-P-5-Pr et (f) Ga-P-5-Ph (left) and powder XRD patterns of (a) Ga-F-0 (b) Ga-F-5-Me (c) Ga-F-10-Me (d) Ga-F-15-Me (e) Ga-F-5-Pr et (f) Ga-F-5-Ph (right)

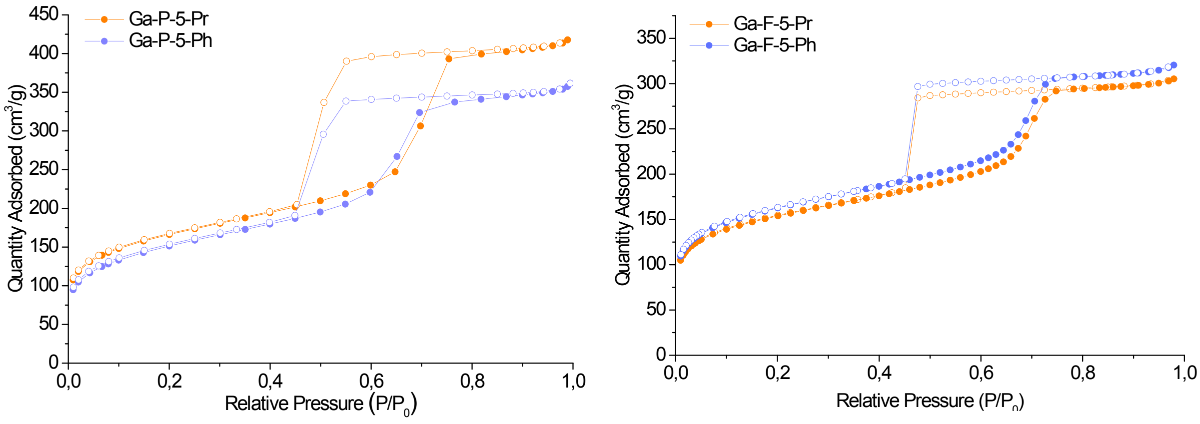


Figure S8: Nitrogen adsorption/desorption isotherms of Ga-P-5-Pr and Ga-P-5-Ph (left) and Ga-F-5-Pr and Ga-F-5-Ph (right)

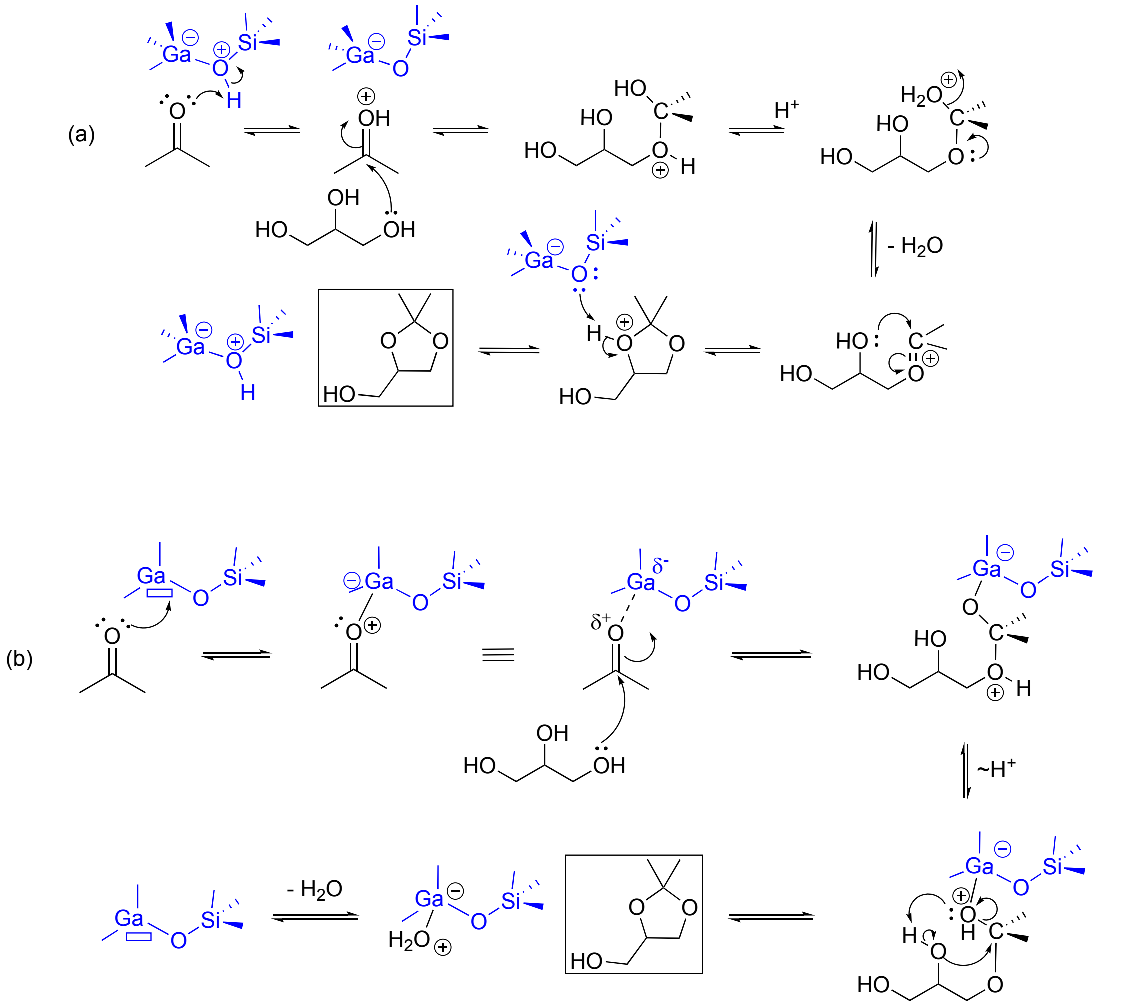


Figure S9: proposed mechanism for glycerol ketalization catalyzed by (a) Brønsted acid catalyst and (b) Lewis acid catalyst

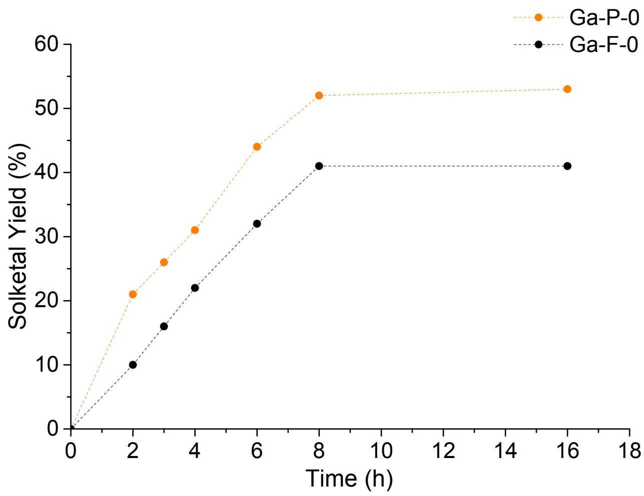


Figure S10: Evaluation of the catalytic activity over time with Ga-P-0 or Ga-F-0 as catalysts. Conditions of the catalytic tests: 10 mg of catalyst, 50°C, Glycerol : Acetone = 1 (0.01 mol) : 4.

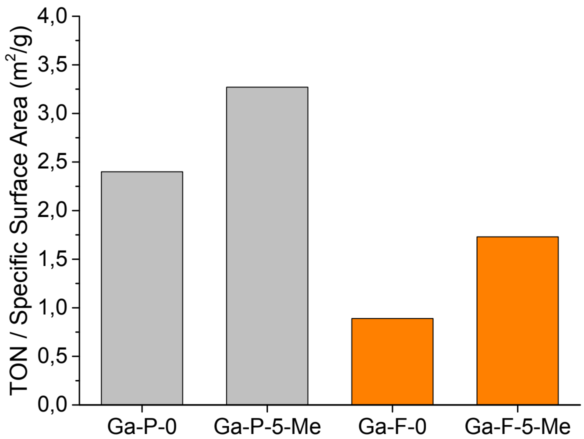


Figure S11: Evaluation of the TON normalized by the BET specific surface area for Ga-P-0, Ga-P-5-Me, Ga-F-0 and Ga-F-5-Me

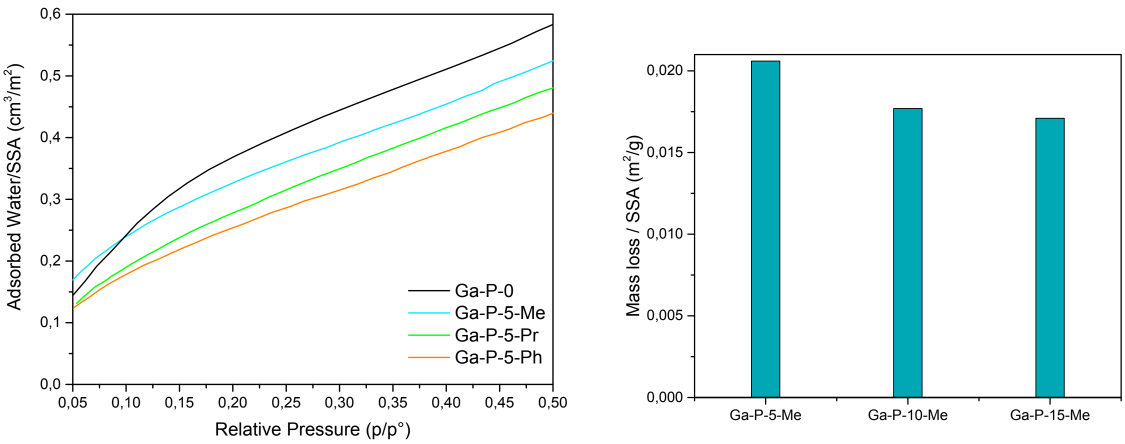


Figure S12: Vapor water adsorption isotherms normalized by the BET specific surface area in the low relative pressure range for Ga-P-0, Ga-P-5-Me, Ga-P-5-Pr and Ga-P-5-Ph (left) and mass loss at 140°C normalized by the BET specific surface area extracted from TGA curves of Ga-P-5-Me, Ga-P-10-Me and Ga-P-15-Me (right).

Table S3: Quantity of adsorbed water normalized by the BET specific surface area at a relative pressure of 0.15 for Ga-P-0, Ga-P-5-Me, Ga-P-5-Pr and Ga-P-5-Ph.

Entry	Material	Adsorbed water/SSA (cm^3/m^2)
1	Ga-P-0	0.32
2	Ga-P-5-Me	0.29
4	Ga-P-5-Pr	0.24
5	Ga-P-5-Ph	0.22

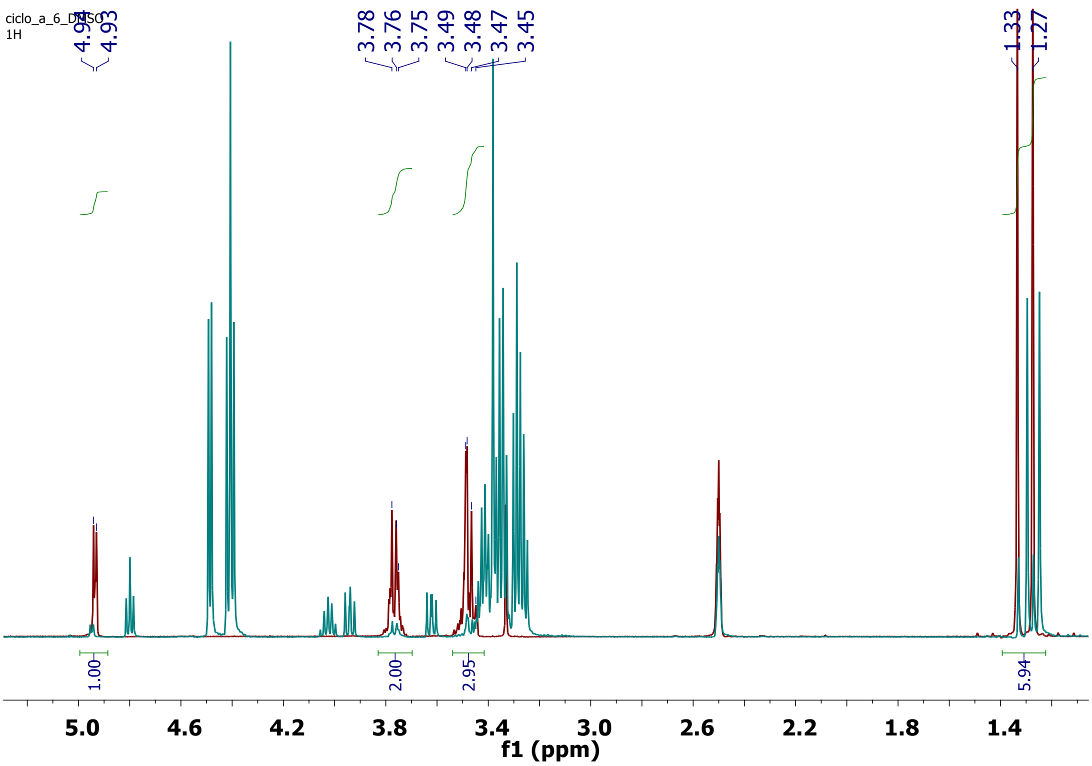
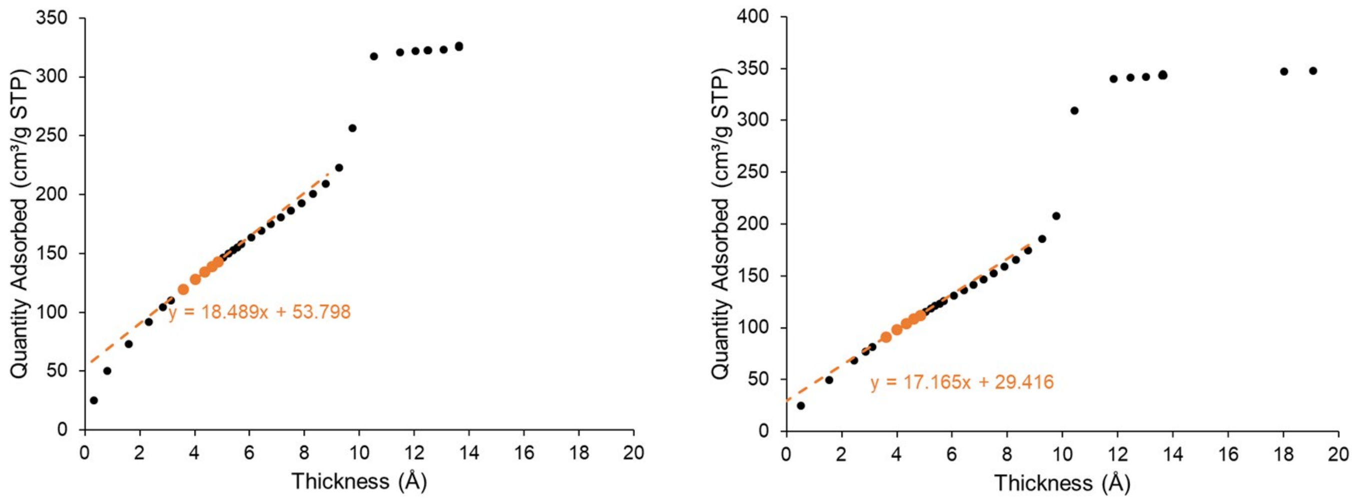


Figure S13: [1]H liquid state NMR of the reaction mixture (blue) and 2,2-Dimethyl-1,3-dioxan-5-ol (red). Solvent: dmso-d6.



(a) (b)

Figure S14: T-plots based on the adsorption branch of the isotherms of (a) Ga-F-0 et (b) Ga-P-0. The micropore volume is given by the intercept of the linear regression calculated in the thickness range of 3.5–5.0 Å.

Table S4: Catalytic activity of Ga-silicates in the conversion of glycerol to solketal. Conditions of the catalytic tests: 10 mg of catalyst, 50°C, 8 hours, Glycerol : Acetone = 1 (0.01 mol) : 4.

Entry	Material	Y_{SK} (%)	$Sel._{SK}$ (%)[1]	TON[2]
1	Ga-P-0	52	95	2599
2	Ga-P-5-Me	55	95	2918
3	Ga-F-0	41	90	1984
4	Ga-F-5-Me	42	91	2276

[1] $Sel._{SK}$ = mol solketal / (mol solketal + mol 2,2-Dimethyl-1,3-dioxan-5-ol). The presence of the by-product (2,2-Dimethyl-1,3-dioxan-5-ol) was identified via ^1H liquid state NMR (Figure S10) [2]TON (TurnOver Number) here defined as mol of solketal/mol of Ga after 2 hours of reaction.

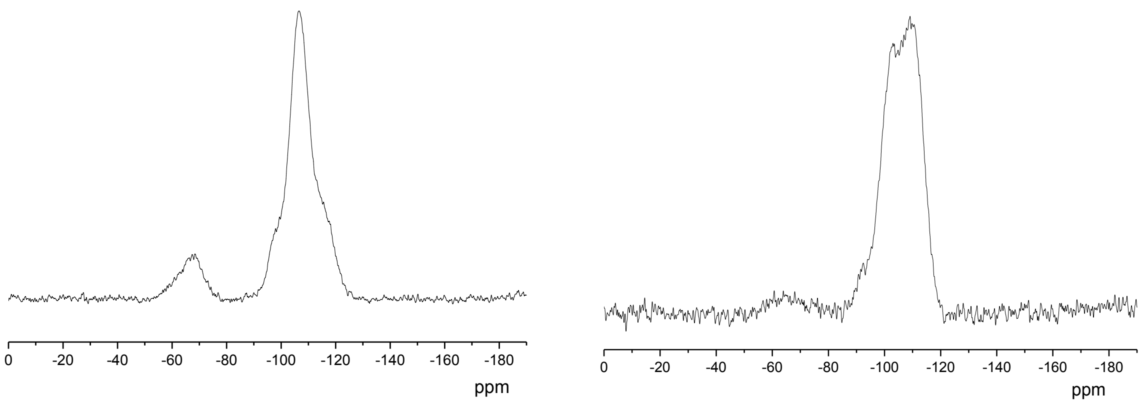


Figure S14: Solid-state cross-polarization (left) and direct excitation (right) ^{29}Si MAS NMR spectra of Ga-P-5-Me calcined at 300°C for 2 hours. The % of functionalization [100 * $\left(\frac{T^i}{\sum_i T^i + Q^i}\right)$] is equal to 4%.

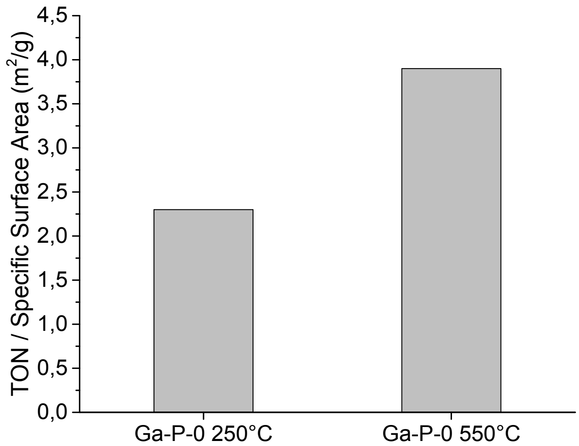


Figure S15: Evaluation of the TON normalized by the BET specific surface area for Ga-P-0 calcined at 250°C and 550°C

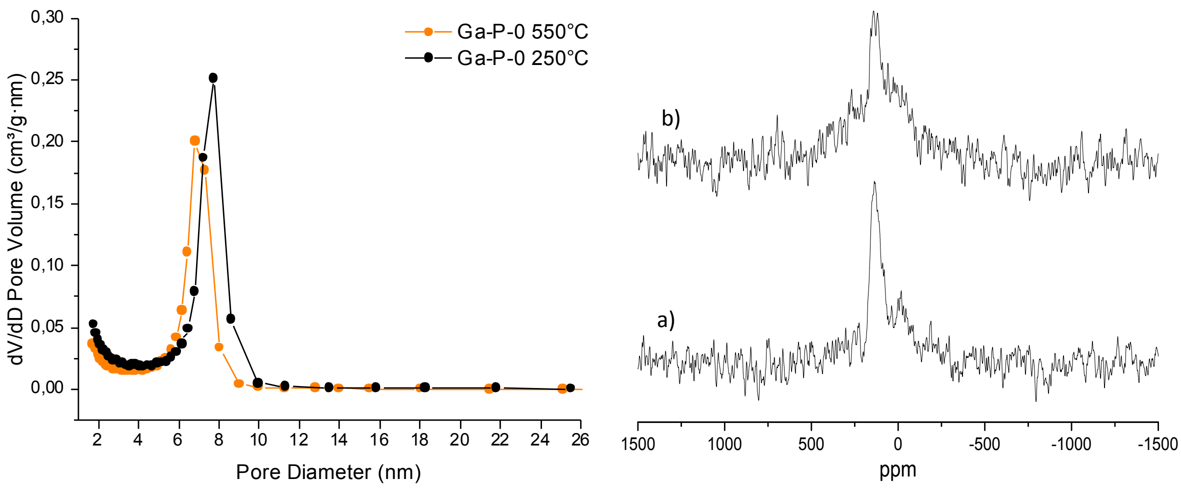


Figure S16: BJH pore size distribution of Ga-P-0 calcined at 250°C and 550°C (left) and solid state ^{71}Ga MAS NMR spectra of (a) Ga-P-0 calcined at 250°C and (b) Ga-P-0 calcined at 550°C (right). The ^{71}Ga MAS NMR spectra were recorded using a Hahn echo sequence (see experimental)