Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for:

$Ga[OSi(O^tBu)_3]_3$•THF, a thermolytic molecular precursor for high surface area gallium-containing silica materials of controlled dispersion and stoichiometry

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Discussion of NMR Spectra

The NMR analysis of **1** is complicated by the presence of overlapping peaks in the ^{1}H NMR and ^{13}C NMR spectra. The ^{1}H NMR spectrum of **1** in benzene-d_6 contains a broad singlet at 4.42 ppm associated with THF, and overlapping peaks at 1.51 ppm associated with THF and the *t*-butoxy groups. A 2D-COSY spectrum of **1** clearly indicates a correlation between the protons at 4.42 ppm and the signal at 1.51 ppm. The ^{13}C NMR spectrum of **1** contains three singlets at 72.20, 32.41 and 25.34 ppm. The upfield signal at 25.34 ppm was assigned to the carbon atoms distal to the ether linkage in THF and the signal downfield at 72.20 ppm was assigned to the carbon atoms directly bound to oxygen. The peak at 32.41 was assigned to the methyl carbons of the *t*-butoxy groups. No signal was observed for the quaternary carbon of the *t*-butoxy group. A 2D-HSQC NMR experiment show correlation between the signals at 25.34 ppm and 32.41 ppm and the singlet at 1.51 ppm in the ^{1}H NMR spectrum. It is also observed that the signal at 72.20 ppm correlates with the signal at 4.42 ppm. This sets the assignment of peaks as presented in this manuscript. A 2D-HMBC NMR spectrum of **1** shows indirect correlation between the carbon signals at 32.41 ppm and 72.20 ppm with the proton signal at 1.51 ppm. This could be interpreted in two ways; either the THF carbon signal at 72.20 ppm is correlating with the overlapping THF proton peak at 1.51 ppm, or there is an overlapping *t*-butoxy carbon at 72.20 which is correlating to the *t*-butoxy methyl protons at 1.51. The related complexes $Al[OSi(O^tBu)_3]_3$•THF and $Ta(O^iPr)_2[OSi(O^tBu)_3]_3$ report chemical shifts for the quaternary carbon atom at 71.76 ppm and 72.91 ppm, respectively, which suggests that this carbon signal should be observable and located in the range of the 72.20 ppm signal assigned to THF.[1,2] The other possibility is simply that the carbon signal for the *t*-butoxy group is unobserved in these spectra.

Figure S 1 ^{1}H NMR spectrum of molecular precursor **1**

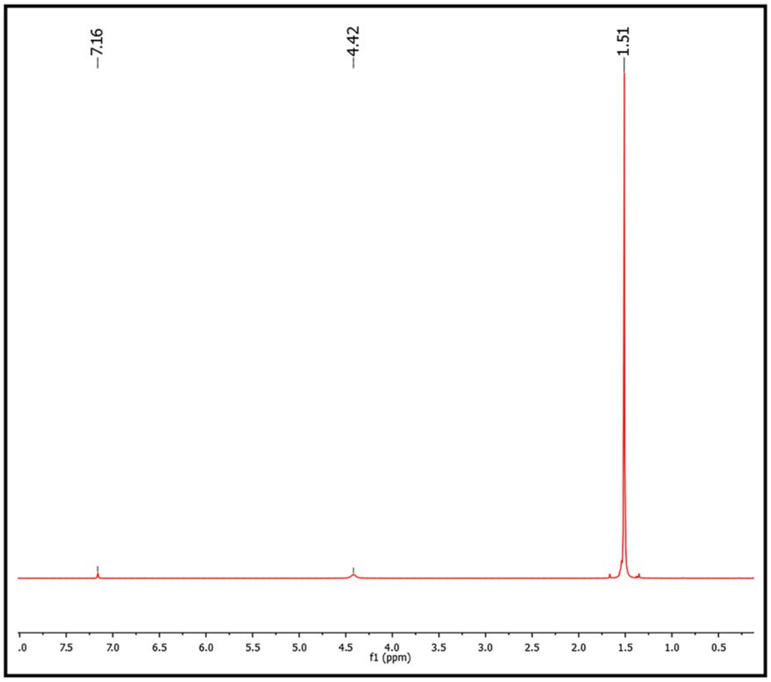


Figure S 2 ^{13}C NMR spectrum of molecular precursor **1**

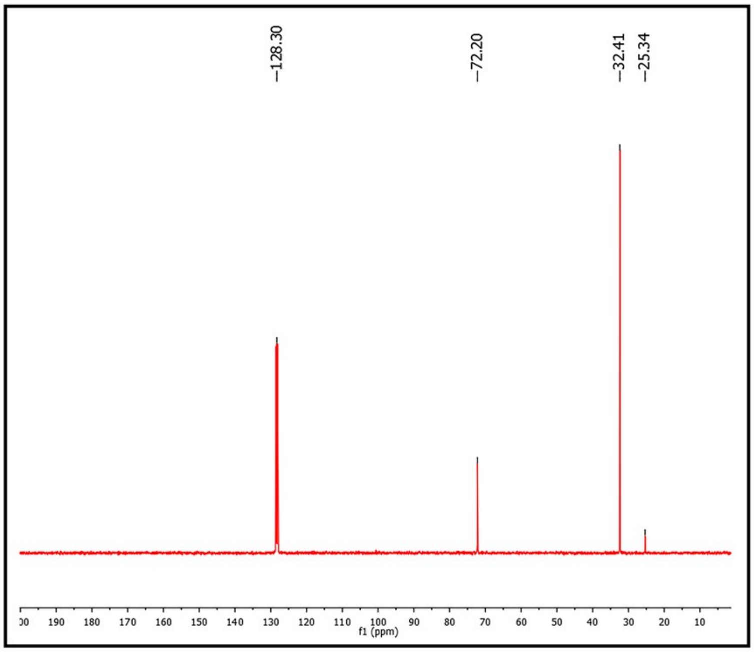
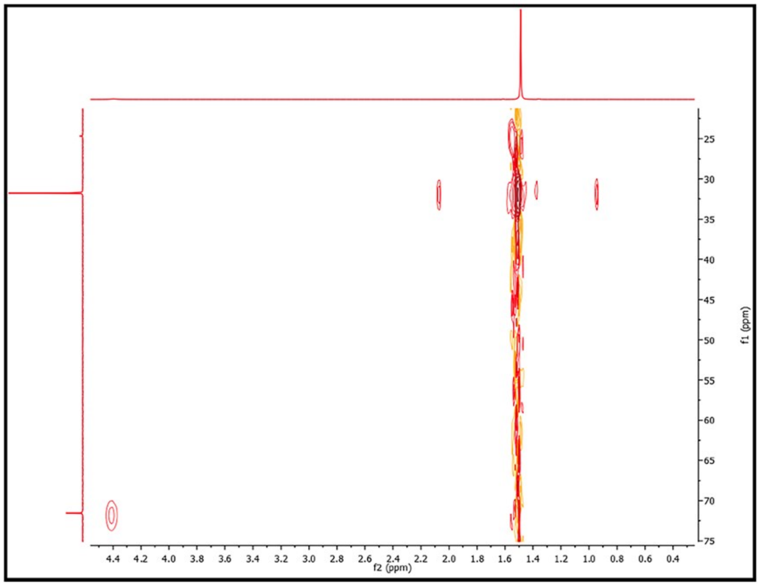
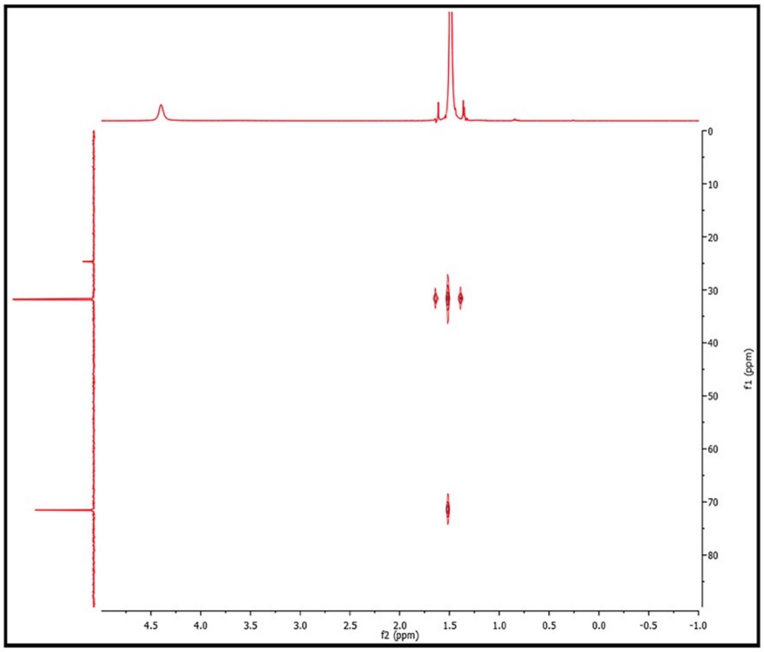
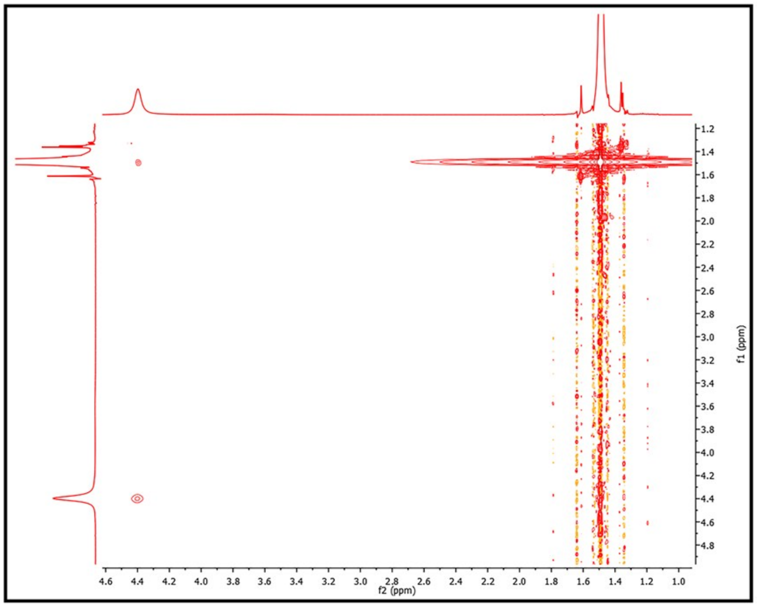


Figure S 3 2D NMR Spectra of molecular precursor **1** (HSQC, HMBC, COSY)





4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f2 (ppm)
0
10
20
30
40
50
60
70
80
f1 (ppm)



4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
f2 (ppm)
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
f1 (ppm)

Figure S 4 ^{29}Si NMR spectrum of molecular precursor **1**

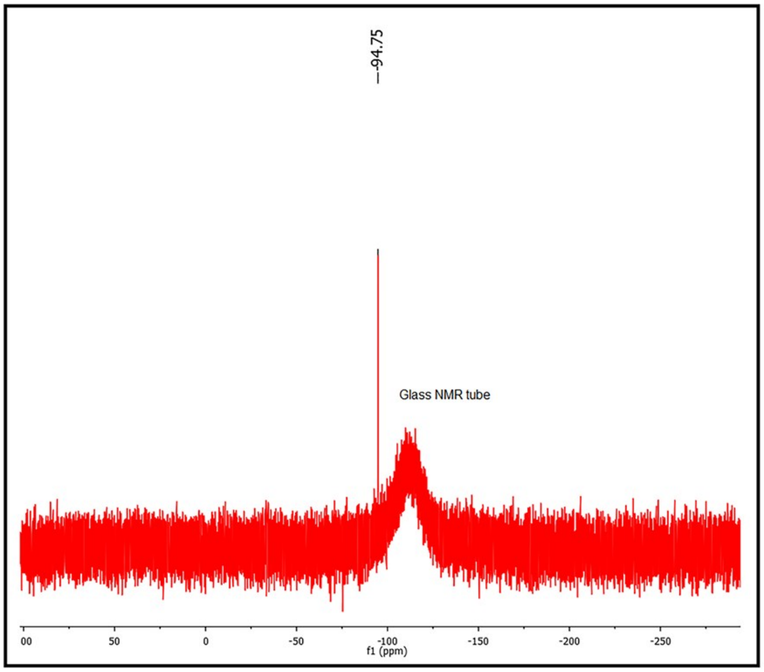


Figure S 5 pXRD spectra of **Ga_2O_3·$3SiO_2$** and **UCB1-GaSi$_{1\text{-}3}$**

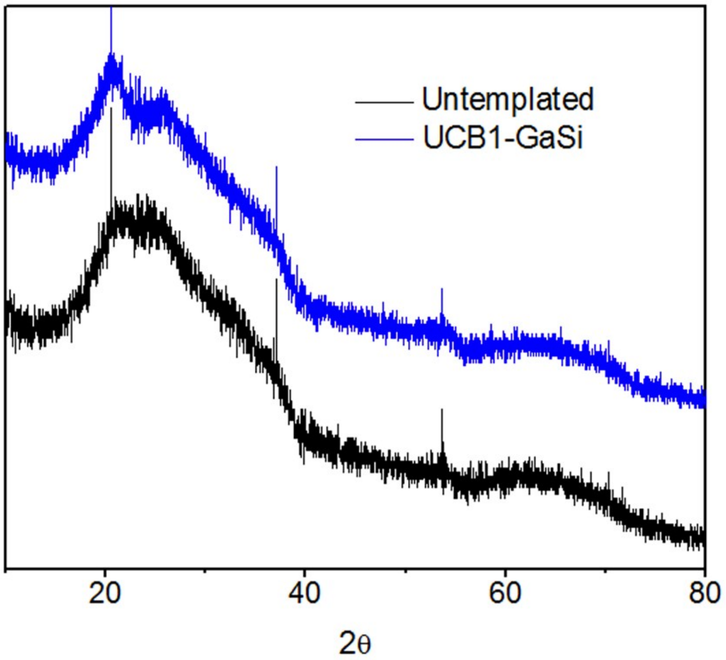


Figure S 6 pXRD spectra of **UCB1-GaSi$_3$** (1:3), **UCB1-GaSi$_{10}$** (1:10), **UCB1-GaSi$_{20}$** (1:20), and **UCB1-GaSi$_{50}$** (1:50)

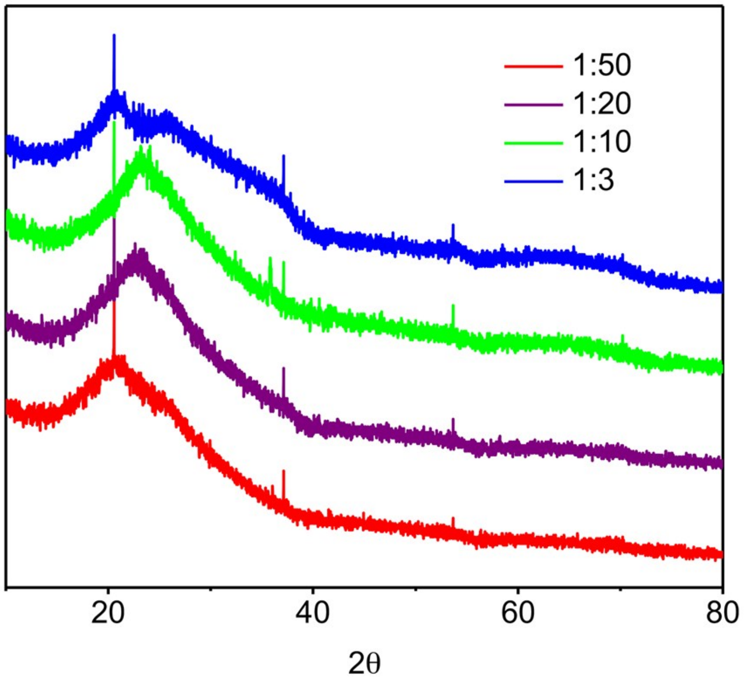


Figure S 7 pXRD spectra of **UCB1-GaSi$_{1\text{-}3}$** calcined at varying temperatures (un-calcined at 20 °C, calcined at 200 °C, calcined at 500 °C, calcined at 800 °C, and calcined at 1000 °C). It should be noted that for the sample calcined at 200 °C the sample was brown following calcination while all other samples appeared white. This is attributed to carbaceous contaminants remaining in the sample. The higher temperature calcinations indicate growth of gallium oxide phases. Between 800 °C and 1000 °C a potential melting event occurred although a corresponding endotherm in the TG/DTA of the precursor was not evident. This was suggested by fusing of the material to the quartz glass of the sample holder.

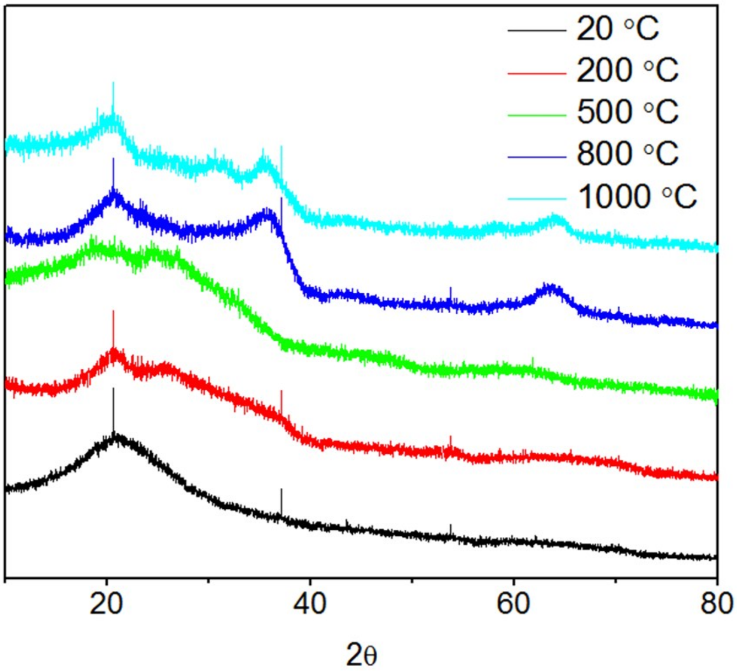
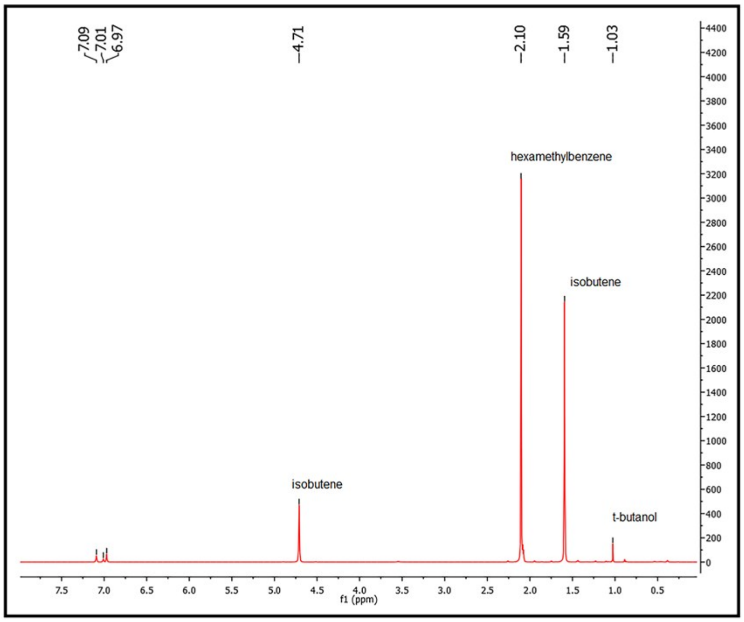


Figure S 8 Thermolysis of **1** and ($^tBuO)_3SiOH$ in toluene-*d8* at 135 °C for 24h. Spectra shown for Ga:Si ratios of 1:20 and 1:50 indicating that even at these dilutions consumption of all silanol and **1** is observed generating only ^{t}BuOH and isobutene as observable products along with a small peak potentially attributable to water. A singlet partially overlapping with the toluene-*d8* methyl signal is for hexamethylbenzene.[3] **Ga:Si = 1:50 followed by Ga:Si = 1:20**



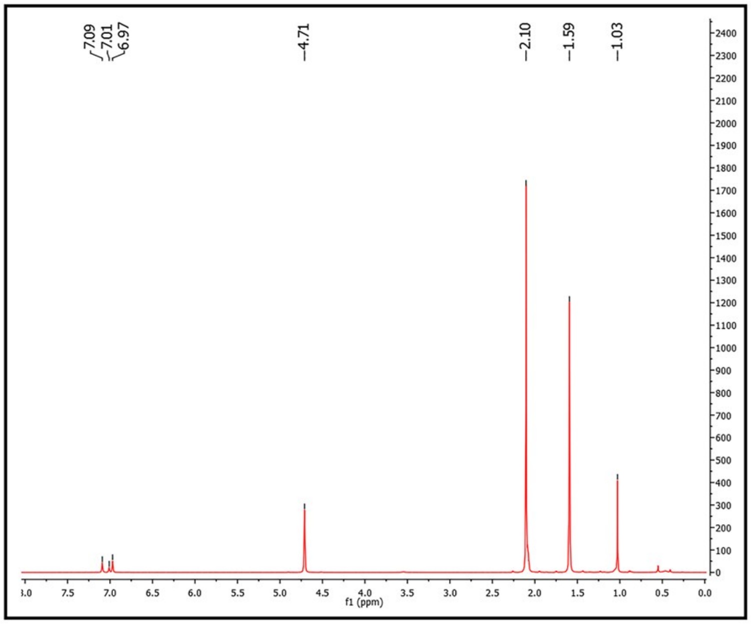


Figure S 9 Raman spectra (500-2000 cm^{-1}) of **1** taken in air at different exposure times and under nitrogen within two hours of removal from a -20 °C freezer (to prevent thermal decomposition and hydrolysis). For comparison the spectrum of tri(*tert*-butoxy)silanol is provided suggesting the changes observed are in part due to the formation of free tri(*tert*-butoxy)silanol by hydrolysis of **1**. All signals are preserved between the precursor **1** and tri(*tert*-butoxy)silanol except for three: a peak appears at 650 cm^{-1} which can be attributed to THF, and a peak appears at 535 cm^{-1} with loss of a signal at 618 cm^{-1} found in tri(*tert*-butoxy)silanol.[4,5] This peak has been previously assigned to an O–Si–O deformation mode in tri(*tert*-butoxy)silanol and substantial shifts to lower wavenumbers have been reported for this mode in molybdenum and tungsten siloxy molecular precursors.[4] The peak at 535 cm^{-1} is therefore tentatively assigned to an O–Si–O deformation mode present for a Ga(OSiO)$_3$ tetrahedral moiety. This peak is observed to broaden and shift to higher wavenumbers as decomposition of **1** occurs

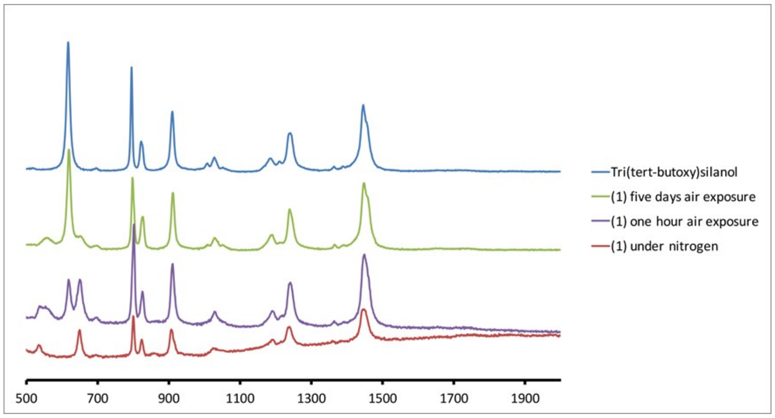
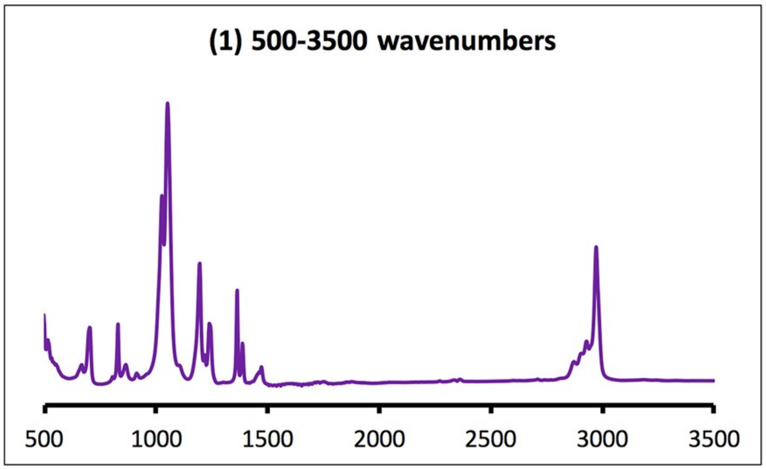


Figure S 10 Infrared spectrum of **1**. Sample was prepared as a pentane film between NaCl plates. Samples compared to previous reports of tri(*tert*-butoxy)silanol and THF.[4,5]



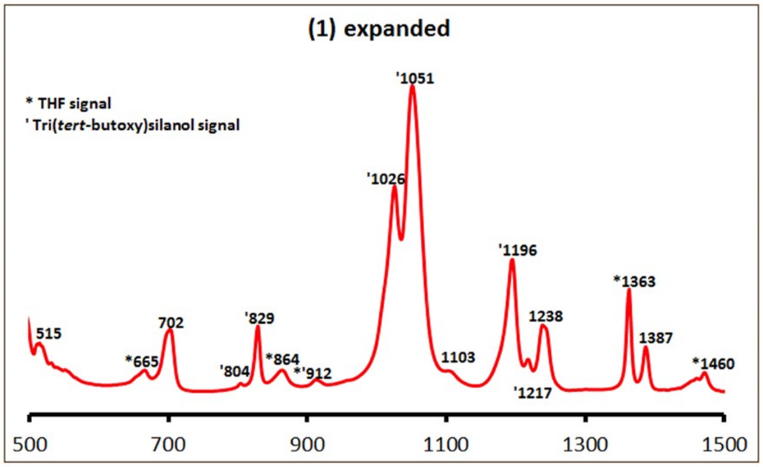


Figure S 11 Un-normalized pore size distributions for **UCB1-GaSi$_{1:3}$ (1:3), UCB1-GaSi$_{1:10}$ (1:10), UCB1-GaSi$_{1:20}$ (1:20), and UCB1-GaSi$_{1:50}$ (1:50)**

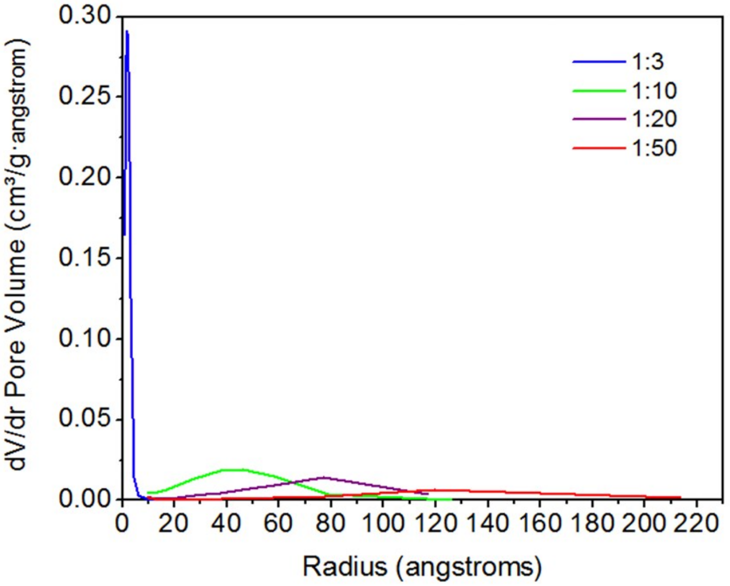


Figure S 12 TG/DTA curves of solid mixtures of **1** and HOSi(O^{t}Bu)$_3$ to generate Ga:Si ratios of 1:10, 1:20, 1:50. Mass losses before 500 °C shown below. Losses measured for a Ga:Si ratio of 1:10, 1:20, and 1:50 were 77.5%, 76.4% and 79.2%, respectively. Calculated mass losses in forming Ga_2O_3•20SiO_2, Ga_2O_3•40SiO_2, Ga_2O_3•100SiO_2 are 75.1%, 76.2% and 76.9%, respectively. The close correspondence between calculated and measured mass losses further supports the conclusion that free silanol is consumed completely in generating low gallium loading materials. The sharp single event suggests in addition that all mass losses occur at temperatures below those used in the synthesis of **UCB1-GaSi** materials eliminating the possibility that significant *tert*-butoxide groups remain in the gels formed prior to calcination.

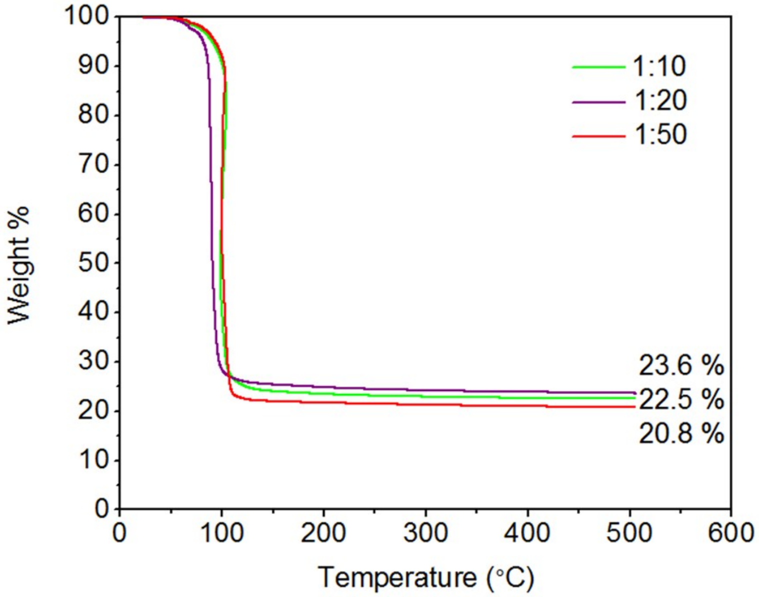
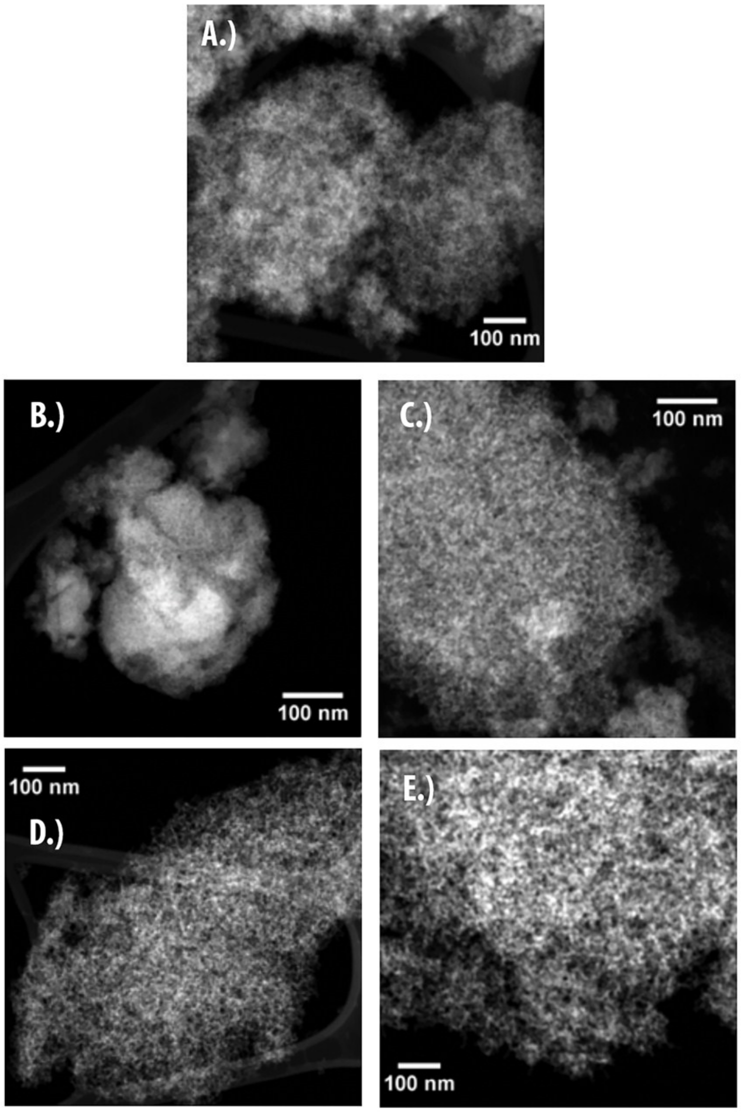


Figure S 13 HAADF-STEM images of A.) untemplated **Ga_2O_3•$6SiO_2$** from **1**, B.) **UCB1-$GaSi_{1:3}$**, C.) **UCB1-$GaSi_{1:10}$**, D.) **UCB1-$GaSi_{1:20}$**, E.) **UCB1-$GaSi_{1:50}$**.



X-ray Crystallographic Analysis of 1

Table 1. Crystal data and structure refinement for **1**.

Identification code	shelx	
Empirical formula	C40 H89 Ga O13 Si3	
Formula weight	932.10	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 18.0537(8) Å	a= 63.017(2)°.
	b = 25.2459(12) Å	b= 89.975(2)°.
	c = 26.1016(12) Å	g = 89.758(2)°.
Volume	10601.5(9) Å^3	
Z	8	
Density (calculated)	1.168 Mg/m^3	
Absorption coefficient	0.639 mm^{-1}	
F(000)	4048	
Crystal size	0.140 x 0.080 x 0.060 mm^3	
Theta range for data collection	1.427 to 25.462°.	
Index ranges	-21<=h<=21, -29<=k<=30, -31<=l<=31	
Reflections collected	213090	
Independent reflections	38525 [R(int) = 0.0458]	
Completeness to theta = 25.000°	99.1 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	38525 / 12 / 2161	
Goodness-of-fit on F^2	1.200	
Final R indices [I>2sigma(I)]	R1 = 0.1484, wR2 = 0.3505	
R indices (all data)	R1 = 0.1577, wR2 = 0.3544	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.805 and -1.492 e.Å^{-3}	

References

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5. H. F. Shurvell, M. C. Southby, *Vibrational Spectroscopy*, 1997, **15**, 137.