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Supporting Information

Organometallic model complexes elucidate the active gallium species in alkane dehydrogenation catalysts based on ligand effects in Ga K-edge XANES

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Additional Preparation and Evaluation of $Ga\text{-}SiO_2$ Catalysts

As mentioned in the main text, successful preparation of single site $Ga\text{-}SiO_2$ depends upon the details of the solution chemistry used during catalyst synthesis. In the main text, only the catalyst prepared using gallium nitrate with citric acid is discussed. We present here a comparison of all three catalyst synthesis procedures considered, including synthetic approach, characterization by XANES and EXAFS, and catalytic evaluation for propane dehydrogenation and propylene hydrogenation activity.

The three Ga/SiO_2 catalysts were prepared by incipient wetness impregnation (IWI) method. Catalyst Ga-N was prepared from impregnating gallium(III) nitrate aqueous solution onto SiO_2 followed by drying at 110 °C overnight and calcination at 550 °C for 3 hours. Catalyst Ga-AC was similarly prepared using an ethanol solution of $Ga(acac)_3$. The use of the organic ligand and organic solvent was intended to give a variation in the structure of Ga surface species. A similar strategy was used to synthesize catalyst Ga-CA, in which excess citric acid was used as a complexing ligand in order to mitigate the aggregation of Ga into oxide clusters. ICP analysis showed that the Ga loading of all the three catalysts were similar: 2.64% for Ga-N, 2.64% for Ga-AC, and 2.46% for Ga-CA

Synthesis of $Ga\text{-}SiO_2$ Catalysts

Ga-N: 0.76 g of $Ga(NO_3)_3{\cdot}xH_2O$ (N) was dissolved in 5 mL of DI H_2O, which was impregnated onto 5.0 g of SiO_2. After drying at 110 °C overnight, the catalyst was calcined at 550 °C for 3 hours. Elemental analysis of Ga: 2.64 %.

Ga-CA: 3.00 g of $Ga(NO_3)_3{\cdot}xH_2O$ and 3.00 g of citric acid (CA) were dissolved in 15 mL of DI H_2O, and then 4 mL of NH_4OH was added to adjust the pH to 11. The solution was impregnated onto 20.0 g of SiO_2. After drying at 110 °C overnight, the catalyst was calcined at 550 °C for 3 hours. Elemental analysis of Ga: 2.46 %.

Ga-AC: 1.00 g of gallium(III) acetylacetonate, $Ga(acac)_3$ (AC), was dissolved in 8 mL of ethanol, and then the solution was impregnated onto 5.0 g of SiO_2. After drying at 110 °C overnight, the catalyst was calcined at 550 °C for 3 hours. Elemental analysis of Ga: 2.64 %.

XAS Analysis

Previous studies have shown that tetrahedral (T_d) and octahedral (O_h) geometries could be distinguished and quantified from the Ga K-edge XANES spectra.[56] An edge energy of 10374-10375 eV, a maximum X-ray absorbance near 10377 eV, and a shoulder near 10381 eV are characteristic of T_d gallium in a GaO_4 coordination environment, while an edge energy above 10376 eV with a relatively symmetric absorption maximum at 10380 eV and no shoulder are characteristic of O_h gallium in a GaO_6 coordination environment. Figure S1a shows the XANES spectra of T_d standard Ga-MFI (Ga in the MFI framework), O_h standard $Ga(acac)_3$, and Ga_2O_3 which has 50% T_d sites and 50% O_h sites.[42] As shown in the XANES spectra in Figure S1b, all of the $Ga(III)/SiO_2$ catalysts show two maxima at about 10376 and 10380 eV. Linear combination fits of the XANES spectra were used to estimate the ratio of T_d and O_h sites. Ga-MFI was selected as the T_d standard, and Ga_2O_3 was also used as a reference (50% T_d and 50% O_h sites). The fractional coordination geometry of Ga-CA was 0.95 T_d with a small amount (0.05) O_h sites, indicating that addition of citric acid during synthesis allows preparation of a Ga-

SiO_2 catalyst containing almost exclusively tetrahedral GaO_4. The fraction of T_d sites in Ga-Ac and Ga-N were similar at 0.80 and 0.77, respectively.

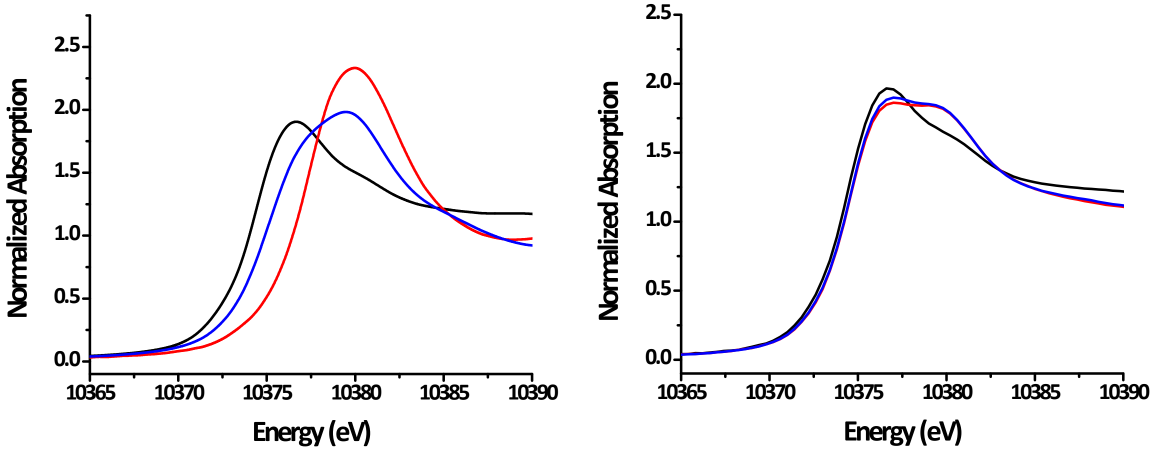

Figure S1. At left: The Ga K-edge XANES from 10365 to 10390 eV for Ga^{3+} standards: T_d Ga-MFI (Black), O_h $Ga(AcAc)_3$ (red), and 0.5 T_d + 0.5 O_h Ga_2O_3 (Blue). At right: XANES spectra of Ga-SiO_2 catalysts: Ga-CA (Black), Ga-AC (Red) and Ga-N (Blue).

The EXAFS spectra of the three catalysts were also fit in order to extract the first-shell Ga-O coordination parameters. The fit of the standard Ga_2O_3 gave an average bond distance of 1.90 Å with a coordination number of 5.1. These results are consistent with its crystal structure which has a fractional T_d occupancy of 0.5 at Ga(T_d)-O bond distance of 1.83 Å and 0.5 O_h occupancy with a Ga(O_h)-O bond distance of 2.00 Å. The average bond distance in Ga_2O_3, therefore, is 1.91 Å consistent with the EXAFS fits. As shown in Table 6, the Ga-O coordination number of Ga-CA was 4.1, while that of Ga-AC and Ga-N were slightly higher consistent with increased amounts of O_h Ga-O bonds compared to Ga-CA. The average Ga-O bond distance in Ga-Ac and Ga-N were also slightly longer than that in Ga-CA consistent with increased amounts of O_h Ga oxide in these catalysts.

Table S1. EXAFS fitting results of the catalysts and standard compounds (k^2: $\Delta k = 2.6 – 10.5$ Å^{-1} and $\Delta R = 0.8 – 1.8$ Å; N ± 10%, R ± 0.02 Å)

Sample	N	R(Å)	$\Delta\sigma^2$	ΔE_o, eV
Ga-CA	4.1	1.81	0.002	-3.43
Ga-AC	4.4	1.84	0.002	-2.18
Ga-N	4.6	1.84	0.002	-2.73
Ga_2O_3	5.1	1.90	0.005	-0.62

Propane dehydrogenation

The test conditions used to compare propane dehydrogenation activity among Ga-SiO_2 catalysts Ga-N, Ga-CA, and Ga-AC differ from those used in the main text to examine the time-on-stream performance of Ga-CA presented in Figure 1. A larger amount of catalyst (1.0 g vs. 0.5 g), a lower gas flow rate (15 mL/min vs 60 mL/min), and a single temperature (550°C) were used to compare relative activities in propane dehydrogenation.

The catalytic performance testing was conducted in a vertical, 1/2" quartz tube reactor equipped with mass flow controllers. About 0.5 g of the catalyst Ga-N was used for initial catalyst testing at various temperatures with a constant flow rate of 15 mL/min (2.3% propane/Ar) in order to determine the reaction temperature for comparison testing of the three Ga/SiO_2 catalysts. 550 °C was chosen as the temperature for catalyst comparisons, and approximately 1 g of catalyst (2.8 mL/g) was supported on quartz wool with an internal thermal couple positioned at the top of the catalyst bed. Initially, the catalyst was purged with He (99.999%, Airgas), which had been further purified with an oxygen trap, at 50 mL/min at room temperature, and heated to the reaction temperature. The conversion was varied by changing the flow rate. Additionally, catalysts were tested under constant conditions overnight in order to determine the conversion stability. Propane dehydrogenation was conducted with 2.3 % propane/Ar at 55 mL/min giving a contact time of 3.0 sec. Blank tests with the silica support at identical flow rates of the catalyst tests were also conducted, and the conversion and selectivity due to thermal cracking were subtracted from those obtained with the catalyst. Product composition was determined by on-line gas chromatography using a 50 m GS-Alumina capillary column and a flame ionization detector (FID) using H_2 (99.999%, Airgas) and air (<2ppm H_2O, Airgas).

The catalyst performance of the three Ga/SiO_2 catalysts at 550 °C is summarized in Table S2. The propylene selectivity of all catalysts was higher than 95% at all conversions, even for those approaching equilibrium. The turnover rate (TOR), based on the total amount of Ga, is given for the catalysts under steady state conversion. The Ga-N reaction rate was 20 $mmol{\cdot}h^{-1}{\cdot}g^{-1}$ (Ga), or a turn-over rate (TOR) of 1.4 h^{-1}. The catalyst Ga-AC had a higher reaction rate, 32 $mmol{\cdot}h^{-1}{\cdot}g^{-1}$ (Ga) and a TOR of 2.2 h^{-1}; while Ga-CA gave the highest rate of 55 $mmol{\cdot}h^{-1}{\cdot}g^{-1}$ (Ga), with a TOR of 3.9 h^{-1}. It should be noted that the yield of propylene was 26% in the Ga-CA case, which approaches the equilibrium conversion for propane dehydrogenation at this temperature, ca. 30%.

Table S2. Rates and selectivity of different Ga/SiO_2 catalysts for propane dehydrogenation at 550 °C

Catalyst	% Conversion	% Selectivity	Rate [$mmol{\cdot}h^{-1}{\cdot}g^{-1}$ (Ga)]	TOR (h^{-1})
Ga-N	9.8	97	20	1.4
Ga-CA	25.5	97	55	3.9
Ga-AC	15.2	98	32	2.2

An interpretation consistent with XAS and catalytic testing results is that only tetrahedral Ga^{3+} sites are active for propane dehydrogenation.

Infrared spectra of pyridine adsorption

The infrared spectrum of adsorbed pyridine is characteristic of the types of acid sites, e.g., Lewis or Brønsted acid sites.[57] In order to evaluate the types of acid sites present on Ga-SiO_2, the Ga-CA catalyst was preheated at 200 °C under vacuum (<5 mTorr), cooled to room temperature and slight stoichiometric excess of pyridine to the moles of Ga was injected onto the catalyst under vacuum through a septum using a syringe. Subsequently, the catalyst was heated under vacuum at 200 °C for 1 h to remove physisorbed pyridine, cooled to RT and mounted in an infrared cell having CaF_2 windows. Nitrogen gas was used to purge the sample chamber as well as the spectrometer. The FTIR spectra were recorded using a Nicolet Nexus 670 FTIR spectrometer coupled to an MCT detector with 2 cm^{-1} resolution.

The infrared spectra in the 1400-1600 cm^{-1} region for Ga-CA catalyst before and after pyridine adsorption are compared in Figure S2. In the absence of Ga(III), the silica support does not adsorb pyridine. After exposure to pyridine, the Ga-CA catalyst shows IR absorption bands at 1459 cm^{-1} and 1492 cm^{-1} that are attributed to pyridine adsorbed on Lewis acid sites. Additionally, there are a small number of Brønsted sites at 1551 cm^{-1}. [57] This small population of Brønsted sites may be responsible for the formation of coke observed during propane dehydrogenation experiments conducted at temperatures above 500°C.

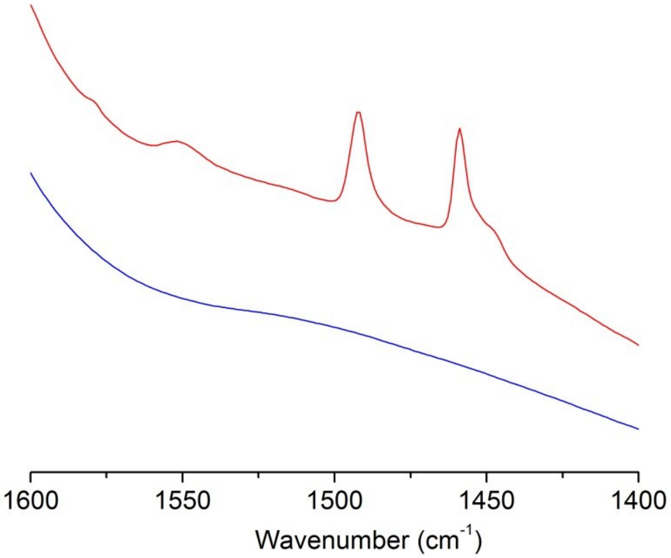

Figure S2. IR absorption spectra in the 1400-1600 cm^{-1} region for Ga-CA before (bottom) and after (top) pyridine adsorption.

Additional Preparation and XANES Analysis of Ga^{3+} Molecular Models

The XANES spectra of Ga-HBEA before and after treatment in H_2 at 500°C (repeated from Figure 1a) are compared to spectra of Ga-SiO_2 before and after treatment in H_2 at 650°C (repeated from Figure 3a) in Figure S3. This figure highlights the systematic 0.8 eV shift in the position of the first absorbance maximum between the as-prepared Ga-HBEA and Ga-SiO_2 catalysts arising from the difference in the character of the bonds between gallium and the support: relatively ionic Ga-O bonds to Si-O-Al anion sites in the zeolite, vs. relatively covalent Ga-O-Si bonds on the silica support. The edge energies between these two as-prepared catalysts likewise differ by 0.7 eV. As Figure S3 shows, the systematic offset is maintained after treatment in H_2.

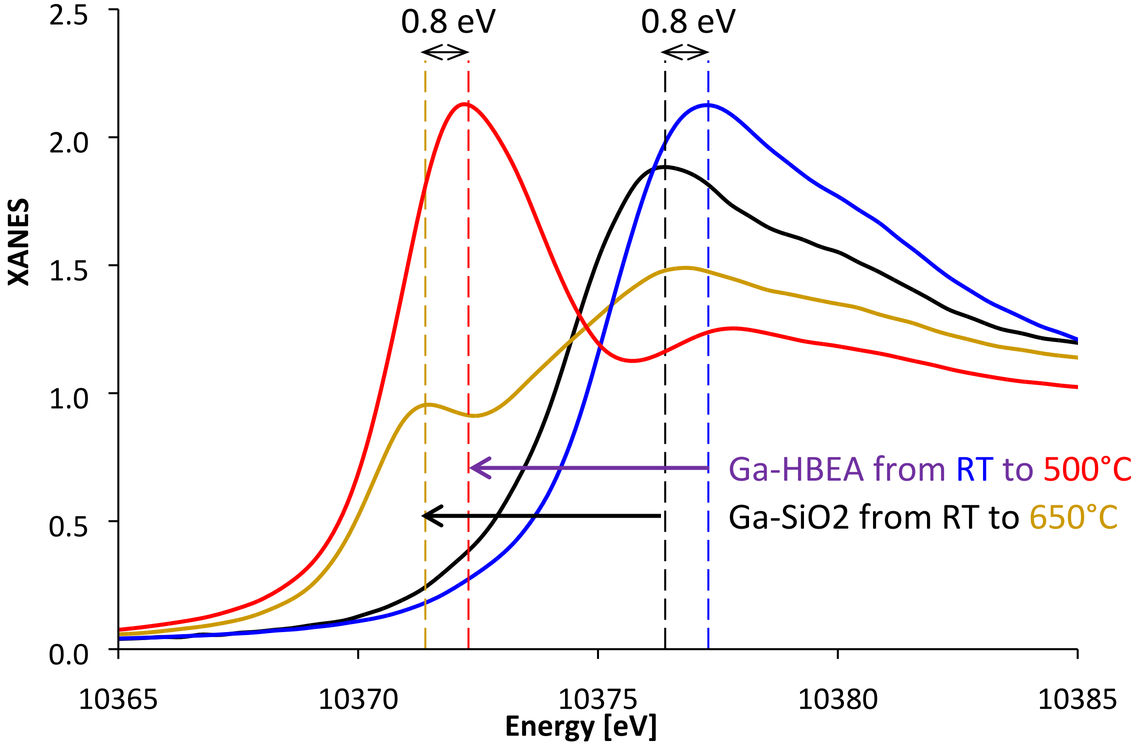

Figure S3: XANES spectra of Ga-HBEA at RT (blue) and in H_2 at 500°C (red) repeated from Figure 1a, compared to those of Ga-SiO_2 at RT (black) and in H_2 at 650°C (gold) repeated from Figure 3a. The difference in bond character between gallium and the support – ionic for Ga-HBEA, covalent for Ga-SiO_2 – gives rise to a systematic 0.8 eV difference in the energies of the absorption maxima in the as-prepared catalysts that is maintained after treatment in hydrogen.

The XANES spectra of molecular model compounds **(4)**, **(6)**, **(3)**, and **(1)** are presented in Figure 6 in the main text. For clarity, the spectra of model compounds **(5)** and **(2)** were omitted from Figure 6. An expanded version of Figure 6 including these latter compounds is presented here as Figure S4.

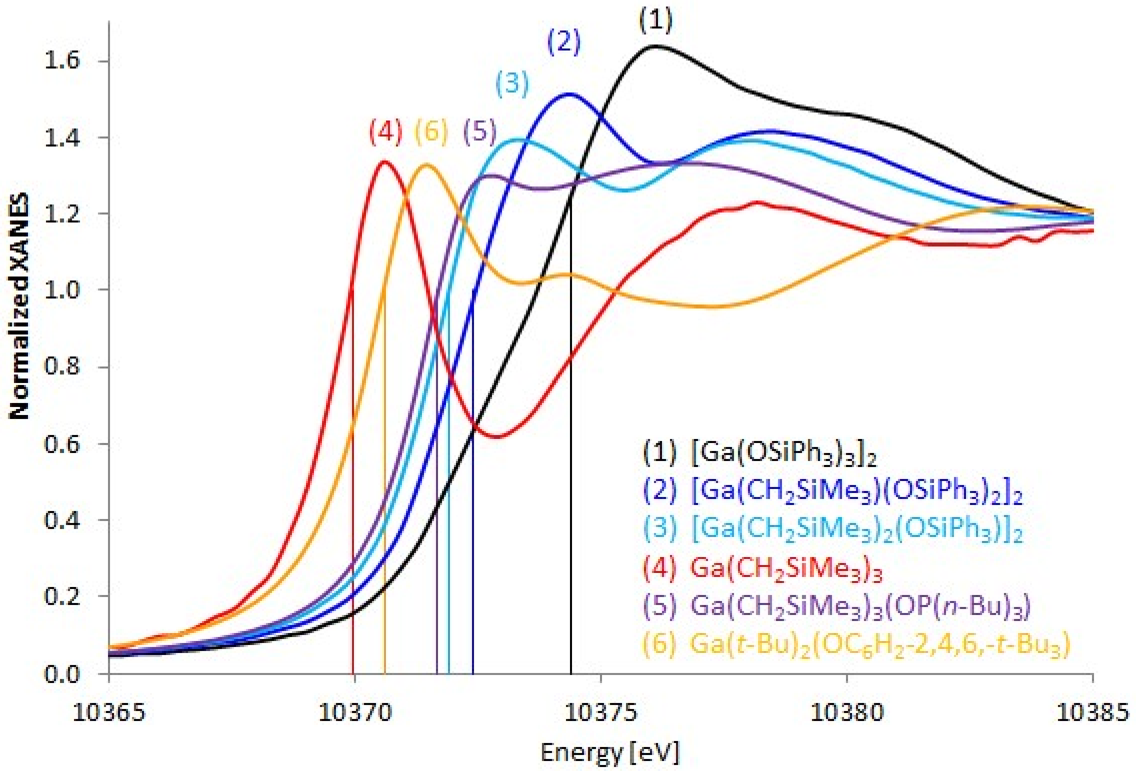

Figure S4: XANES spectra for molecular model compounds **(1)-(6)**. The edge energy for each compound, defined as the energy of the (first) inflection point in the absorption edge, is noted by a vertical line and tabulated in Table 2 in the main text.

Preparation of model compounds **(2)** and **(3)** proceeded from synthetic intermediates $[Ga(CH_2SiMe_3)Cl_2]_2$ and $[Ga(CH_2SiMe_3)_2Cl]_2$. The XANES spectra of these intermediates were also acquired, and are presented here in Figure S5. It is clear from this figure that replacement of Ga-C bonds by Ga-Cl bonds produces shifts in the XANES edge energy similar to those resulting from replacement of Ga-C bonds by Ga-O bonds.

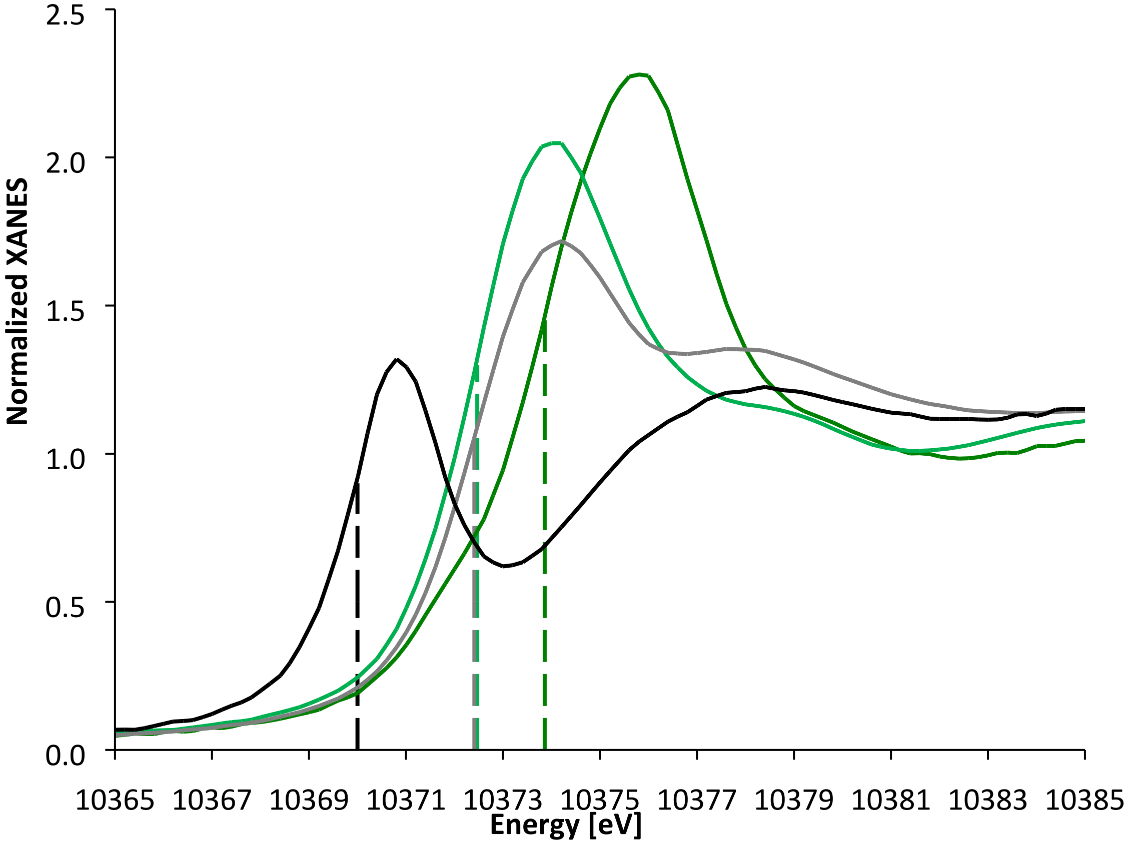

Figure S5: XANES spectra of $Ga(CH_2SiMe_3)_3$ (black), $[Ga(CH_2SiMe_3)_2Cl]_2$ (gray), $[Ga(CH_2SiMe_3)Cl_2]_2$ (light green), and $[GaCl_3]_2$ (dark green). XANES edge energies, marked by dashed vertical lines are 10370.0 eV, 10372.4 eV, 10372.5 eV, and 10373.9 eV respectively.

To support the assertion that –H and sp^3-C substituents have similar effects on XANES edge energies, the consequences of single substitution of Cl by H or by sp^3-C were compared. Single substitution of Cl by H was examined by comparing the spectra of $KGaCl_4$ and $KGaHCl_3$. As shown in Figure S6 at top, this replacement results in a 1.5 eV decrease in the XANES edge energy. Single substitution of Cl by sp^3-C was examined by comparing the spectra of $[GaCl_3]_2$ and $[Ga(CH_2SiMe_3)Cl_2]_2$ (Figure S6, bottom, repeated from Figure S5). This substitution results in a nearly identical 1.4 eV decrease in XANES edge energy, confirming that H and sp^3-C ligands exert similar effects on XANES edge energies.

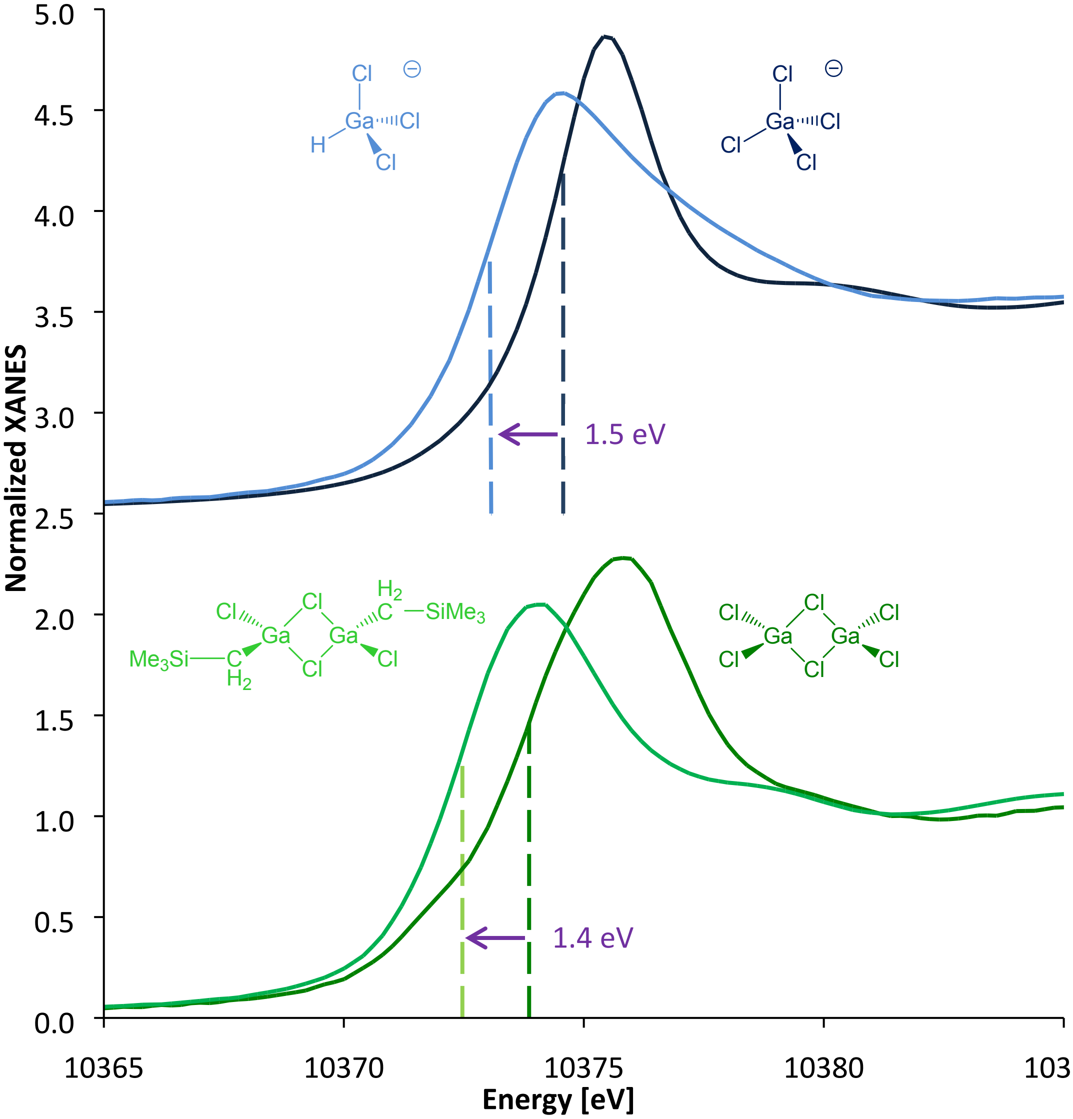

Figure S6: XANES spectra of $KGaCl_4$ (dark blue, top), $KGaHCl_3$ (light blue, top), $[GaCl_3]_2$ (dark green, bottom) and $[GaCl_2(CH_2SiMe_3)]_2$ (light green, bottom). Edge energies, marked by dashed vertical lines, are 10374.6 eV, 10373.1 eV, 10373.9 eV, and 10372.5 eV respectively.

Model compound **(4)** was also grafted to thermally treated silica, and impregnated into the acid form of beta zeolite. The XANES spectrum of the former is shown in Figure 7 in the main text. The XANES spectrum of the latter is shown here as Figure S7. The close agreement between the spectra of **(4-2)** and model compound **(3)** support the expectation that grafting $Ga(CH_2SiMe_3)_3$ to acidic beta zeolite produces a $Ga(CH_2SiMe_3)_2(OZ)_2$ (Z=zeolite framework site) structure with a GaC_2O_2 local coordination environment similar to that of $[Ga(CH_2SiMe_3)_2(OSiPh_3)]_2$. The spectrum of **(4-2)** does not, however, match the spectrum of Ga-HBEA heated to 500°C in hydrogen. As discussed in the main text, Ga-HBEA in hydrogen at 500°C likely contains a three-coordinate $GaH_2(OZ)$ species, which by virtue of its lower coordination number and empty Ga $4p_z$ orbital has a lower XANES edge energy and more prominent absorbance maximum than are expected for four-coordinate **(4-2)**.

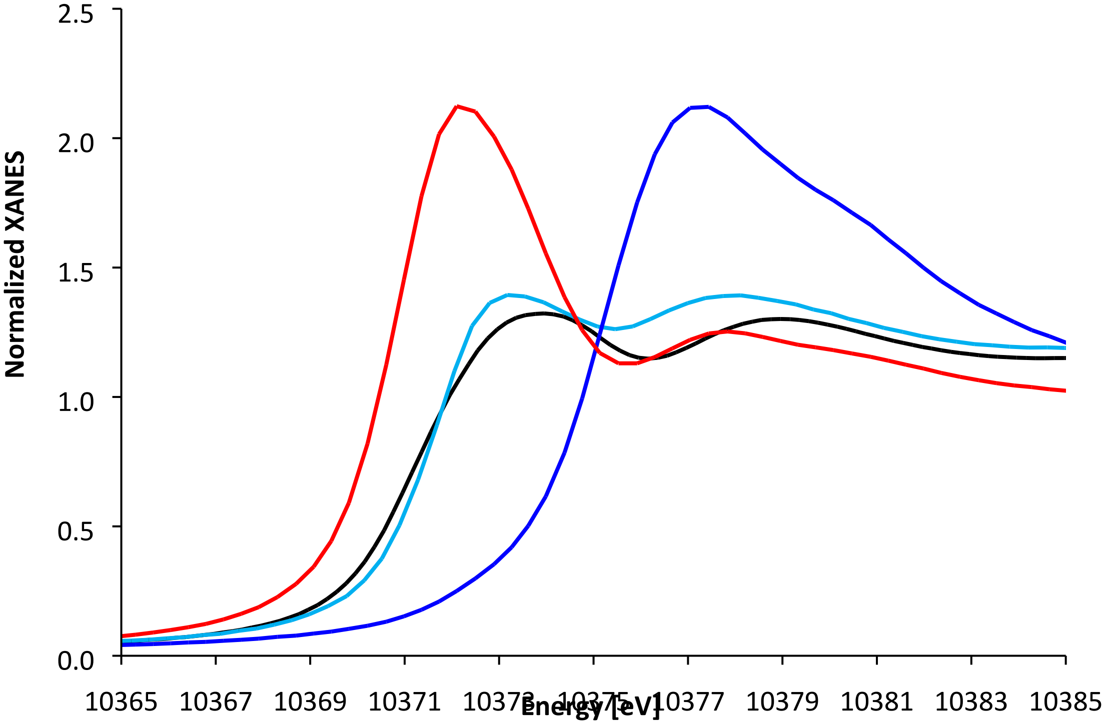

Figure S7: Normalized XANES spectra of **(4-2)** (expected structure $Ga(CH_2SiMe_3)_2(OZ)_2$ for Z=zeolite framework site) prepared by impregnating HBEA zeolite with $Ga(CH_2SiMe_3)_3$, in black, compared to the spectrum of $[Ga(CH_2SiMe_3)_2(OSiPh_3)]_2$ in light blue. The close agreement between the two spectra support the expectation that grafting **(4)** to HBEA produces a gallium species with a GaC_2O_2 coordination environment similar to that of **(3)**. Also shown for comparison are the spectra of Ga-HBEA in hydrogen at 140°C (blue) and 500°C (red).

In order to interrogate the XANES edge energy of an authentic Ga^+ cation, the XANES spectrum of commercially available Ga_2Cl_4 was acquired. Although sold as "Gallium(II) chloride," this material actually comprises the mixed valence ionic salt $Ga^+[GaCl_4]^-$, containing Ga(I) cations and tetrachlorogallate(III) anions. The contribution of the tetrachlorogallate(III) ions can be subtracted by comparison with the XANES spectrum of isostructural $KGaCl_4$. Figure S8 presents the XANES spectra of Ga_2Cl_4 and $KGaCl_4$, and the Ga^+ contribution to the Ga_2Cl_4 spectrum generated by subtracting the $KGaCl_4$ spectrum from that of Ga_2Cl_4. The subtraction is for visual purposes only: the edge energy of the mathematically derived Ga^+ contribution is identical to that of Ga_2Cl_4 at 10371.4 eV. The edge energy of $KGaCl_4$ is 10374.6 eV.

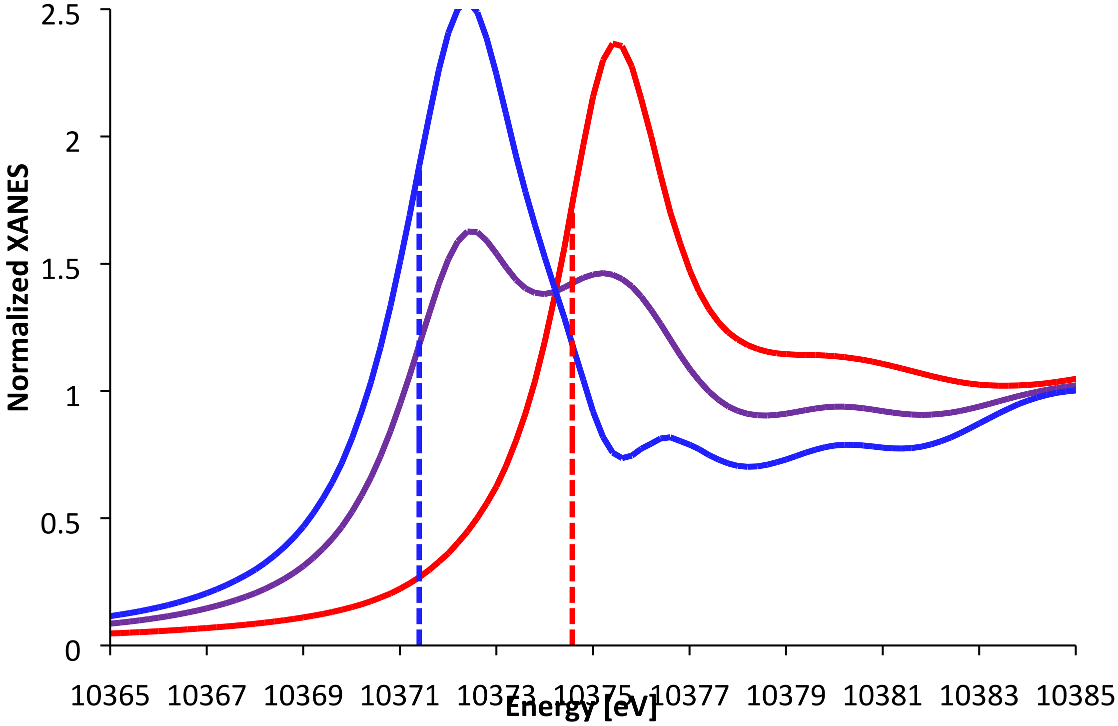

Figure S8: XANES spectra of Ga_2Cl_4 (purple), $KGaCl_4$ (red), and the Ga^+ contribution to the Ga_2Cl_4 spectrum (blue), isolated by subtracting the spectrum of $KGaCl_4$ from that of Ga_2Cl_4. Edge energies for Ga^+ and Ga^{3+} at 10371.4 eV and 10374.6 eV respectively are marked with dashed vertical lines.