Towards Quantitatively Probing the Al Distribution in Zeolites

Aleksei Vjunov,[†] John L. Fulton,[,†] Thomas Huthwelker,[‡] Sonia Pin,[‡] Donghai Mei,[†] Gregory K. Schenter,[†] Niranjan Govind,[§] Donald M. Camaioni,[†] Jian Zhi Hu,[†] Johannes A. Lercher[†,¶,*]*

[†]Institute for Integrated Catalysis, Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99352 (United States)

[‡]Paul Scherrer Institut (PSI), Swiss Light Source, Laboratory for Catalysis and Sustainable Chemistry (LSK), 5232 Villigen (Switzerland)

[§]Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99352 (United States)

[¶]Department of Chemistry and Catalysis Research Institute, TU München, Lichtenbergstrasse 4, 85748 Garching (Germany)

Supporting Information

Table of contents

Al EXAFS data fitting for α-alumina and sodium aluminate

In addition to the MD-EXAFS results reported in the main document, the experimental spectra for α-alumina and sodium aluminate were also fit using conventional EXAFS scattering path analysis. Figures 1S a) and b) show the $k^2\,\chi(k)$ plot for α-Al_2O_3 and the magnitude and imaginary Fourier transforms of this function in the form of $|\tilde{\chi}(R)|$ and $\mathrm{Img}[\tilde{\chi}(R)]$ plots. The fitting was performed to demonstrate that the conventional EXAFS analysis can also be used to describe the main features in the experimental spectra. A structural model using scattering paths derived from the known crystal structure, fits all the relevant features of both $\chi(k)$ and $\tilde{\chi}(R)$. This model includes Al-O single scattering paths for the 2nd and 4th shells and Al-Al scattering paths for the 3rd and 5th shells in order to fit the features in $|\tilde{\chi}(R)|$ up to 5.5 Å in Figure 1S.

The fitted parameters including the bond distances for a combination of Al-O and Al-Al single and multiple scattering paths are shown in Table 1S.

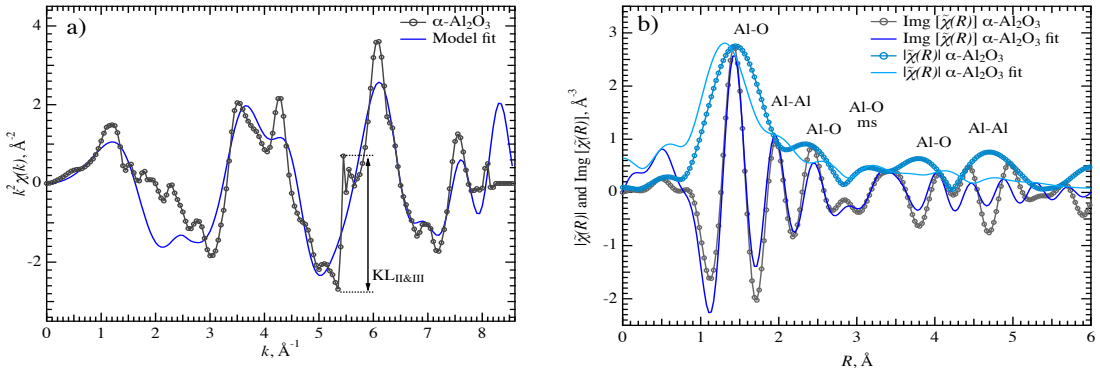

Figure 1S. EXAFS k^2-weighted $\chi(k)$ (a) and $|\tilde{\chi}(R)|$ and $\mathrm{Img}[\tilde{\chi}(R)]$ (b) plots for α-alumina with simple model fits starting from crystallographic data.

Table 1S. Scattering paths used for fitting to the α-alumina standard. The number (between atoms) indicates the scattering angle. An EXAFS fit is applied that uses a simple linear

expansion model applied to the set of Al-O or Al-Al crystallographic distances. The Debye-Waller factors (DWF) for all paths used in the fitting are reported.

#	Path	Fitted distances (Å)	DWF	Scattering path	Crystallographic distances (Å)
1	Al – 180° – O	1.81±0.020	0.0005	single	1.855
2	Al – 180° – O	1.92±0.021	0.0005	single	1.972
3	Al – 180° – Al	2.62±0.024	0.003	single	2.655
4	Al – 180° – Al	2.76±0.025	0.003	single	2.792
5	Al – 180° – Al	3.18±0.029	0.003	single	3.219
6	Al – 180° – O	3.22±0.036	0.002 (set)	single	3.222
7	Al – 180° – O	3.34±0.037	0.004 (set)	single	3.429
8	Al – 180° – Al	3.45±0.032	0.008	single	3.499
9	Al – 180° – O	3.46±0.038	0.004 (set)	single	3.559
10	Al – 180° – O – 180° – Al – 180° – O – 180° – Al	3.61±0.040	0.002	multiple	3.710
11	Al – 180° – O	3.76±0.042	0.01	single	3.865
12	Al – 180° – O – 180° – Al – 180° – O – 180° – Al	3.84±0.042	0.002	multiple	3.943
13	Al – 180° – O	4.05±0.045	0.01	single	4.162
14	Al – 180° – O	4.26±0.047	0.01	single	4.377
15	Al – 180° – O	4.55±0.050	0.01	single	4.677
16	Al – 180° – Al	4.70±0.043	0.0005 (set)	single	4.760
17	Al – 180° – Al	5.06±0.067	0.0005 (set)	single	5.129
18	Al – 180° – Al	5.38±0.071	0.0005 (set)	single	5.450

The same overall analysis procedure was applied to $Na_2Al_2O_4$ as shown in Figure 2S. All relevant features of both $\chi(k)$ and $|\tilde{\chi}(R)|$ are captured in the model. The first shell Al-O bond distances were determined to be 1.76 Å, which is in excellent agreement with the crystallographic value (1.76Å).[1] The fitted bond distances are shown in Table 2S for sodium aluminate.

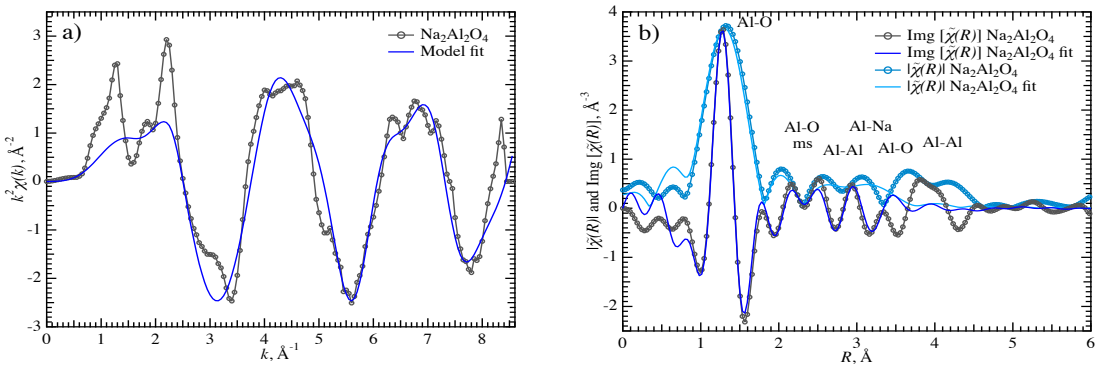

Figure 2S. EXAFS k^2-weighted $\chi(k)$ (a) and $|\tilde{\chi}(R)|$ and Img$[\tilde{\chi}(R)]$ (b) plots for $Na_2Al_2O_4$ with simple model fits starting from crystallographic data.

Table 2S. Scattering paths used for fitting to the α-alumina standard. The number (between atoms) indicates the scattering angle. An EXAFS fit is applied that uses a simple linear expansion model applied to the set of Al-O or Al-Al crystallographic distances. The Debye-Waller factors (DWF) for all paths used in the fitting are reported.

#	Path	Fitted distances (Å)	DWF	Scattering path	Crystallographic distances (Å)
1	Al – 180° – O	1.75±0.0012	0.0002	single	1.759
2	Al – 180° – Na	3.19±0 (set)	0.03	single	3.191
3	Al – 180° – Al	3.25±0.092	0.01	single	3.215
4	Al – 180° – Na	3.37±0 (set)	0.05	single	3.369
5	Al – 180° – O	3.49±0.0024	0.0002	single	3.517
6	Al – 180° – O	3.69±0.0025	0.0002	single	3.722
7	Al – 180° – O	3.88±0.0027	0.0002	single	3.905

EXAFS measurements of $Al^{3+}(H_2O)_6$

The measurements were performed in a liquid cell equipped 1.5 mm diameter window, 800 nm thick CVD diamond X-ray windows (Applied Diamond, Inc. Wilmington, DE). The cell design can be found elsewhere.[2] An aqueous 2 M $AlCl_3$ solution was used to perform EXAFS measurements in transmission mode wherein the sample chamber was held at 800 mbar He.

Zeolite Beta polymorphs

Zeolite Beta is composed of polymorphs A, B and C.[3] The composition of HBEA150 and HBEA25 is studied by analyzing the powder X-ray diffraction (PXRD) patterns (Figure 3S a) and comparing to the literature references.[4,5] The composition was determined as a 50/50 mixture of polymorphs A and B. We emphasize that both polymorphs are constructed from the same centrosymmetric tertiary building units that are arranged in layers.[6,7] As these are long-range structural features, the EXAFS analysis that probes only the local geometry about the target atom is not affected by the presence of the two polymorphs. To demonstrate this we have calculated the DFT EXAFS for the 9 T-sites of the all-siliceous zeolite Beta using the polymorph structures reported previously.[8] As shown in the $\mathrm{Img}[\tilde{\chi}(R)]$ plot in Figure 3S b) the two polymorphs are very similar from the EXAFS point of view. Note that the T-sites in polymorph A and polymorph B are compared based on their geometric position in the framework in such a way that the T-sites shown in identical colors in Figure 3S b) represent structurally equivalent conformations. It is likely, that after the published crystallographic structures are optimized using MD simulation, that minor observed differences would be even further reduced. 100% pure phases of A and B have not yet been synthesized, their structures have been extrapolated from the refinement of the 50/50 mixture in zeolite Beta so there remain uncertainties in the refined atomic positions. The equivalency of A and B is supported by previous NMR studies and pair distribution function (PDF) measurements that are reported below. The results demonstrate the strong similarity of the T-sites in the two different polymorphs.

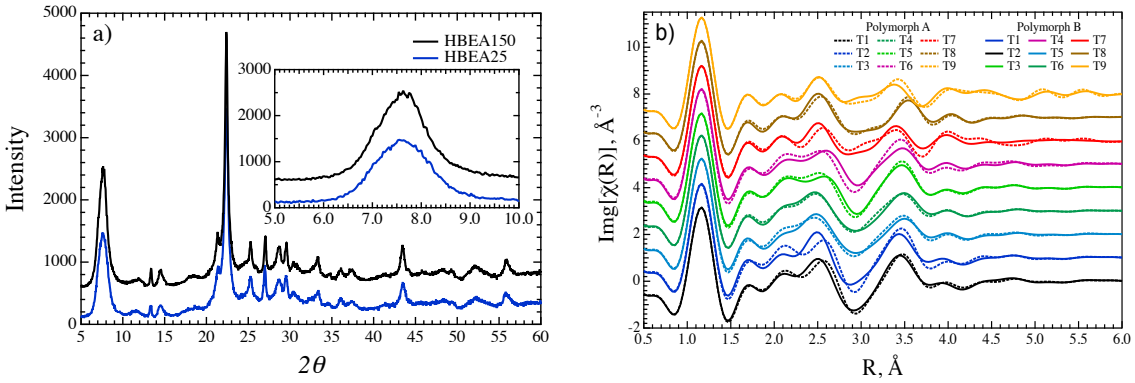

Figure 3S. The PXRD patterns for HBEA150 and HBEA25 (a) and the calculated DFT EXAFS $\mathrm{Img}[\tilde{\chi}(R)]$ plot (b) for the nine T-sites of the all-siliceous Polymorph A and Polymorph B of zeolite Beta, see legend for details. The standard σ^2 (disorder) parameter was set to 0.003 for all Al T-sites. The position of these peaks is mostly independent of the choice of the disorder parameter.

Previous reports on ^{29}Si NMR studies of zeolite Beta (50% polymorph mixture)[9,10] show the existence of 9 distinct NMR signals. In addition the T-site degeneracy (2 of 9 sites having degeneracy of ½ times the other 7)) is captured in these NMR spectra. This strongly suggests that the local T-site environment between "A" and "B" polymorphs are nearly identical in their local structure from an NMR spectroscopy point of view.

A recent pair distribution function (pdf) analysis from a corefinement of both X-ray and neutron scattering data[11] shows that the total pair distribution functions for polymorphs A and B are nearly identical up to about 4.5 Å, and thereafter, there are only small differences (see Figure 4S). We have previously collected pdf spectra for our HBEA150 at the Advanced Photon Source, Sector 11 ID C (Argonne National Laboratory). Figure 4S compares the HBEA150 to this earlier published data for zeolite Beta. We find that the HBEA150 is in quantitative agreement over the full R-range. These pdf's contain the local structural information from all tetrahedral sites in

polymorph A and B. Importantly, the region of these pdf's up to about 5 Å is the same region sampled by EXAFS.

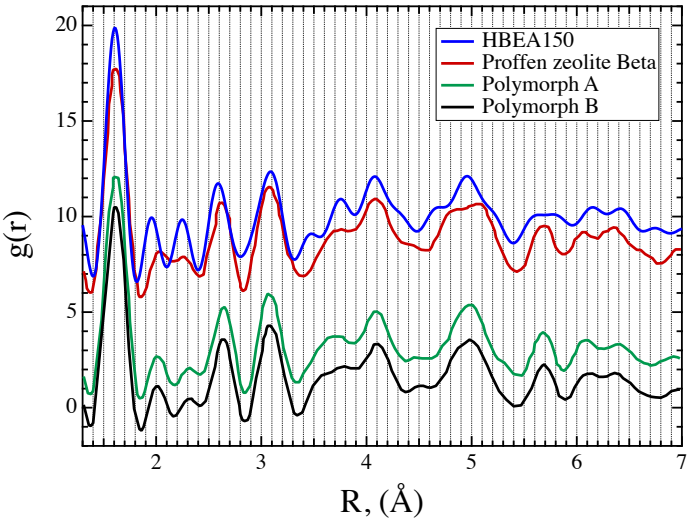

Figure 4S. The PDF spectrum of HBEA150 used in this study is compared to prior measurements by Proffen *et.al* for zeolite Beta and their refinement of the two polymorphs A and B.[11] The HBEA150 spectrum was taken at somewhat higher spatial resolution, however, it reproduces the earlier reported structure nearly quantitatively. Polymorphs A and B have nearly the same structure up to about 6 Å.

We have used XRD crystal parameters[7] for polymorph "A" and "B" to determine the atomic structure and atom distances about the specific T-sites in the framework. We provide here an example of statistics comparing T-site 3 to 7. We calculated the absolute average distance deviation (AAD) between the atoms surrounding T-sites 3 and 7. In EXAFS, the region of sensitivity for detecting T-site structure is the range from about 2.5 to 4.5 Å. For the 16 atoms that lie within this range, the AAD between T-site 3 and 7 is 0.17Å ± 0.16. In contrast the AAD between polymorph A and B for this same set of atoms is 0.029Å ±0.02. In other words, the differences in the polymorph distances are only about 15% of the distance differences between

the different T-sites. Hence the dominant structure differences occur as a result of the local T-site geometry and not as a result of differences between polymorphs. This result is elucidated in further detail by the plots in Figure 5S.

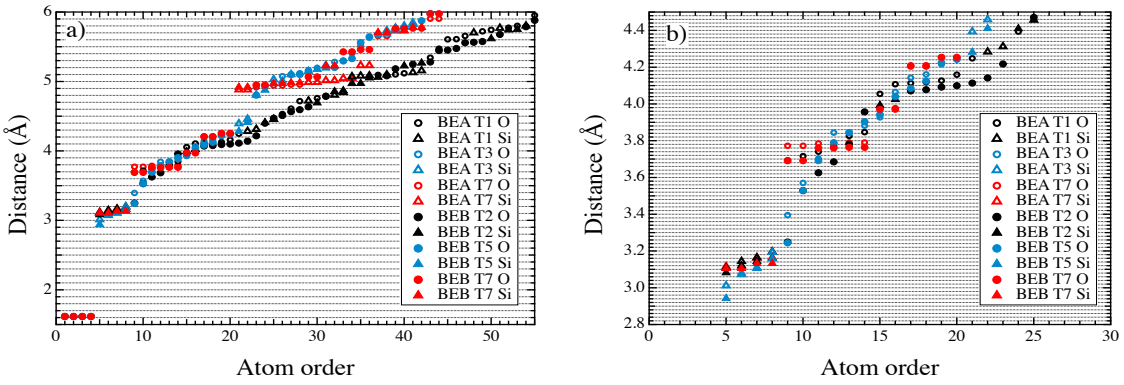

Figure 5S. The Si-O and Si-Si bond distances are shown in a) and enlarged for the 2.8 – 4.5 Å region in b). See legend for detail.

DFT optimized Al T-site model

A single BEA unit cell contains 64 T-sites. Substituting one Al for Si corresponds to Si/Al ratio of 63 corresponding by definition to HBEA126, which is a satisfactory model for the experimental sample HBEA150 (Si/Al = 75) that on average has less than one Al^{3+} per unit cell, each separated by multiple shells of Si T-sites. The model is also representative of the Al T-sites within HBEA25 (Si/Al = 12.5), provided Al-O-Si-O-Al pairs are excluded in either case. To exclude the possibility of Al-O-Si-O-Al pairs in the studied HBEA samples, ^{29}Si MAS NMR spectra were obtained (see Figure 6S). Note that at least three peaks are observed indicative of tetrahedral Si^{4+} in different environments.[9,10] The signals between –110 and –115 ppm are attributed to sites with Si^{4+} ions bonded to four oxygens which are in turn bonded to Si^{4+} ions, $Si(OSi)_4$ sites. The signal at –103 ppm corresponds to a $Si(OSi)_3OAl$ site in which one second

shell Si^{4+} ion is substituted by an Al^{3+} ion.[12,13] The signal for $Si(OSi)_2(OAl)_2$ site, which shows up at –98 ppm,[14] if present, is weak (0.6% and 2.4% total Si for HBEA150 and HBEA25, respectively). At this level, the frequency of Al-O-Si-O-Al pairs in the HBEA samples is too low to affect the Al distribution analysis.

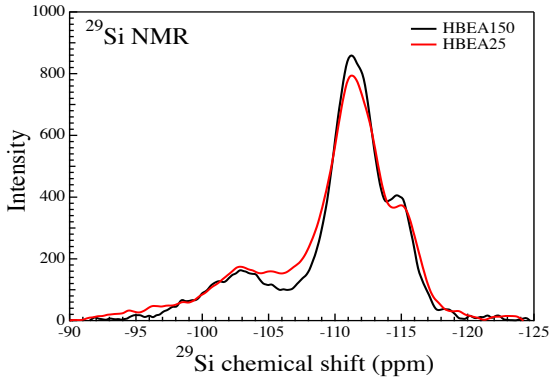

Figure 6S. ^{29}Si MAS NMR spectra of HBEA150 (black) and HBEA25 (red).

EXAFS calculation and Al T-site grouping based on DFT optimized Al T-site structures

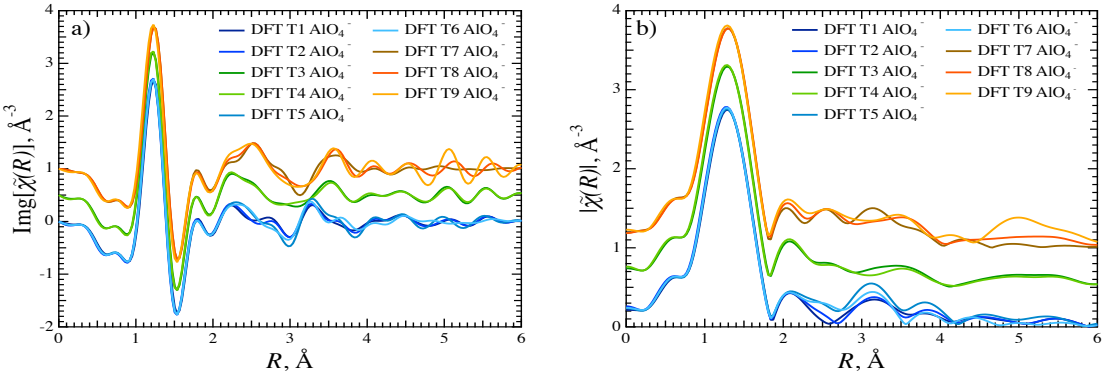

Figure 7S. DFT optimized AlO_4^- EXAFS $\mathrm{Img}[\tilde{\chi}(R)]$ plot (a) and $|\tilde{\chi}(R)|$ plot (b) plots for the nine T-sites of HBEA, see legend for details. The standard σ^2 (disorder) parameter was set to 0.003 for all Al T-sites. The T-sites are grouped as Set A (T1, T2, T5, T6), Set B (T3, T4) and Set C (T7, T8, T9). The groupings are based primarily upon the positions of the various

scattering peaks in the range from 2 to 5 Å. The position of these peaks is mostly independent of the choice of the disorder parameter.

Table 3S. Al-O bond distances from DFT optimization of 9 different Al T-sites for the dissociated Brønsted acidic proton ($[AlO_4]^-$) and the bound proton (AlO_4H) located on the bridging O atom.

T-site	$[AlO_4]^-$		AlO_4H		
	Al-O bonds, Å	*Avg(4)*	Al-O bonds, Å	*Avg(3)*	Al-O(H) bonds, Å
T1	1.72, 1.73, 1.74, 1.75	1.74	1.70, 1.70, 1.70	1.70	1.92
T2	1.72, 1.74, 1.71, 1.72	1.72	1.71, 1.70, 1.69	1.70	1.91
T3	1.74, 1.72, 1.74, 1.72	1.73	1.71, 1.71, 1.71	1.71	1.87
T4	1.73, 1.73, 1.71, 1.71	1.72	1.71, 1.70, 1.71	1.71	1.88
T5	1.71, 1.74, 1.71, 1.72	1.72	1.71, 1.70, 1.70	1.70	1.89
T6	1.72, 1.74, 1.72, 1.73	1.73	1.71, 1.71, 1.70	1.71	1.89
T7	1.75, 1.75, 1.73, 1.73	1.74	1.70, 1.70, 1.70	1.70	1.96
T8	1.75, 1.74, 1.75, 1.72	1.74	1.70, 1.70, 1.69	1.70	1.94
T9	1.74, 1.72, 1.74, 1.72	1.73	1.70, 1.69, 1.69	1.69	1.94

Linear combination fit for HBEA25

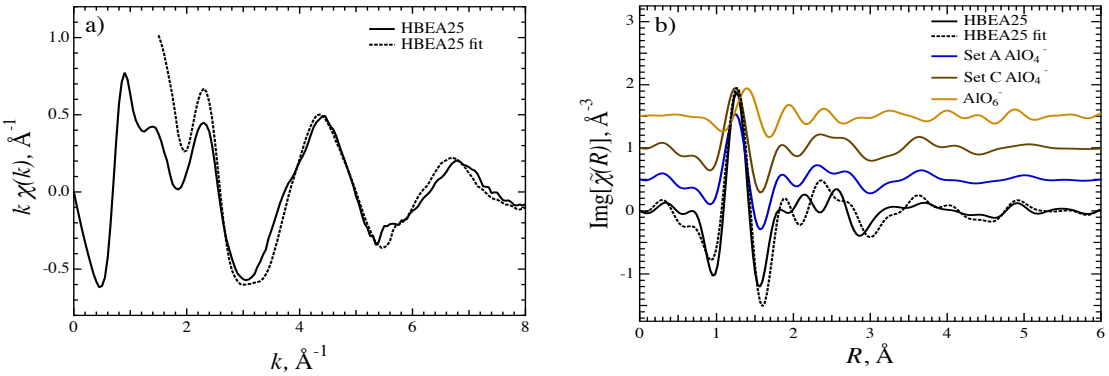

Figure 8S. EXAFS *k*-weighted $\chi(k)$ plot (a) for experimental HBEA25 and simulated using a linear combination of MD EXAFS for T1 and T3 sites for Sets A and B of Al T-sites and a measured aqueous $Al(H_2O)_6^{3+}$ EXAFS for octahedral Al; Img[$\tilde{\chi}(R)$] plot (b) for experimental and simulated HBEA25 (black) with the calculated component spectra for T-sites A (T1, blue) and B (T7, brown) and octahedral sites (gold).

^{27}Al DFT NMR calculations

In the past there were reports of a useful relationship between the ^{27}Al NMR chemical shift of the tetrahedral site to the mean Al-O-Si bond.[15,16]

$$\delta_{Al} = -0.50\theta_{avg} + 132 \qquad (1)$$

Where θ_{avg} is the average of four Al-O-Si angles at each T-site. Based upon the calculated Al-O-Si bond angles from the DFT optimized structures the chemical shifts according to Equation 1 are shown in Figure 9S. For comparison to this empirical model, the DFT-NMR calculations of ^{27}Al chemical shifts for Al in the framework were performed based on DFT-optimized crystal structures for all potential Al positions referenced to the isotropic chemical shift of aqueous Al^{3+}. The MAS NMR shielding calculation results as well as corresponding bond angles for each T-

site are shown in Table 4S. The DFT-NMR values are also plotted in Figure 4S. Note that the empirical bond angle model (Equation 1) mostly captures the trends of the chemical shift versus T-site. However the overall span of the shifts is significantly smaller and there is some reordering of the series for certain T-sites (especially T7). The chemical shifts calculated from DFT suggest that perhaps there is a significant error in the simple average bond angle relationship (Eq1). A similar level of error is also observed in fitting eq1 to the original set of 17 crystalline standards.[15] The chemical shift is thus suggested dependent upon more complete representation of the local structure than solely the average bond angle.

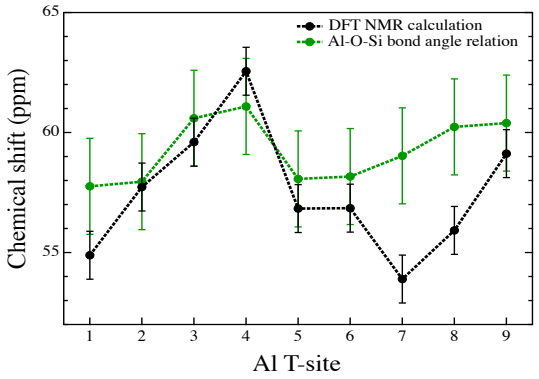

Figure 9S. The calculated ^{27}Al DFT NMR chemical shifts for tetrahedral Al^{3+}.

Table 4S. Calculated ^{27}Al NMR chemical shifts as well as Al-Si-O angles for 9 potential Al T-site positions.

T-site	Average Al-O-Si angle (°)	Predicted NMR chemical shifts (ppm) based on Al-O-Si angle relation	Calculated ^{27}Al MAS NMR isotropic chemical shift for Al-$(O\text{-}Si\text{-}OH)_4^-$	^{27}Al NMR chemical shift (ppm) for Al-O-Si-O-H	^{27}Al NMR chemical shift (ppm) for Al-O-Si-O-H offset by +1 ppm
1	148.5	57.76	517.5	53.9	54.9
2	148.1	57.95375	514.7	56.7	57.7
3	142.8	60.59625	512.8	58.6	59.6
4	141.8	61.0875	509.9	61.5	62.5
5	147.9	58.07	515.5	55.8	56.8
6	147.7	58.16625	515.6	55.8	56.8
7	145.9	59.02875	518.5	52.9	53.9
8	143.5	60.235	516.5	54.9	55.9
9	143.2	60.395	513.3	58.1	59.1

Table 5S. Average first shell Al – O bond distances, O – O atom distances and O – Al – O angles for the 9 T-sites of HBEA. The atoms are labeled in accordance with the crystallographic reference.

T1				
Distance O-O	**Distance (Å)**	**O-Al-O angles (°)**	**Distance Al-O**	**Distance (Å)**
O94-O93	2.84312	110.0633	Al-O94	1.72386
O94-O89	2.76244	106.0856	Al-O188	1.73961
O94-O188	2.86498	111.6239	Al-O93	1.74558
O93-O89	2.87633	111.5498	Al-O89	1.73314
O93-O188	2.79928	106.8721		
O89-O188	2.85707	110.7143		
T2				
Distance O-O	**Distance (Å)**	**O-Al-O angles (°)**	**Distance Al-O**	**Distance (Å)**
O93-O91	2.89337	113.3576	Al-O91	1.72325
O93-O189	2.81247	108.6766	Al-O95	1.71126
O93-O95	2.82369	109.8306	Al-O93	1.73934
O91-O189	2.76613	106.8013	Al-O189	1.72225
O91-O95	2.78067	108.1181		
O189-O95	2.81248	109.9941		
T3				
Distance O-O	**Distance (Å)**	**O-Al-O angles (°)**	**Distance Al-O**	**Distance (Å)**
O82-O148	2.83954	109.4104	Al-O82	1.73878
O82-O150	2.81146	108.8308	Al-O148	1.74024
O82-O149	2.85793	111.6097	Al-O150	1.71823
O148-O150	2.83913	110.3529	Al-O149	1.71642
O148-O149	2.81597	109.1035		
O150-O149	2.77017	107.5178		
T4				

Distance O-O	Distance (Å)	O-Al-O angles (°)	Distance Al-O	Distance (Å)
O85-O151	2.85812	112.1994	Al-O85	1.7296
O85-O152	2.80846	109.4533	Al-O151	1.71386
O85-O148	2.81638	108.7672	Al-O152	1.7104
O151-O152	2.7116	104.7228	Al-O148	1.73486
O151-O148	2.8617	112.152		
O152-O148	2.81266	109.4473		

T5

Distance O-O	Distance (Å)	O-Al-O angles (°)	Distance Al-O	Distance (Å)
O153-O149	2.82277	109.5793	Al-O153	1.74
O153-O154	2.80382	108.4398	Al-O149	1.71482
O153-O188	2.87486	111.2404	Al-O154	1.71605
O149-O188	2.80063	108.1617	Al-O188	1.74335
O149-O154	2.74319	106.1763		
O188-O154	2.88622	113.0861		

T6

Distance O-O	Distance (Å)	O-Al-O angles (°)	Distance Al-O	Distance (Å)
O151-O153	2.88293	112.5771	Al-O151	1.72084
O151-O155	2.7689	107.2465	Al-O153	1.74483
O151-O189	2.77844	107.2106	Al-O155	1.71822
O153-O189	2.83677	109.4068	Al-O189	1.73085
O153-O155	2.81118	108.535		
O155-O189	2.8576	111.8923		

T7

Distance O-O	Distance (Å)	O-Al-O angles (°)	Distance Al-O	Distance (Å)
O158-O83	2.87119	110.4222	Al-O158	1.74677
O158-O94	2.78954	106.8219	Al-O83	1.74931
O158-O169	2.87554	111.4085	Al-O94	1.7274
O83-O169	2.84003	109.2423	Al-O169	1.73391
O83-O94	2.8713	111.3514		
O94-O169	2.7923	107.5528		

T8

Distance O-O	Distance (Å)	O-Al-O angles (°)	Distance Al-O	Distance (Å)
O161-O84	2.88082	110.7239	Al-O161	1.75228
O161-O90	2.89878	112.2637	Al-O84	1.74914
O161-O170	2.81449	108.1705	Al-O90	1.73886
O84-O170	2.83927	109.7232	Al-O170	1.72281
O84-O90	2.82977	108.4434		
O90-O170	2.79069	107.446		

T9

Distance O-O	Distance (Å)	O-Al-O angles (°)	Distance Al-O	Distance (Å)
O167-O92	2.76762	107.2083	Al-O167	1.71858
O167-O87	2.84203	110.7091	Al-O92	1.71973
O167-O162	2.82798	109.8806	Al-O87	1.73597
O92-O162	2.84438	110.7782	Al-O162	1.73625
O92-O87	2.78762	107.5433		
O87-O162	2.85542	110.6435		

The ^{27}Al NMR calculations were performed using NWChem software package, the shielding property for the target Al T-site was determined for a DFT optimized Al-cluster. 6-311+G**

basis set was used for all atoms. The determined isotropic chemical shift values are compared to H-Mordenite (H-MOR), see Figure 10S and Table 6S. Note that the experimental value for H-MOR chemical shift is in very good agreement with previous reports.[15] The single signal in MAS NMR is explained by the nature of the samples. HMOR sample is a naturally occurring zeolite with Al T-sites distributed among T1 and T3 sites, which as seen in Figure 10S, cannot be distinguished in NMR. The calculated chemical shift, however, assumes all four T-sites are equally populated in the framework.

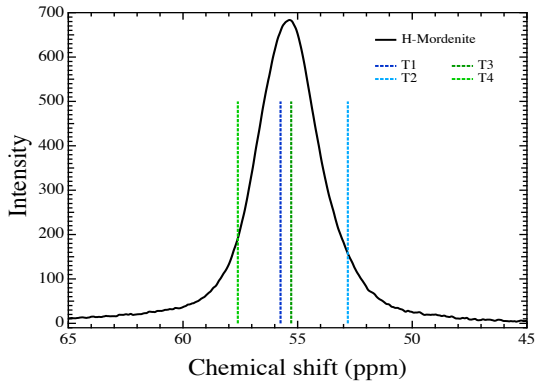

Figure 10S. Measured ^{27}Al MAS NMR spectrum (tetrahedral Al signal range) as well as chemical shift calculated for the 4 T-sites of H-Mordenite reference (calculated shifts in Table 6S were centered on the experimental peak by subtracting 1.0 ppm).

Table 6S. Calculated ^{27}Al NMR chemical shifts for the 4 Al T-site positions of H-Mordenite.

T-site	^{27}Al NMR isotropic chemical shift for Al-O-Si-O-H	^{27}Al NMR chemical shift (ppm) for Al-O-Si-O-H	Measured ^{27}Al MAS NMR chemical shift (ppm)
1	515.7	56.7	55.4
2	518.6	53.8	
3	516.1	56.2	
4	513.8	58.6	
		Average: 56.3 ± 2.0	

HBEA T-site thermodynamic stability calculation

The thermodynamic stability of the nine HBEA T-sites as well as the Boltzmann probabilities of Al to populate the sites as function of temperature are listed in Table 7S and graphically depicted in Figure 11S. The probabilities of the occupying the sites are equivalent to the equilibrium distribution since the internal entropies and zero point energies of the various Al T-sites are expected to be similar.

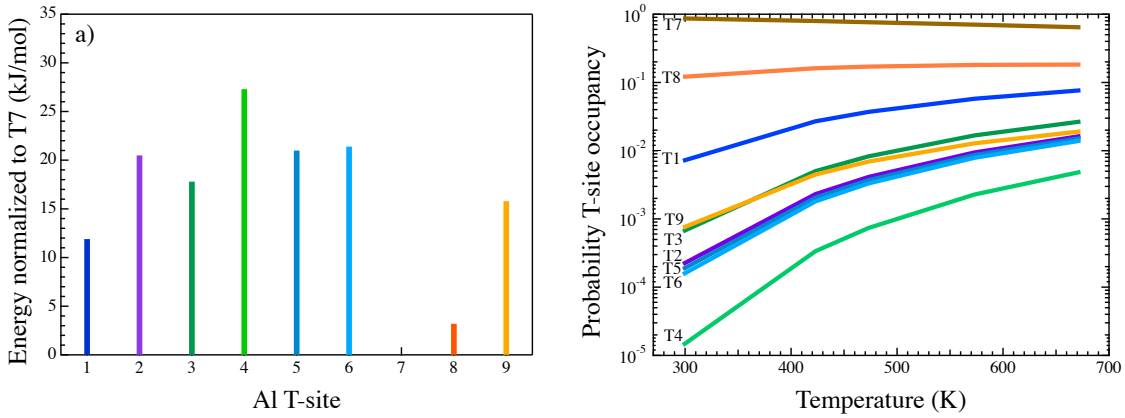

Figure 11S. Calculated relative thermodynamic stability of individual Al T-sites (a) and the T-site occupancy probability for different temperatures (b), see legend for detail.

Table 7S. The relative energies of the T-sites calculated by DFT and the probability of Al distribution among T-sites are shown. Note: the degeneracy is derived from the BEA crystal unit cell.

HBEA T-site	Energy (hartree)	Energy norm. to T7 (kJ/mol)	Degen.	Probability				
				298	423 K	473 K	573 K	673 K
T1	-2312.059399	11.9	8	7.13E-03	2.70E-02	3.71E-02	5.78E-02	7.67E-02
T2	-2312.056111	20.5	8	2.19E-04	2.32E-03	4.13E-03	9.45E-03	1.64E-02
T3	-2312.057151	17.8	8	6.59E-04	5.04E-03	8.27E-03	1.68E-02	2.67E-02
T4	-2312.053532	27.3	8	1.42E-05	3.38E-04	7.38E-04	2.28E-03	4.89E-03
T5	-2312.055950	21.0	8	1.84E-04	2.05E-03	3.71E-03	8.64E-03	1.52E-02
T6	-2312.055784	21.4	8	1.55E-04	1.81E-03	3.32E-03	7.89E-03	1.41E-02
T7	-2312.063932	0.0	8	8.70E-01	7.95E-01	7.65E-01	7.03E-01	6.44E-01
T8	-2312.062726	3.2	4	1.21E-01	1.62E-01	1.71E-01	1.81E-01	1.83E-01
T9	-2312.057925	15.8	4	7.47E-04	4.49E-03	6.93E-03	1.28E-02	1.92E-02

XANES experimental data

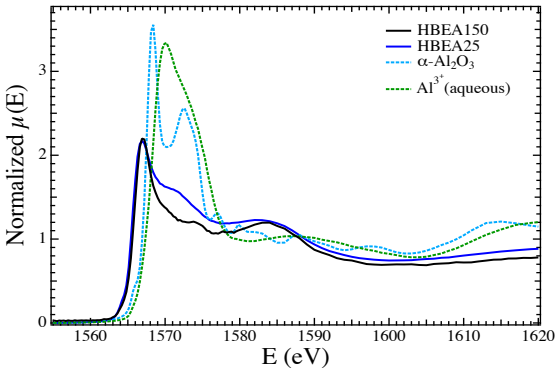

Figure 12S. XANES plot for the measured HBEA150 (black), HBEA25 (dark blue), α-alumina (dashed light blue) and Al^{3+} aqueous (dashed green).

XANES calculation data

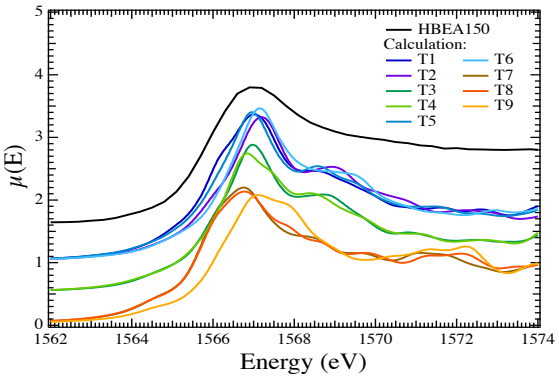

Figure 13S. XANES plots for HBEA150 and DFT optimized AlO_4^- XANES plots calculated for individual Al T-sites, see legend for details.

T-site atom coordinates used in Al-[O-Si-$(OH)_3]_4^-$ cluster ^{27}Al NMR calculations for HBEA

Table 8S. T-site atom coordinates used in Al-[O-Si-$(OH)_3]_4^-$ cluster ^{27}Al NMR calculations for HBEA.

Geometry T1

No.	Tag	Charge	X	Y	Z
1	Al	13.0000	1.05858558	-0.81493188	-0.50899565
2	O	8.0000	2.12653720	-2.00435970	0.13628623
3	O	8.0000	2.04689976	0.26538269	-1.43634920
4	O	8.0000	-0.17243771	-1.53258113	-1.50694476
5	O	8.0000	0.23809888	0.01914420	0.78654041
6	Si	14.0000	2.13039030	1.83256349	-1.53943127
7	Si	14.0000	2.13994048	-3.32255990	0.98026900
8	Si	14.0000	-1.70479845	-1.68469568	-1.83574586
9	Si	14.0000	-0.66737039	0.84808216	1.76966286
10	O	8.0000	1.58101391	2.64193215	-0.22272233
11	O	8.0000	0.76539332	-4.21846579	0.86810065
12	O	8.0000	-2.72301125	-0.85320698	-0.83026051
13	O	8.0000	1.31776682	2.38483446	-2.87240919
14	O	8.0000	2.42519717	-2.99301914	2.57268355
15	O	8.0000	-2.26875434	0.67175474	1.41912824
16	O	8.0000	-0.32908941	2.45536109	1.68388552
17	O	8.0000	3.71287910	2.21104088	-1.64664365
18	O	8.0000	3.36104747	-4.23295149	0.37310322
19	O	8.0000	-2.12565125	-3.26881068	-1.78215662
20	O	8.0000	-2.07265335	-1.21734126	-3.36816365
21	O	8.0000	-0.43593258	0.39976455	3.33654871
22	Si	14.0000	0.48486867	3.43454637	0.68704085
23	Si	14.0000	-3.33352887	-0.02768127	0.42248818
24	H	1.0000	0.47441501	2.44830745	-3.32664362
25	H	1.0000	-0.03776561	-4.64447293	1.17640839
26	H	1.0000	-1.99952639	-0.48113935	-3.97993092
27	H	1.0000	-0.44850827	-0.34128183	3.94670617
28	H	1.0000	2.16917762	-2.90430842	3.49365282
29	H	1.0000	-2.52499312	-3.86841965	-1.14765276
30	O	8.0000	-0.59230563	4.27564662	-0.24099345
31	O	8.0000	-4.26544935	-1.03766904	1.31354940
32	O	8.0000	-4.29929670	1.15370701	-0.15429696
33	O	8.0000	1.29837168	4.48934833	1.63931957
34	H	1.0000	-1.24531322	4.19721198	-0.94029961
35	H	1.0000	4.32372911	2.93448539	-1.80504287
36	H	1.0000	4.05238250	-4.86214053	0.59168277
37	H	1.0000	-4.35949294	-1.98630607	1.42687897
38	H	1.0000	-4.35881416	1.97761365	-0.64341404
39	H	1.0000	1.82458489	5.28299169	1.51754160

Geometry T2

No.	Tag	Charge	X	Y	Z
1	Al	13.0000	1.09283799	0.74285790	-0.48087385
2	O	8.0000	2.14655558	1.93187409	0.15511476
3	O	8.0000	-0.03803654	1.47242388	-1.55558562

4	O	8.0000	2.03059699	-0.35874682	-1.41716139
5	O	8.0000	0.21780628	-0.02279259	0.81272638
6	Si	14.0000	2.11449821	-1.92715943	-1.48408123
7	Si	14.0000	2.18138158	3.25153622	0.99118828
8	Si	14.0000	-1.55402241	1.70767661	-1.87399213
9	Si	14.0000	-0.74104046	-0.80102292	1.78402923
10	O	8.0000	1.49631979	-2.69296282	-0.14719525
11	O	8.0000	-2.56458490	0.89474849	-0.88336869
12	O	8.0000	0.84763580	4.19545228	0.83028970
13	O	8.0000	2.39054251	2.91290539	2.58546919
14	O	8.0000	1.34470604	-2.50981021	-2.83235179
15	O	8.0000	-2.32046571	-0.49367615	1.43849560
16	O	8.0000	-1.90506811	3.29679997	-1.75207236
17	O	8.0000	-0.47132399	-2.42541816	1.68898630
18	O	8.0000	3.70315513	-2.31112827	-1.56511605
19	O	8.0000	3.45657908	4.11019640	0.42203580
20	O	8.0000	-1.91130405	1.28312497	-3.42276565
21	O	8.0000	-0.53578788	-0.35186155	3.35309582
22	Si	14.0000	0.35112791	-3.43364223	0.71951870
23	Si	14.0000	-3.33373399	0.16601084	0.35696672
24	H	1.0000	0.50765015	-2.52735053	-3.30206422
25	H	1.0000	0.06348542	4.66374546	1.12594098
26	H	1.0000	-1.81848020	0.54516977	-4.02973011
27	H	1.0000	-0.51004726	0.38161790	3.97192158
28	H	1.0000	2.16329371	2.84720854	3.51586798
29	H	1.0000	-2.33664139	3.92991539	-1.17370451
30	O	8.0000	-0.70793316	-4.21005729	-0.28039627
31	O	8.0000	-4.31425718	1.22435454	1.14364423
32	O	8.0000	-4.32316118	-0.97906276	-0.26342347
33	O	8.0000	1.08843338	-4.52367978	1.70312504
34	H	1.0000	-1.36370010	-4.13033648	-0.97696954
35	H	1.0000	4.26079588	-3.07312442	-1.73831723
36	H	1.0000	4.16232829	4.70661532	0.68242500
37	H	1.0000	-4.35033986	2.16970964	1.30674472
38	H	1.0000	-4.39754918	-1.78514232	-0.77946821
39	H	1.0000	1.63347907	-5.30826525	1.60851617

Geometry T3

No.	Tag	Charge	X	Y	Z
1	Al	13.0000	0.73473130	-1.22275070	0.45320371
2	O	8.0000	1.83118156	-0.32221253	1.41905245
3	O	8.0000	1.49091566	-2.71708552	0.06894838
4	O	8.0000	-0.74875579	-1.54594231	1.30066003
5	O	8.0000	0.38814975	-0.32874936	-0.99913039
6	Si	14.0000	1.02916566	-3.93363384	-0.80480164
7	Si	14.0000	2.32996097	1.15321114	1.61292461
8	Si	14.0000	-2.00698273	-0.81772955	1.89756395
9	Si	14.0000	-0.30169974	0.75282930	-1.91994405
10	O	8.0000	-0.57802013	-4.25598465	-0.64095031
11	O	8.0000	1.99083807	2.17110509	0.37121446
12	O	8.0000	-2.70441168	0.32330969	0.94286859
13	O	8.0000	1.40990746	-3.71548605	-2.39749010
14	O	8.0000	-1.66952793	-0.05283071	3.31104587
15	O	8.0000	-1.91948705	0.86782289	-1.60936827
16	O	8.0000	1.70141735	1.81587560	2.98043785
17	O	8.0000	0.36616827	2.24984541	-1.81841680

18	O	8.0000	3.95450399	1.10014814	1.75502218
19	O	8.0000	1.86087805	-5.21350869	-0.23996441
20	O	8.0000	-3.15008636	-1.95404976	2.17003734
21	O	8.0000	-0.17228761	0.36687089	-3.50969357
22	Si	14.0000	-3.00875680	1.11634086	-0.44407492
23	Si	14.0000	1.27037618	3.08331870	-0.75987903
24	H	1.0000	-1.42736461	-4.50162098	-1.01495131
25	H	1.0000	1.20635493	-3.62096225	-3.33088799
26	H	1.0000	-0.43330214	-0.39762555	-4.02836168
27	H	1.0000	1.09832005	2.43070246	3.40453875
28	H	1.0000	-1.71935019	0.60258653	4.01072150
29	O	8.0000	-3.04567435	2.71420185	-0.07515697
30	O	8.0000	0.31035376	4.22195323	-0.07196236
31	O	8.0000	-4.45332390	0.61546612	-1.04447017
32	O	8.0000	2.44697722	3.83742867	-1.59854268
33	H	1.0000	2.37333436	-6.01308108	-0.38022319
34	H	1.0000	4.76758517	1.58601541	1.91132955
35	H	1.0000	-3.99082850	-2.28775626	2.49158458
36	H	1.0000	-0.07649268	4.54597148	0.74471505
37	H	1.0000	-3.20014472	3.47513088	0.48940120
38	H	1.0000	3.19320978	4.44090894	-1.57512177
39	H	1.0000	-5.39820917	0.47652847	-0.94706308

Geometry T4

No.	Tag	Charge	X	Y	Z
1	Al	13.0000	-0.73204601	-1.18140096	0.39384421
2	O	8.0000	-1.50633388	-2.64897824	-0.02112100
3	O	8.0000	-1.86209889	-0.35775134	1.38477052
4	O	8.0000	0.74245417	-1.52443982	1.23030093
5	O	8.0000	-0.36100212	-0.29549202	-1.05096713
6	Si	14.0000	-0.98844074	-3.90183049	-0.81091779
7	Si	14.0000	-2.38280906	1.10909274	1.57438943
8	Si	14.0000	1.95896331	-0.82249527	1.91665096
9	Si	14.0000	0.37262982	0.77844082	-1.94343021
10	O	8.0000	0.62145237	-4.20232606	-0.70837071
11	O	8.0000	-2.02412929	2.14660828	0.35071245
12	O	8.0000	2.67568406	0.32288892	0.98286089
13	O	8.0000	1.50029655	-0.05598695	3.29526647
14	O	8.0000	-1.35887798	-3.83514265	-2.40904311
15	O	8.0000	1.99087391	0.95302639	-1.59247052
16	O	8.0000	-1.80854615	1.75795011	2.96287794
17	O	8.0000	-0.36391953	2.24225642	-1.83342826
18	O	8.0000	-1.77290099	-5.16007181	-0.14403502
19	O	8.0000	-4.00189518	1.04311696	1.70544838
20	O	8.0000	3.05776100	-1.98967712	2.24478565
21	O	8.0000	0.25004569	0.34474180	-3.52210796
22	Si	14.0000	-1.27987957	3.05461674	-0.76838975
23	Si	14.0000	3.02905674	1.15156314	-0.36451389
24	H	1.0000	1.47542627	-4.47200995	-1.05420185
25	H	1.0000	0.48034473	-0.42623705	-4.04570511
26	H	1.0000	-1.16246734	-3.69889144	-3.33880570
27	H	1.0000	-1.22150133	2.37563187	3.40497253
28	H	1.0000	1.57467841	0.58760184	4.00368782
29	O	8.0000	-0.28978854	4.15915688	-0.06031942
30	O	8.0000	3.07631593	2.74366962	0.03428956
31	O	8.0000	-2.45013229	3.82966402	-1.60600501

32	O	8.0000	4.49487853	0.61919376	-0.87285001
33	H	1.0000	-2.23831387	-5.97493680	-0.34648476
34	H	1.0000	-4.81966310	1.51469064	1.88001616
35	H	1.0000	3.89361487	-2.34609908	2.55448177
36	H	1.0000	0.04676511	4.50039496	0.77147876
37	H	1.0000	3.20865744	3.50148295	0.60857579
38	H	1.0000	-3.22397717	4.39653138	-1.56824910
39	H	1.0000	5.44055773	0.48251651	-0.78005895

Geometry T5

No.	Tag	Charge	X	Y	Z
1	Al	13.0000	-1.05852229	-0.79884562	0.48606018
2	O	8.0000	-2.06989609	0.33510446	1.28100580
3	O	8.0000	-2.10203301	-1.99350880	-0.16882053
4	O	8.0000	-0.22479004	-0.01720581	-0.82608960
5	O	8.0000	0.06450284	-1.43903892	1.65581341
6	Si	14.0000	-2.14882755	1.88332869	1.49965360
7	Si	14.0000	-2.10596681	-3.31268695	-1.00468738
8	Si	14.0000	1.60791626	-1.66854915	1.90444367
9	Si	14.0000	0.70836130	0.81367248	-1.78230335
10	O	8.0000	-1.56172247	2.79255639	0.23071846
11	O	8.0000	2.57294002	-0.83410120	0.84912391
12	O	8.0000	-0.75284139	-4.22609352	-0.84555918
13	O	8.0000	-1.37703707	2.36453671	2.88756554
14	O	8.0000	-2.34237674	-2.99046872	-2.60167479
15	O	8.0000	2.29961220	0.62022655	-1.40834214
16	O	8.0000	2.03819646	-3.25106139	1.77688492
17	O	8.0000	0.37706876	2.42352532	-1.71284405
18	O	8.0000	-3.74839286	2.18471846	1.65057950
19	O	8.0000	-3.35177981	-4.19864658	-0.42988769
20	O	8.0000	2.00459094	-1.22382617	3.44994077
21	O	8.0000	0.51521752	0.37101248	-3.35036913
22	Si	14.0000	-0.42093039	3.42551316	-0.71978373
23	Si	14.0000	3.31860789	-0.07608390	-0.36822407
24	H	1.0000	-0.53033185	2.46464706	3.32877772
25	H	1.0000	0.03945465	-4.67672934	-1.14688016
26	H	1.0000	1.90255574	-0.48707246	4.05688624
27	H	1.0000	0.53719811	-0.37388205	-3.95555423
28	H	1.0000	-2.06450093	-2.91582703	-3.51754249
29	H	1.0000	2.46759737	-3.87623143	1.18834666
30	O	8.0000	0.64970347	4.26714771	0.19232528
31	O	8.0000	4.26481961	-1.11500078	-1.21741339
32	O	8.0000	4.29274512	1.08985630	0.23566491
33	O	8.0000	-1.15310762	4.49413405	-1.70184675
34	H	1.0000	1.27664968	4.19576422	0.91581878
35	H	1.0000	-4.04495501	-4.82019978	-0.66393846
36	H	1.0000	-4.32669238	2.94297259	1.76112514
37	H	1.0000	4.37241080	-2.06224288	-1.33035822
38	H	1.0000	4.34799485	1.90686498	0.73670811
39	H	1.0000	-1.67522119	5.29291452	-1.59721801

Geometry T6

No.	Tag	Charge	X	Y	Z
1	Al	13.0000	-1.01737447	0.85229364	0.44039399
2	O	8.0000	-2.01758135	2.09447437	-0.19920088
3	O	8.0000	-2.03634172	-0.22328105	1.31569389

4	O	8.0000	0.14997546	1.47430475	1.55673887
5	O	8.0000	-0.19368321	0.06720487	-0.88246089
6	Si	14.0000	-2.24505444	-1.76633290	1.46710961
7	Si	14.0000	-1.96705208	3.44341249	-0.98818495
8	Si	14.0000	1.67833665	1.59983538	1.87710087
9	Si	14.0000	0.70283687	-0.87378584	-1.77843277
10	O	8.0000	-1.67874600	-2.64337901	0.20474742
11	O	8.0000	2.60487860	0.69894047	0.85841348
12	O	8.0000	-0.54877776	4.25797887	-0.86286673
13	O	8.0000	-1.60408533	-2.34684702	2.87063100
14	O	8.0000	-2.30758312	3.26119263	-2.59001880
15	O	8.0000	0.25704424	-2.45452741	-1.70160198
16	O	8.0000	2.30362245	-0.83868623	-1.37448746
17	O	8.0000	2.16717929	3.15935344	1.79155692
18	O	8.0000	-3.84597555	-2.01300984	1.56739073
19	O	8.0000	-3.12787600	4.38887649	-0.33897468
20	O	8.0000	1.96371243	1.13284588	3.42779193
21	O	8.0000	0.61417087	-0.43975692	-3.36003733
22	Si	14.0000	-0.56926197	-3.42987561	-0.70216287
23	Si	14.0000	3.33099741	-0.12505202	-0.33684038
24	H	1.0000	-0.75837651	-2.44726553	3.31368033
25	H	1.0000	0.27239811	4.65629512	-1.16054836
26	H	1.0000	1.82338706	0.39835472	4.02981479
27	H	1.0000	0.59613888	0.33004343	-3.93334551
28	H	1.0000	-1.98567393	3.09803024	-3.47959876
29	H	1.0000	2.63465313	3.76189560	1.20845217
30	O	8.0000	0.47371480	-4.29008975	0.24767919
31	O	8.0000	4.30660165	0.89209011	-1.18612607
32	O	8.0000	4.27842783	-1.29446016	0.32781478
33	O	8.0000	-1.37923298	-4.48158870	-1.65504938
34	H	1.0000	-3.77195393	5.04824594	-0.60729452
35	H	1.0000	1.09058229	-4.24100466	0.98161730
36	H	1.0000	-4.46379655	-2.73031332	1.72667952
37	H	1.0000	4.46231054	1.83476331	-1.27951764
38	H	1.0000	4.29263590	-2.11748507	0.82180681
39	H	1.0000	-1.96975235	-5.23389271	-1.57182954

Geometry T7

No.	Tag	Charge	X	Y	Z
1	Al	13.0000	0.61147080	-0.05407367	-0.01356282
2	O	8.0000	1.63614797	1.25839372	0.44624328
3	O	8.0000	1.63162159	-1.36044561	-0.52260549
4	O	8.0000	-0.32098787	-0.48626988	1.39895074
5	O	8.0000	-0.44837834	0.39646148	-1.33027977
6	Si	14.0000	1.59234536	-2.93090104	-0.48669860
7	Si	14.0000	1.74065205	2.82014571	0.39059172
8	Si	14.0000	-1.70688758	-0.52211434	2.15235295
9	Si	14.0000	-1.83943065	0.62445488	-2.03692016
10	O	8.0000	1.43502202	-3.53942101	1.03723306
11	O	8.0000	0.35045098	-3.54187824	-1.40730567
12	O	8.0000	1.59330483	3.43973705	-1.12299721
13	O	8.0000	-2.90181432	-1.05521095	1.16798926
14	O	8.0000	0.59949221	3.55012150	1.32238304
15	O	8.0000	-2.89533305	1.31794882	-0.99511162
16	O	8.0000	-2.16748895	0.95059424	2.68479054
17	O	8.0000	-2.56826514	-0.74359829	-2.57923934

18	O	8.0000	3.03366190	-3.46820221	-1.04988696
19	O	8.0000	3.22753452	3.26620855	0.89571013
20	O	8.0000	-1.65592968	-1.52159254	3.46724562
21	O	8.0000	-1.72211902	1.61917292	-3.35757011
22	H	1.0000	-2.89261152	-1.63937083	-2.46095587
23	H	1.0000	1.02318257	-4.11177419	1.68869304
24	H	1.0000	-2.53016245	1.83817657	2.63719282
25	H	1.0000	1.17637489	4.05068573	-1.73497037
26	H	1.0000	-0.36762602	-4.04575636	-1.79727008
27	H	1.0000	-0.02972965	4.08781685	1.80876106
28	H	1.0000	-3.62088283	-1.59493428	0.83147892
29	H	1.0000	-3.57003868	1.86677141	-0.58870532
30	H	1.0000	-1.45692932	-2.43391208	3.69011761
31	H	1.0000	-1.52537316	2.52948891	-3.59041311
32	H	1.0000	3.37112855	-4.04697495	-1.73744669
33	H	1.0000	3.67877643	3.79887655	1.55468322

Geometry T8

No.	Tag	Charge	X	Y	Z
1	Al	13.0000	0.61423912	-0.00504792	0.04434308
2	O	8.0000	1.52639152	1.34542520	-0.51439900
3	O	8.0000	1.74485571	-1.24348299	0.50434213
4	O	8.0000	-0.38356351	-0.62105936	-1.25348295
5	O	8.0000	-0.37560601	0.52336935	1.39030705
6	Si	14.0000	1.69600997	-2.81126783	0.42218036
7	Si	14.0000	1.58642605	2.90626559	-0.43756600
8	Si	14.0000	-1.78436368	0.52721073	2.09424633
9	Si	14.0000	-1.71394817	-0.61980664	-2.09675159
10	O	8.0000	1.35282819	-3.40179853	-1.08646467
11	O	8.0000	0.54696403	-3.40231380	1.41667476
12	O	8.0000	1.43486664	3.50579582	1.09308549
13	O	8.0000	-2.92620262	1.09402029	1.05246271
14	O	8.0000	0.42979679	3.57974662	-1.38665573
15	O	8.0000	-2.98169801	-1.18321519	-1.22226579
16	O	8.0000	-2.21088877	0.84247287	-2.66765728
17	O	8.0000	-2.34473501	-0.91559811	2.62836658
18	O	8.0000	3.06043398	3.35585150	-0.98421488
19	O	8.0000	3.15771406	-3.37101561	0.88418421
20	O	8.0000	-1.70716809	1.48300192	3.43405079
21	O	8.0000	-1.54928755	-1.57717710	-3.42347659
22	H	1.0000	-2.64946511	-1.82172028	2.54071853
23	H	1.0000	-2.62489542	1.70418534	-2.58019229
24	H	1.0000	1.00713344	4.06434874	1.74627991
25	H	1.0000	-0.11238983	-3.98956951	1.79348135
26	H	1.0000	-3.56698846	-1.79694470	-0.77240897
27	H	1.0000	-3.61506340	1.64156848	0.66871566
28	H	1.0000	-0.26195866	4.10230164	-1.79897921
29	H	1.0000	1.26345623	-4.17062118	-1.65437698
30	H	1.0000	-1.52924274	2.39544927	3.67359703
31	H	1.0000	3.43311681	3.96687298	-1.62402756
32	H	1.0000	3.60404362	-3.96507853	1.49203219
33	H	1.0000	-1.92952217	-2.13177652	-4.10863432

Geometry T9

No.	Tag	Charge	X	Y	Z
1	Al	13.0000	-0.60711130	0.01057242	-0.01288291

2 O	8.0000	-1.57795036	1.32677196	-0.54061974
3 O	8.0000	-1.67512464	-1.23114185	0.51161698
4 O	8.0000	0.33056777	-0.62658603	-1.32758131
5 O	8.0000	0.42671159	0.52252973	1.28460942
6 Si	14.0000	-1.66960516	-2.79685823	0.44069110
7 Si	14.0000	-1.59140578	2.88334386	-0.40959226
8 Si	14.0000	1.69625210	-0.61136046	-2.10299707
9 Si	14.0000	1.78568368	0.53181141	2.06558327
10 O	8.0000	-1.35778595	-3.38649985	-1.07546275
11 O	8.0000	-1.27594788	3.40145333	1.12878408
12 O	8.0000	-0.51949333	-3.43099094	1.41625750
13 O	8.0000	-0.42409476	3.53264102	-1.35495084
14 O	8.0000	2.19514837	0.85512604	-2.64656198
15 O	8.0000	3.05021841	1.02534278	1.10696995
16 O	8.0000	2.98795288	-1.17480427	-1.23578709
17 O	8.0000	2.27800572	-0.90840116	2.68868655
18 O	8.0000	-3.07419611	3.39894617	-0.88158481
19 O	8.0000	1.47275263	-1.59284910	-3.39587039
20 O	8.0000	-3.12569952	-3.31521957	0.96365047
21 O	8.0000	1.58668080	1.54799587	3.33991272
22 H	1.0000	2.60626161	-1.80080716	2.55655178
23 H	1.0000	2.61890506	1.71335107	-2.57253440
24 H	1.0000	0.27568233	4.06478933	-1.74060638
25 H	1.0000	0.13468068	-4.03441925	1.77616117
26 H	1.0000	3.58401713	-1.77587340	-0.78299210
27 H	1.0000	-1.27174936	-4.14906560	-1.65225664
28 H	1.0000	-1.13545906	4.17989049	1.67274958
29 H	1.0000	3.68724600	1.61244107	0.69331375
30 H	1.0000	-3.45982992	4.05258320	-1.46950079
31 H	1.0000	-3.56135386	-3.95803415	1.52809242
32 H	1.0000	1.89922610	-2.10803150	-4.08457023
33 H	1.0000	2.02725721	2.03669632	4.03895800

T-site atom coordinates used in Al-[O-Si-$(OH)_3$]$_4^-$ cluster ^{27}Al NMR calculations for HMOR

Table 9S. T-site atom coordinates used in Al-(O-Si-$OH)_4^-$ cluster ^{27}Al NMR calculations for HMOR.

Geometry T1

No.	Tag	Charge	X	Y	Z
1	Al	13.0000	0.02632965	0.14821512	0.03866058
2	O	8.0000	1.12902311	-0.70119446	-0.98203262
3	O	8.0000	0.87099861	1.20925218	1.11075422
4	O	8.0000	-0.89980882	-0.87002157	1.09182628
5	O	8.0000	-0.97920203	0.96470135	-1.11733734
6	Si	14.0000	-2.41196568	1.61664028	-1.16085257
7	Si	14.0000	1.80780731	2.46638923	1.10956558
8	Si	14.0000	-1.52073995	-2.28427057	1.35791615
9	Si	14.0000	2.18086605	-1.83416578	-1.23978749
10	O	8.0000	-2.80851839	2.44154895	0.20631021
11	O	8.0000	1.19308681	3.73054880	0.26793151
12	O	8.0000	2.78252600	-2.46447357	0.15548434
13	O	8.0000	3.26282314	2.20979806	0.41666145
14	O	8.0000	-2.38003945	-2.88895433	0.10265189
15	O	8.0000	-0.35203361	-3.37826282	1.71069690
16	O	8.0000	-3.66323688	0.55506153	-1.32112745
17	O	8.0000	1.60840123	-3.08129261	-2.13057637
18	O	8.0000	3.41032414	-1.23282600	-2.12951132
19	O	8.0000	-2.39735714	2.64028108	-2.43717810
20	O	8.0000	2.02413505	2.90325041	2.66610577
21	O	8.0000	-2.59510328	-2.18416914	2.58281280
22	H	1.0000	-2.42845631	-3.05523686	-0.84159698
23	H	1.0000	-2.75726360	3.25657458	0.71099444
24	H	1.0000	0.55107958	4.44249403	0.31853497
25	H	1.0000	-3.95507480	-0.18932209	-1.85246883
26	H	1.0000	4.11875167	1.77970535	0.35336366
27	H	1.0000	3.11041992	-2.83783537	0.97687739
28	H	1.0000	0.90692993	-3.72939628	-2.22804260
29	H	1.0000	0.26430604	-4.00569925	2.09546820
30	H	1.0000	4.26759655	-0.80407530	-2.07606184
31	H	1.0000	-2.81226830	-2.36674786	3.49993023
32	H	1.0000	-2.60133947	3.35561555	-3.04404530
33	H	1.0000	2.51260075	3.21836064	3.43011284

Geometry T2

No.	Tag	Charge	X	Y	Z
1	Al	13.0000	-0.10489980	-0.00039656	0.54938472
2	O	8.0000	-0.17392130	1.35968379	1.59137875
3	O	8.0000	-1.20368571	-1.13661294	1.22223098
4	O	8.0000	1.50924401	-0.60791056	0.51010096
5	O	8.0000	-0.60417467	0.42887966	-1.05731443
6	Si	14.0000	-0.17582363	2.92205488	1.55796319
7	Si	14.0000	-1.73998230	-2.59149636	1.03663112
8	Si	14.0000	2.82214422	-1.14599942	-0.15169607
9	Si	14.0000	-0.97792303	0.78527582	-2.54346981

10	O	8.0000	-1.36410865	3.52661163	0.60791817
11	O	8.0000	-0.55608324	-3.70884383	1.15165244
12	O	8.0000	-2.51543040	-2.77043629	-0.39448735
13	O	8.0000	1.20352741	3.60790908	1.03246411
14	O	8.0000	2.59825807	-2.23350025	-1.36485067
15	O	8.0000	3.72740082	0.03185336	-0.85246577
16	O	8.0000	-0.87985976	-0.49884370	-3.54893705
17	O	8.0000	3.66919858	-1.84496707	1.06970423
18	O	8.0000	-2.52780890	1.32306947	-2.66495753
19	O	8.0000	0.01504166	1.89161161	-3.24337809
20	O	8.0000	-0.32012029	3.45471573	3.08348938
21	O	8.0000	-2.75712575	-2.91010256	2.26082050
22	H	1.0000	1.80462718	3.66100518	0.28583176
23	H	1.0000	2.01261282	-2.91278693	-1.70717982
24	H	1.0000	-0.88329921	-1.45883554	-3.55089773
25	H	1.0000	0.06004447	-4.37255459	0.83310155
26	H	1.0000	-3.31086234	1.67218459	-2.23304789
27	H	1.0000	4.13871915	0.88632537	-0.70315129
28	H	1.0000	-2.97124911	-2.85636464	-1.23499054
29	H	1.0000	-2.13705771	3.91755896	0.19402212
30	H	1.0000	0.39507544	2.76548752	-3.12712304
31	H	1.0000	-0.90070638	3.84430054	3.74132177
32	H	1.0000	4.34733095	-2.47110019	1.33370009
33	H	1.0000	-3.60435560	-3.24321859	2.56550934

Geometry T3

No.	Tag	Charge	X	Y	Z
1	Al	13.0000	0.18703461	0.63774958	-0.45045914
2	O	8.0000	0.75811222	-0.36042401	-1.72143574
3	O	8.0000	-1.10603026	1.56090470	-1.12657779
4	O	8.0000	1.57542882	1.56621720	-0.00985486
5	O	8.0000	-0.42033520	-0.23610272	0.92240146
6	Si	14.0000	0.90704146	-1.87557939	-2.08136790
7	Si	14.0000	-2.02658479	2.81692498	-0.92240598
8	Si	14.0000	2.08329410	2.82445976	0.78020538
9	Si	14.0000	-0.86211392	-1.27995165	2.01097332
10	O	8.0000	0.45085748	-3.00630667	-0.97283172
11	O	8.0000	-2.30904752	3.28134896	0.62624521
12	O	8.0000	1.18755598	3.28657426	2.07510963
13	O	8.0000	-1.39245769	4.18084703	-1.59894774
14	O	8.0000	2.10903109	4.18599158	-0.14959607
15	O	8.0000	0.01562988	-2.13884509	-3.42611430
16	O	8.0000	2.49009117	-2.13002935	-2.39344022
17	O	8.0000	-0.67747055	-2.83123876	1.55472114
18	O	8.0000	-3.43288383	2.41081591	-1.65245948
19	O	8.0000	3.59532249	2.42179451	1.25719485
20	O	8.0000	0.01454890	-1.13249867	3.39126400
21	O	8.0000	-2.45762011	-1.14068121	2.37082734
22	Si	14.0000	-0.14947771	-3.74388107	0.33938165
23	H	1.0000	-2.47388978	3.14076863	1.56148005
24	H	1.0000	0.64493565	3.14335580	2.85398809
25	H	1.0000	2.26938230	4.42468523	-1.06551792
26	H	1.0000	-0.86064821	4.42150428	-2.36109127
27	H	1.0000	0.32918637	-0.47091800	4.01167861
28	H	1.0000	-3.09514807	-0.46493914	2.61275864
29	O	8.0000	-1.43758265	-4.66049060	-0.07711704

30	O	8.0000	1.04172845	-4.67722417	0.95152192
31	H	1.0000	-0.23524142	-2.63110444	-4.21119030
32	H	1.0000	3.21229510	-2.62662400	-2.78512280
33	H	1.0000	-4.31940101	2.66430891	-1.91972078
34	H	1.0000	4.41023020	2.67837907	1.69501878
35	H	1.0000	1.70302613	-5.34065894	0.74142743
36	H	1.0000	-1.72510815	-5.34541093	-0.68523975

Geometry T4

No.	Tag	Charge	X	Y	Z
1	Al	13.0000	-0.09076027	-0.70517222	0.60542145
2	O	8.0000	-0.29017509	0.41981942	1.86858335
3	O	8.0000	1.33230463	-1.60408553	0.98851154
4	O	8.0000	-1.55407037	-1.62275501	0.62121527
5	O	8.0000	0.13745081	0.07201531	-0.93449973
6	Si	14.0000	2.18586642	-2.75540581	0.35860725
7	Si	14.0000	-2.21545993	-2.78364701	-0.19590808
8	Si	14.0000	-0.28613888	1.94522523	2.17922111
9	Si	14.0000	0.28240945	1.03948373	-2.15979375
10	O	8.0000	2.05978069	-2.92894893	-1.27015298
11	O	8.0000	-1.68258709	-2.95378222	-1.74106820
12	O	8.0000	-0.18155837	2.98937899	0.92150458
13	O	8.0000	-1.97104538	-4.20984970	0.56601497
14	O	8.0000	1.78553899	-4.18707578	1.03959996
15	O	8.0000	0.95469803	2.28183326	3.18543142
16	O	8.0000	-1.71555325	2.27762124	2.87732743
17	O	8.0000	0.22498568	2.62460864	-1.76808344
18	O	8.0000	3.73829109	-2.40398784	0.68105721
19	O	8.0000	-3.80783380	-2.45311985	-0.26445085
20	O	8.0000	-0.92868009	0.82177607	-3.24946434
21	O	8.0000	1.72950511	0.84498096	-2.91044492
22	Si	14.0000	0.04950780	3.64523040	-0.53039543
23	H	1.0000	1.97848663	-3.01775810	-2.22257316
24	H	1.0000	-1.36400287	-3.04221148	-2.64233640
25	H	1.0000	-1.37104849	0.23683743	-3.86894556
26	H	1.0000	2.30317919	0.26064557	-3.41149402
27	H	1.0000	-1.77456799	-5.14022065	0.69794876
28	H	1.0000	1.57738790	-5.12059291	1.12217651
29	O	8.0000	1.39337767	4.57330092	-0.49766564
30	O	8.0000	-1.25550818	4.57695013	-0.82946762
31	H	1.0000	-2.31017425	2.91406624	3.28101497
32	H	1.0000	1.40701521	2.92877520	3.73176034
33	H	1.0000	4.67550365	-2.61097259	0.70080417
34	H	1.0000	-4.71223532	-2.69038509	-0.48208149
35	H	1.0000	-1.81633196	5.34002770	-0.67202146
36	H	1.0000	1.26160928	5.34658323	-1.05108371

References

[1] J. A. Kaduk, S. Pei, *J. Solid State Chem*. **1995***, 115*, 126–139.

[2] J. L. Fulton, M. Balasubramanian, V.-T. Pham, G. S. Deverman, *J. Synchrotron Rad*. **2012**, *19*, 949-953

[3] A. Corma, M. Moliner, A. Cantín, M. J. Díaz-Cabañas, J. L. Jordá, D. Zhang, J. Sun, K. Jansson, S. Hovmöller, X. Zou, *Chem. Mater*. **2008,** *20,* 3218–3223.

[4] J. M. Newsam, M. M. J. Treacy, W. T. Koetsier, C. B. de Gruyter, *Proc. R. Soc. Lond. A* **1988**, *420*, 375-405.

[5] T. Willhammar, X. Zhou, *Z. Kristallogr*. **2013**, *228*, 11–27.

[6] P. A. Wright, W. Zhou, J. Perez-Pariente, M. Arranz, *J. Am. Chem. Soc*. **2005**, *127*, 494-495.

[7] M. M. J. Treacy, J. M. Newsam, *Nature* **1988**, *332*, 249-251.

[8] A. Andersen, N. Govind, L. Subramanian, *Mol. Simul*. **2008**, *34*, 1025–1039.

[9] C A. Fyfe, H. Strobl, G. T. Kokotailo, C. T. Pasztor,G. E. Barlow, S. Bradley, *Zeolites* **1988**, *8*, 132-136.

[10] M. A. Camblor, A. Corma, S. Valencia, *Chem. Comm*. **1996**, 2365-2366.

[11] M. M. Martinez-Iñesta, I. Peral, T. Proffen, R. F. Lobo, Micropor. *Mesopor. Mater*. **2005**, *77*, 55-66.

[12] L. Čapek, J. Dědeček, B. Wichterlová, *J. Catal*. **2004**, *227*, 352–366.

[13] J. Pérez-Pariente, J. Sanz, J. Fornés, A. Corma, *J. Catal*. **1990**, *124,* 217.

[14] A. Fyfe, Y. Feng, H. Grondey, G.T. Kokotailo, H. Gies, *Chem. Rev*. **1991**, *91,* 1525.

[15] E. Lippmaa, A. Samoson, M. Mägi, *J. Am. Chem. Soc*. **1986,** *108,* 1730.

[16] J.A. van Bokhoven, A.M.J. van der Berden, D.C. Koningsbeger, *J. Am. Chem. Soc*. **2003**, *125*, 7435-7442.