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Journal Name:	International Research Journal of Pure and Applied Chemistry
Manuscript Number:	2014_IRJPAC_10212
Title of the Manuscript:	Cation-Type Dependences of ^1H and ^{29}Si MAS NMR Chemical Shifts and Desorption Temperatures of Water Molecules in Faujasite-Type Zeolites
Type of the Article	Original Research Article

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PART 1: Review Comments

	Reviewer's comment	Author's comment (if agreed with reviewer, correct the manuscript and highlight that part in the manuscript. It is mandatory that authors should write his/her feedback here)
Compulsory REVISION comments	Faujasite-type zeolites (FAU) with five different ions with varying ratios of Si/Al were synthesized along with range of experiments were performed (XRD, ^1H and ^{29}Si solid-state NMR, TG and DTA). The syntheses of these compounds are straightforward and follow standard procedures with commercially available materials. As much as I could understand none of the results support the conclusion "water molecules form weak hydrogen bonds in Na- and K-type FAU with high Si/Al ratios". The results from the multiple experiments do not correlate with any particular trend, at least from the manner in which the data is presented. Major issues: Water chemical shift is extremely sensitive to micro-environments. The best quantification the authors could come up from the ^1H experiments, a pivot for the analysis is that 'CS was increased'. NMR chemical shifts are always discussed with down or up –field shift related to a good control experiment. With the resolution allowed by the SSNMR such observations are difficult, but not impossible. The spectra provided do not warranty such a conclusion. The authors	Thank you very much for many advises and comments. ^1H MAS NMR spectra gave information about hydrogen bonding, we think. We showed inner reference signals on the ^1H MAS NMR spectra and CS values in Table 2 in the 2nd revision. We deleted the figure in the 2nd revision.



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	undermine the intelligence of the readers by providing the same figure (# 7/8), where one is a transpose of the other. Careful investigation of these figures suggests that there may be additional features that could be important, but ignored. Statements such as “All spectra of ^1H and ^{29}Si nucleus were obtained from free-induction-decay signals which were recorded after a $\pi/2$ pulse” (line 120-121) and “^{29}Si MAS NMR was designed with a ^1H decoupling pulse (line 122) are wrong. Experimental information provided for NMR is insufficient. ^{29}Si NMR, XRD, TG and DTA data inclusive at large. There may be additional features that might point of trends within a particular study that are completely ignored. Line 152: XRD lines also suggest that lattice constants of the FAUs are independent on cation: No result supports this conclusion. Figure 1 misses data for Si/Al ratios of 1.2 and 2.4 for the Li, K, Rb and Cs. No explanation is provided. Line 158: What is a Gauss function? I suppose it is a Gaussian function. Why not Lorentians?	I cannot understand why you suggest these sentences are wrong. ^1H and ^{29}Si NMR spectra displayed in this draft were obtained by FT of FID obtained after a $\pi/2$ pulse. This method is very popular. In addition, no ^{29}Si NMR spectra can be obtained; if no ^1H decoupling pulses are applied in solid samples. Since ^{29}Si and TG/DTA data showed complex dependences, both spectra are need in this study. Na1.2 and Na2.4 were commercial samples; in contrast three specimens of Na1.0, Na1.7, and Na3.5 were prepared in this study. Therefore, their XRD spectra are displayed in Fig. 1. The powder patterns observed in Na1.2 and Na2.4 are also shown in the figure to compare with those synthesized in this study Thank you for your supporting. We modified "Gaussian function". The reason why we employed Gaussian function is line shapes of ^{29}Si NMR signals. As you know, NMR spectra with narrow line-widths can be fitted by Lorentz function. However, ^{29}Si lines showed broad peak top. Therefore, we used Gaussian function.
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	How was the lineshapedeconvoluted into multiple Gaussians? What parameters were used in the process? How reliable is the method under MAS conditions? Are there any residual proton couplings influence the analysis? What are the actual results of the process? Lines 168-170: It is confusing: How is it possible to compare the XRD data and the NMR spectra to suggest this conclusion, particularly when neither of the experiments was analyzed in detail. Qualitatively looking at the spectra, a large up-field shift is noted on the K (Si/Al=1) and that trend tends to be diminished as the ratio increases. Why the peak shapes differ with increase in Si/Al ratios? Why the spectral feature at Si/Al ratio of 3.5 is much simpler than at 2.4? There are more questions than answers, yet the conclusion drawn from this data does not make sense.	We used a computer software. Since some parameters e.g. line-height and -width aren't need to determine Si/Al ratios, I didn't list them in the draft. Because ^1H decoupling pulse sequences were employed in this study, dipole interactions of ^1H atoms to the Si NMR spectra weren't considered. ^{29}Si NMR lines cannot obtain without MAS method because of large line-widths caused by chemical shift anisotropy of Si atoms. Many scientists employ the same method to estimate Si/Al ratio. We need Si/Al ratios, therefore absolute values of the spectral area were needed (relative areas were need). I modified the text. Since each peak correspond to a Si site, it can be considered that 5 peaks can be recorded on a ^{29}Si NMR spectrum: if 4 Al atoms bonding to SiO_4 (this site is displayed as $\text{Si}(4)$), a ^{29}Si NMR signal is observed at the highest CS, in contrast, when 4 Si atoms bonding to SiO_4 ($\text{Si}(0)$ site), a ^{29}Si NMR signal is observed at the lowest CS. Therefore, 5 peaks ($\text{Si}(0)$, $\text{Si}(1)$, $\text{Si}(2)$, $\text{Si}(3)$, $\text{Si}(4)$) can be observed. However, the higher Si/Al ratio results in the lower ratios of $\text{Si}(4)$ and $\text{Si}(3)$ sites and the higher of $\text{Si}(0)$ site. In a case of $\text{Si/Al} = 3.5$, it can be
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	Figure 4 & 5 are exactly the same, except repotted. Some of the obvious observations are unexplained. What is the reason for a significant difference in the data for Na at Si/Al=1.0? The effects seem too random and do not follow any trend or pattern, at least not provided. DTA, TG and DTG data are worse than the others: What is the reason for secondary peaks with increasing Si/Al ratios? Some of the isotherms are so broad (K-FAU 1, Rb FAU 1), yet it is possible to identify a slope within 10th of a degree? In addition to the comments described earlier regarding the ¹H NMR data, why there are additional peaks for Li 1.0 (spinning sidebands?). Plot the spectra overlapping with each other that can highlight the change in the chemical shifts. If the hypothesis that Si/Al ratio increases the relative hydrophobicity, why the water should shift up-field? What is the rationale? The simulation results were least accurate. The authors fail to properly describe the role of the simulations in the study, yet draw strong conclusions. Considering the symmetry of the molecules there are multiple equivalent sites (Figure 9). Chemical shift	considered that there is no Si(4) site. Therefore, the result that line-shapes of M3.5 is simpler than those of M2.4 is reasonable. I deleted Fig. 4 and modified the text. The reason of secondary peak is unknown. K-DTG curves of FAU 1 and Rb-FAU 1 showed broad peaks, however we can determine the peak tops. I deleted the number at the first decimal place. It is methanol peak, we think. Methanol was employed to rinse sample tubes. The inner diameter of the sample tube is ca. 1mm; therefore, it can be considered that a little amount of methanol was remained. ¹H MAS NMR measurements were carried out with MAS = 30 kHz, therefore spinning side bands can be recorded at ca. ±50 ppm. Absolute values in any calculation are rarely agreed with experimental values. Therefore, only tendency is discussed. There are some reports [17, 20-23] using more simple model. In this study, supercage model is employed for
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	predictions are notoriously difficult, particularly in complex systems such as FAUs. Absolute chemical shifts have no meaning these calculations. Further the model is not a good representation of the experimental conditions, either Si/Al ratio or different ions. There is no discussion section. Results need to be looked at carefully and analyzed consistently across the multiple sample conditions. Conclusions drawn are not supported by the experimental results. One of core deficiencies of the manuscript is the rationale. Unfortunately making 25 different samples and running multitude of experiments do not qualify to be a research article, just a collection of data. Last but not the least, the manuscript is written rather poorly. Incomplete sentences with several grammatical mistakes and typos. I am not sure whether conversion of the word document to PDF messes up the format, but several words are jumbled together and making it difficult to read.	MO estimation, because it can be considered that the linking number of water molecules on cations is important. I modified the figure of ¹H MAS NMR spectra. Discussions are described in section 3.5. New data which ¹H and ²⁹Si NMR CS values showed complex dependences on cation characters are not only data collection. This result can be explained by computer simulation. I modified the text in conclusion. I cannot understand why many spaces between words were deleted in the draft. I inserted appropriate spaces in the 2nd revision.
<u>Minor</u> REVISION comments		
<u>Optional/General</u> comments		