Prediction of ^{29}Si MAS NMR chemical shifts in zeolites using density functional theory

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Abstract

The sum-over-states density functional perturbation theory has been used to calculate ^{29}Si shielding constants and chemical shifts in zeolites. The calculations were carried out on one-site (1T) $Si(OSiH_3)_4$ and two-site (2T) $R_3SiOSiR_3$ ($R = OSiH_3$) models, including three coordination shells around each site. The ^{29}Si NMR chemical shifts are shown to be very sensitive to the local geometry. A linear correlation between chemical shifts and average SiOSi angles has been established, taking into account two different zeolites, i.e. mazzite and zeolite-β. The use of 1T models allows the assignment of the experimental spectra, whereas that of 2T models, containing eventually four-membered rings, improves considerably the calculation of the absolute ^{29}Si chemical shifts, including those of silicon sites in aluminated zeolites. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

High resolution solid-state NMR techniques, such as magic angle spinning (MAS) have become a powerful tool for the investigation of zeolite structures. This high resolution allows one to detect small structural differences such as those induced by temperature variations or by crystallographically inequivalent environments among the silicon sites. The traditional assignment of ^{29}Si NMR signals of zeolites is essentially based on empirical relations involving the average Si–O distance, the number of next silicon or aluminum neighbors (T) and average values of TOT angles [1]. These empirical predictions have been shown to be useful to determine the distribution of aluminum in the faujasite lattice [2]. Substitution of Si by other elements such as B, Al, Ga also leads to modified ^{29}Si NMR spectra. These spectral changes are correlated with the modifications of the framework geometry and also with the electronic effects of the neighboring T sites. ^{29}Si MAS NMR spectra of zeolites with various Si/Al ratios have been used to determine the ordering of Si and Al atoms in the framework [3–5].

In order to refine the empirical analyses, to interpret and predict NMR spectra, an accurate theoretical approach is necessary. Provided the models used for the description of the Si sites in zeolites are valid, the experimental ^{29}Si NMR

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spectrum can be predicted. With this purpose, we have chosen to study the ^{29}Si spectra of the relatively simple zeolite mazzite, with only two crystallographically distinct T sites and, as a much more challenging example, the zeolite-β, which includes nine crystallographically distinct T sites. Using a density functional theory (DFT)-based methodology [6], we have calculated the ^{29}Si NMR spectra of these zeolites with fully siliceous frameworks and when silicon sites have one aluminum first neighbor. This study has shown that the use of very simple 1T models is sufficient to predict the relative positions of the NMR signals of siliceous systems. However, the description of the absolute chemical shifts necessitates a better description of the silicon environment. A substantial improvement of the accuracy, including for aluminated frameworks, can be achieved using 2T models and a simple averaging technique.

2. Models and methods

There are two and nine crystallographically distinct T sites in mazzite and zeolite-β, respectively. For mazzite, we have followed the structural description given by Galli [7], whereas we considered the experimental structure of polymorph A of zeolite-β, as reported by Newsam et al. [8]. Two kinds of cluster models, have been considered in this study: (i) one-site (1T) clusters (Fig. 1(a) with the formula $Si(OSiH_3)_4$ for each crystallographic site separately; (ii) two-site (2T) clusters including eight SiO_4 units with the formula $R_3Si_x–O–Si_yR_3$ (where $R = OSiH_3$). The number of oxygen and hydrogen atoms in 2T models varies depending on the number of 4-MRs. The number of 4-MRs could be 0 to 2 as shown in Fig. 1(b)–(d), respectively. In zeolite-β, all the three-cluster models were needed to represent the different T sites, whereas only one 2T model including one 4-MR (Fig. 1(c)) was enough to represent the two crystallographic sites in mazzite.

In all the clusters that we have considered, the dangling bonds of Si have been saturated with hydrogen atoms. The Si–H bond distance has been set to 1.50 Å, and the H atoms have been posi-

tioned along the corresponding Si–O bond vectors in the experimental structure. When the structures have been allowed to relax (see Sections 3.2 and 3.3), the terminal H atoms have been kept fixed, in order to simulate the constraints of the surrounding zeolite lattice.

These clusters have been used to simulate the NMR properties of ^{29}Si without any aluminum atom in the next T sites (Si(0Al)) in the usual notation [9]) and also with one aluminum first neighbor (Si(1Al)).

The calculations have been performed within the linear combination of Gaussian type orbitals–density functional formalism (LCGTO–DF) [10–12], using the deMon and deMon properties programs [13–15]. All geometry optimizations have been performed at the gradient-corrected density functional level using the Becke B88 [16] functional for exchange and the Perdew P86 [17] functional for correlation. All-electron basis sets of DZP quality have been used for all heavy atoms whereas the terminal hydrogens have been described on a small DZ basis. In Huzinaga's notation the contraction patterns are (6321/521/1), for Si and Al, (621/41/1) for 0 and (41) for H [18].

^{29}Si NMR chemical shifts have been evaluated from the NMR shielding tensors obtained using the sum-over-states–density functional perturbation theory (SOS–DFPT) in the LOC1 approximation [13], along with the IGLO method for the choice of the gauge origin. We used the IGLO III basis set of Kutzelnigg et al. [19] for all the heavy atoms, keeping the standard (41) basis (Huzinaga's notation) for the terminal H. Only the shielding tensors of the central atoms were considered, because only these atoms have an appropriate local environment. All the shielding tensor calculations were performed using the PW91 functional [20,21]. In order to obtain more precise molecular orbital coefficients, an additional iteration after SCF convergence, using the numerical evaluation of the exchange-correlation potential on an enlarged grid, has been performed. More details concerning the stability of calculations against different basis sets and functionals can be found in Ref. [22].
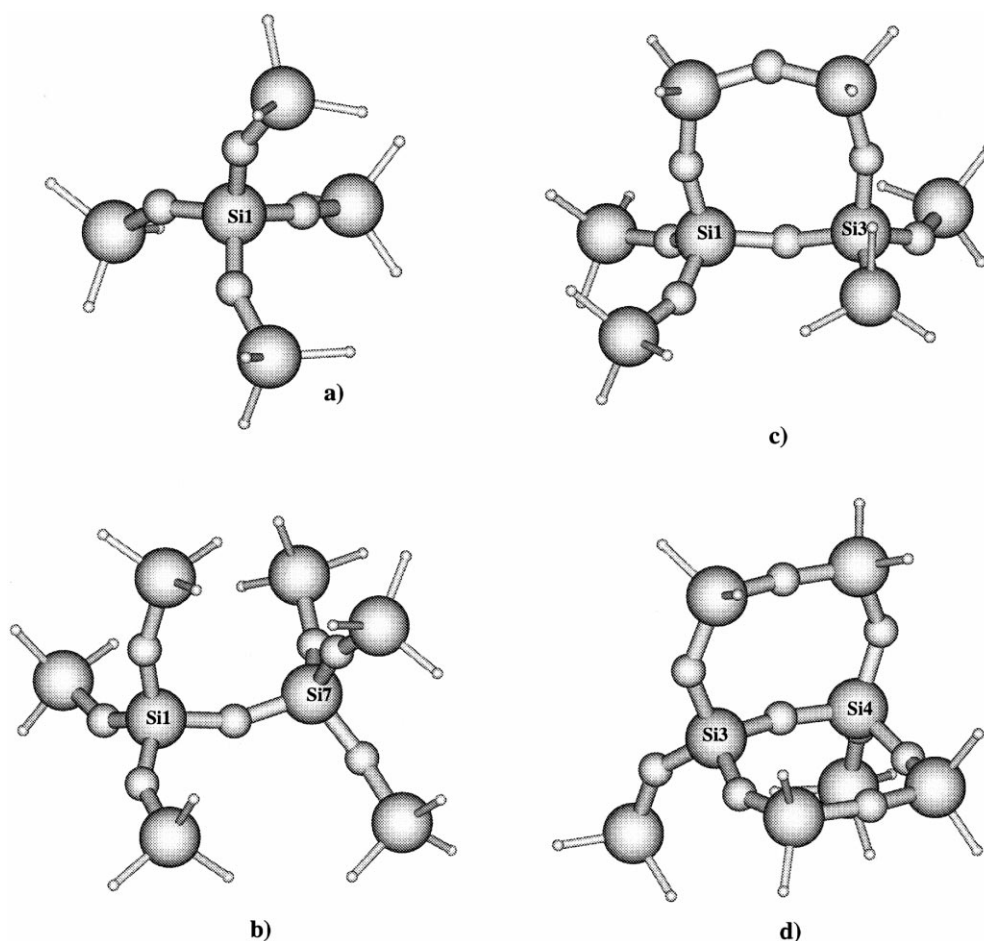
Fig. 1. (a) Typical 1T model representing the Si1 site in polymorph A of zeolite-β and (b)–(d) typical 2T models. These models represent 0, 1 or 2 four-member rings (4-MRs) formed because of different connectivities of adjacent Si sites.

3. Results and discussion

3.1. 1T site cluster models

We first carried out calculations on the 1T models, representing, each, one of the crystallographic sites of the fully siliceous zeolite mazzite and zeolite-β. The average Si–O bond distance in the crystallographically distinct SiO_4 units does not vary significantly. The average $\langle SiOSi \rangle$ bond angles display large variations with the sites, with a difference of 11.2° for mazzite and up to 7.9° for zeolite-β. This variation seems to be the main geometric factor determining the pattern of the NMR spectra. We carried out ^{29}Si NMR shielding

constant calculations as mentioned in the earlier section and a similar calculation was also performed for the tetramethylsilane (TMS), all chemical shifts (δ) reported for the various silicon sites being obtained using TMS as the reference. The calculated ^{29}Si NMR chemical shifts (δ) for the individual sites in mazzite and zeolite-β are compared in Fig. 2 (1T models) with the experimental values for mazzite [23,24] and zeolite-β [25,26]. The experimental and calculated chemical shifts show a qualitative linear correlation with the $\langle SiOSi \rangle$ bond angles. It is gratifying to observe the 1:1 correlation between the experimental and calculated chemical shifts of the various T sites for both zeolites. Small 1T models are thus sufficient
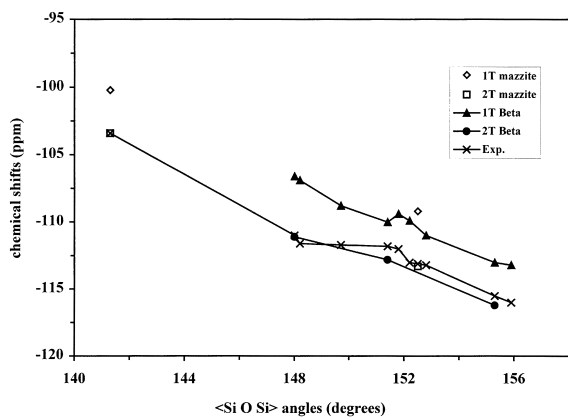
Fig. 2. Variation of δ with $\langle SiOSi \rangle$ angles, for 1T and 2T clusters of mazzite and zeolite-β compared with experimental data, taken from Refs. [23–26].

to describe the relative chemical shifts among the different sites of a given zeolite, even if the error on the absolute δ values can vary from 3 to 5 ppm. These results also prove that the linear correlation assumed between the chemical shift and the average TOT bond angle is valid.

3.2. 2T site cluster models

Larger cluster models with a chemical formula $R_3Si-O-SiR_3$ ($R = OSiH_3$) have also been considered, representing 2T sites in the zeolite lattices. Topographically, the nine T sites in zeolite-β could be grouped into three categories, namely A, B and C as described earlier [27]. In group A, a given T site is not associated with any 4-MR whereas in groups B and C, the T sites belong to one and two 4-MRs, respectively. The T sites 7, 8 and 9 come under group A, 1 and 2 come under group B and 3, 4, 5 and 6 come under group C. Representative sites, namely 1, 3 and 8 have been considered for chemical shift calculations of zeolite-β, whereas one 2T model including the two crystallographic sites has been used for mazzite.

It is shown in Fig. 2 (2T models) that increasing the cluster size to octamers $(H_3SiO)_3$ $Si-O-Si$ $(OSiH_3)_3$ leads to a substantial improvement of the NMR simulations. Mazzite being a highly symmetrical zeolite, a single 2T cluster is sufficient to provide accurate ^{29}Si chemical shifts. In the

case of zeolite-β, the presence of all the neighboring Si sites would imply a large cluster model containing more than 12 Si sites, which is computationally demanding. Hence, we have applied a fragment-averaging technique. The central silicon in a 1T cluster has four silicon neighbors. In order to build a 2T model, one of the four silicon neighbors of a 1T cluster is terminated by $OSiH_3$ groups instead of hydrogens, as shown in Fig. 1(b)–(d). This procedure is applied three more times to create three more octamers, wherein the other three silicon neighbors are saturated with $OSiH_3$ groups instead of hydrogens. Thus, to represent the influence of all the neighboring silicons on the ^{29}Si NMR chemical shift of Si1, we have considered four clusters, namely Si1Si2, Si1Si7, Si1Si8 and Si1Si3. The final chemical shift for site 1 is taken as an average of the four values. The ^{29}Si chemical shifts calculated by this procedure for Si1, Si3 and Si8 of zeolite-β are the three 2T Beta values represented on Fig. 2. The error on the calculated chemical shifts of both zeolites is now reduced to ± 1 ppm with respect to the experimental values. The quantitative prediction of the absolute chemical shift for crystallographically distinct sites is thus possible and this allows confidence in NMR techniques as a structure determining tool.

Prior to the study of zeolites containing aluminum, we have found it useful to analyze the effect of the geometry relaxation on the calculated chemical shifts of the siliceous models. Indeed, geometry optimization cannot be avoided when one wants to describe a structure with aluminum centers, since only average T–O bond lengths and TOT bond angles are provided by crystallographic measurements. The major problem, in this case, concerns the size of the clusters chosen to represent the crystallographic sites: the geometry optimization of too small a cluster generates underestimated bond angles, i.e. underestimated shielding constants [28].

In fact, the critical size of the cluster depends on the zeolitic structure. Indeed, starting from the experimental structure, the geometry optimization of the 2T (Si1Si2) model of mazzite (with fixed border hydrogens as indicated in Section 2) leads to negligible geometric distortions, leaving unchanged the δ shifts of the two sites. In contrast,

the same procedure applied to the Si1Si3 model of zeolite-β (with one 4-MR as mazzite) leads to non-negligible changes in geometry (the average bond angles decrease by around 3°) and to chemical shifts values of -114.5 (Si1) and -108.3 (Si3), instead of -117.2 (Si1) and -111.3 ppm (Si3), corresponding to the experimental geometry.

These results allow us to anticipate that, when Si is replaced by aluminum, the main source of inaccuracy for the NMR chemical shifts will be the inaccuracy of the optimized structure.

3.3. 2T models containing Al

In the case of mazzite, each crystallographic site can, in turn, be substituted by Al, leading to two models, Si1Al2 and Al1Si2. For zeolite-β, there is a large number of possible topologies. We have chosen to limit our study to Si1Al3, Si1Al8, Si8Al1, Si8Al3, Si3Al1 and Si3Al8, i.e. each type of site B (Si1), C (Si3) and A (Si8) being studied with two different aluminum neighbors.

In all cases, the excess negative charge, resulting from the Si→Al substitution has been compensated by a proton associated with the bridging oxygen between the silicon (Sia) and aluminum (Alb) sites. The optimized structural parameters of the SiaOAlb linkages are presented in Table 1, together with the calculated screening constants and chemical shifts of the Sia sites. The corresponding parameters evaluated for the siliceous models SiaSib are also given for comparison.

These results show that the presence of Al in site b generates a decrease of the screening constant of Sia. This decrease is larger and more site-dependent in zeolite-β ($\Delta\sigma = 8$–15 ppm) than in mazzite ($\Delta\sigma = 5$ ppm). Moreover, it is much larger in, zeolite-β, than the difference between the individual crystallographic sites, whereas this is the opposite in mazzite. These conclusions are in agreement with the fact that mazzite has a more rigid and more isotropic local structure than zeolite-β, allowing less relaxation when Si is substituted by Al. It looks reasonable that the response of the local structure around a silicon to the presence of an aluminum neighbor can be more diverse in zeolite-β, where the sites have essentially four different neighbors, than in mazzite with only two distinct sites. This characteristics probably explains why a single 2T model including the two crystallographic sites of mazzite gives a good prediction of its NMR spectrum: the NMR peaks attributed to Si(1Al) are at -107.1 and -98.7 ppm, which correlates very well with the calculated values of -108.6 ppm for site 1 and -97.8 ppm for site 2. This good agreement is a proof, a posteriori, that the geometries of the Si1Al2 and Si2Al1 models are realistic, which is consistent with the stability of the siliceous structure upon geometry optimization (cf. Section 3.2).

In the case of zeolite-β, we expect that the error of 3 ppm, related with the optimization of the Si1Si3 beta model, will be a lower limit error for the systems with one aluminum. The ^{29}Si NMR

Table 1
Geometric parameters (bond lengths in Å, bond angles in degrees) and ^{29}Si NMR shielding constants and chemical shifts (ppm) calculated for SiaAlb (2T) models of mazzite and zeolite-β, compared with the calculated NMR parameters (ppm) of the siliceous SiaSib systems. TMS was used as a reference ($\sigma = 344.9$)

SiaAlb	Sia–O	Alb–O	∠ SiaOAlb	σ, δ (Sia) (SiaAlb)	σ, δ (Sia) (SiaSib)
Beta					
Si1Al3	1.705	1.924	137.5	452.2, -107.3	462.1, -117.2
Si1Al8	1.703	1.949	142.7	446.4, -101.5	459.8, -114.9
Si3Al1	1.716	1.904	135.0	448.1, -103.2	456.2, -111.3
Si3Al8	1.687	1.890	132.9	443.2, -98.3	453.8, -108.9
Si8Al1	1.729	1.962	138.0	444.4, -99.5	457.8, -112.9
Si8Al3	1.692	1.854	132.9	442.2, -97.5	457.1, -112.2
Mazzite					
Si1Al2	1.721	1.918	133.9	453.5, -108.6	458.0, -113.1
Si2Al1	1.707	1.925	139.5	442.7, -97.8	448.3, -103.4

spectrum of a zeolite-β with an Si/Al ratio of 27 (2.4 aluminum atoms for 64 T sites) displays the peaks characteristic of siliceous sites (Si(0Al)) in the −110 to −116 ppm region and an additional broad low-field signal centered at −104 ppm. This signal is attributed to a superposition of a peak due to silanols (already present in the siliceous zeolite) at about −102 ppm and to Si(1Al) sites estimated at −106 ppm [26,29,30]. When more aluminum is incorporated in the framework, the intensity and width of the low-field signal increase, associated with Si(2Al) sites.

It is worth noting that the low-field peak at −104 ppm has a width comparable with that attributed to Si(0Al), i.e. around 6 ppm. Although it includes a silanol contribution, this gives some indication that the range of the calculated chemical shifts (Table 1) is reliable. Their absolute values are certainly too small, as already mentioned, because of the underestimation of the TOT bond angles after geometry optimization. A high-field correction of 3–5 ppm would shift the signals to the region of the experimental spectrum.

Another way to correct the overestimated low-field shift due to geometry optimization, is to apply the same averaging technique as explained above (cf. Section 3.2): the ^{29}Si chemical shifts can be evaluated using one SiaAl and three SiaSi models ($a = 1, 3, 8$). The ^{29}Si chemical shifts obtained with this procedure represent high-field limits to the true chemical shifts, since the three SiaSi values included in each average value do not take into account any relaxation of the structure after incorporation of one aluminum in the surroundings.

These estimated chemical shifts (δ_{av}) are presented in Table 2, together with the average $\langle \text{SiaOT} \rangle$ angles. We see that the chemical shifts calculated with this procedure for Si1, Si3 and Si8 are much less sensitive to the topology of the Al substitution than the individual SiaAl models. The comparison with the fully siliceous results, i.e. −116.2, −112.8 and −111.1 ppm for Si1, Si8 and Si3, respectively, shows a low-field shift of only 3–4 ppm for each type of site. It is worth noting that these calculated δ_{av} values correlate well with the average $\langle \text{SiaOT} \rangle$ angles, following the trend that more negative chemical shifts are associated with

Table 2

Calculated ^{29}Si NMR chemical shifts (ppm) (see the text) and averaged $\langle \text{SiaOT} \rangle$ angles (degrees) for 2T models of zeolite-β containing one Al, and averaged $\langle \text{SiaOSi} \rangle$ angles from the experimental, almost fully siliceous, structure

SiaAlb	δ (Sia)	δ (Sia)$_{av}$	$\langle \text{SiaOT} \rangle_{av}$	$\langle \text{SiaOSi} \rangle_{av}$
Si1Al3	−107.3	−113.8	152.5	155.3
Si1Al8	−101.5	−113.0	152.6	155.3
Si8Al1	−99.5	−109.4	147.6	151.4
Si8Al3	−97.5	−109.0	148.6	151.4
Si3Al1	−103.2	−109.0	144.7	148.0
Si3Al8	−98.3	−108.5	145.2	148.0

larger angles, as it is demonstrated for the fully siliceous zeolite (Fig. 2).

4. Conclusions

The ^{29}Si NMR chemical shifts of the zeolite mazzite and zeolite-β have been calculated using the SOS–DFPT method [13]. We report here the effects of the cluster size on the calculated ^{29}Si chemical shifts for the two sites of mazzite and the nine sites of zeolite-β. We have shown that a good description of the relative position of the NMR peaks is obtained using models with a chemical formula $Si(OSiH_3)_4$. However, larger cluster models with a chemical formula $R_3Si–O–SiR_3$ ($R = OSiH_3$), representing double T sites in the zeolite lattice, must be considered for a more accurate description. Using such clusters, it is also possible to predict the ^{29}Si spectra of Al containing zeolites. In the case of flexible zeolitic structures, geometry optimization may induce a systematic low-field error, related to the limited size of the model cluster. The technique of evaluating the Si chemical shift as the average of values obtained for one SiaAl and three SiaSi models provides a high-field limit to the true chemical shifts. These two approaches are not very accurate but they have the merit of specifying the lower and higher expected limits for the Si(Al) chemical shifts, even in a quite complex system as zeolite-β, requiring a moderate computational effort. We are confident that this procedure can be applied successfully to other zeolitic systems.

Acknowledgements

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