Lattice Energy-Minimization Calculation in the Further Investigation of XRD and NMR Studies of Zeolite Frameworks

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A knowledge of the local structure of zeolite frameworks is an important prerequisite for a detailed and quantitative understanding of e.g. catalytic processes. In the present work the sensitivity of 1D and 2D MAS NMR experiments to the local order of framework T atoms and energy-minimization calculations for the geometrical analysis of the complete zeolite framework structure are combined to provide a most detailed view of their structural properties. Correlations of the chemical shifts, $\delta(^{29}\mathrm{Si})$, with the mean distance between Si and its neighboring Si T atoms, $\bar{d}$(Si−Si), are presented for the three materials MFI, MEL, and MTT. Excellent agreement between experimental and computational results was obtained. In the case of MFI, this most complicated structure was used to demonstrate the viability of the method. The MTT and MEL systems showed that it is possible to deduce the unique assignment of the NMR spectra from energy-minimized structures when it is not possible using the available structural data from X-ray structure analysis. Taken together, all three investigations also demonstrate that improved structural data are obtained from lattice energy minimizations compared to those from Rietveld analysis as long as the topology of the framework is known.

Introduction

Zeolites are porous tectosilicates which are widely used as industrial ion exchangers, sorbents, and catalysts.[1] The remarkable size and shape selectivity of these materials results from their unique framework structures and, thus, a knowledge of their crystal structures is essential to understand current and to evaluate potential applications of these materials.

Although synthetic zeolites are very highly crystalline, they are usually microcrystalline, most often precluding the use of single-crystal techniques and necessitating the deductions of lattice structures from the much more limited powder diffraction data. In general, the framework topologies from successful refinements are correct, but the more quantitative local structural data such as bond length, angles, and even atomic positions are imprecise compared to those from single-crystal studies even when synchrotron sources and Rietveld refinement techniques are used. This makes it difficult to relate these XRD studies quantitatively to the data from other techniques such as NMR. In the past, a number of attempts have been made to correlate the ^{29}Si chemical shifts which reflect the local environment and which are average values with parameters from diffraction studies such as average $\bar{d}$(Si−Si) distances and T−O−T angles. Overall, these studies indicated that the general trends exist but the quality of the average correlations was such that no universally accepted relationship was established.[2]

In recent years, high-resolution ^{29}Si solid-state MAS NMR spectroscopy has developed as an important complementary technique to X-ray diffraction studies for structural investigations of zeolites since the ^{29}Si NMR chemical shift is very sensitive to changes in the geometry of the first (oxygen), second (T atom), and even third coordination spheres surrounding the silicon nuclei.[3] In highly siliceous zeolites, where all T sites have the same Si[OSi]$_4$ local environment, the number, and relative intensities of the resonances in the spectra provide direct information on the number of symmetrically inequivalent silicon atoms in the asymmetric unit and their relative site occupancies. The chemical shifts, therefore, reflect subtle differences in the local geometry of the framework structure.

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(1) Jansen, J. C., Stöcker, M., Karge, H. G., Weitkamp, J., Eds. *Advanced Zeolite Science and Applications*, Studies in Surface Science and Catalysis 85, Elsevier Science B. V. Amsterdam, 1994.

(2) (a) Higgins, J. B. Woessner, D. E. *EOS* **1982**, *63*, 1139. (b) Smith, J. V.; Blackwell, C. S. *Nature* **1983**, *303*, 223. (c) Grimmer, A. R.; Radeglia, R. *Chem. Phys. Lett.* **1984**, *106*, 262. (d) Thomas, J. M.; Klinowski, J.; Ramdas, S.; Hunter, B. K.; Teenakoon, D. T. B. *Chem. Phys. Lett.* **1983**, *102*, 158. (e) Mägi, M.; Lippmaa, E.; Samoson, A.; Engelhardt, G.; Grimmer, A. R. *J. Phys. Chem.* **1984**, *88*, 1518. (f) Ramdas, S.; Klinowski, J. *Nature* **1984**, *308*, 521. (g) Janes, N.; Oldfield, E. *J. Am. Chem. Soc.* **1985**, *107*, 6769. (h) Engelhardt, G.; Radeglia, R. *Chem. Phys. Lett.* **1984**, *108*, 271. (i) Fyfe, C. A.; Feng, Y.; Grondey, H. *Microporous Materials* **1993**, *1*, 393.

(3) Engelhardt, G. *High-Resolution Solid State NMR of Silicates and Zeolites*; John Wiley & Sons: Chichester, 1987.

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A step forward was made with the introduction of two-dimensional NMR techniques such as COSY and INADEQUATE, making it possible to determine the three-dimensional Si−O−Si connectivity patterns.[4] Combining these data with a knowledge of the framework topology from structural studies has yielded detailed assignments of the ^{29}Si NMR signals to distinct sites in the crystal structure for a number of zeolite frameworks.[5] Most importantly, it was now possible to correlate and assign ^{29}Si chemical shifts for complex frameworks even where the sites are of equal occupancy. In the case of zeolite ZSM-5, it was possible to assign the resonances in all of the different forms for which single-crystal diffraction data were available from the work of van Koningsveld and co-workers. Excellent correlations were found of the ^{29}Si shifts with the parameters from single-crystal studies but the correlations were much worse for the other structures derived from powder data.[2i] This suggested that the main limitation in these chemical shift/structure correlations would be the accuracy of the X-ray derived parameters, particularly those derived from powder diffraction data.

In previous work, lattice energy-minimization calculations have been used to obtain valuable structural information on zeolites. The technique has been applied for e.g. studying details of nonframework cation distributions in zeolites,[6] and to predict framework structures and stabilities .[7,8] Close agreement with experimentally determined lattice parameters, bond lengths, and interatomic angles are obtained. In addition, a recent study[9] suggested that the local structural parameters from energy-minimized geometries could give good correlations with ^{29}Si NMR chemical shifts. In an evaluation of energy-minimized zeolite framework structures in comparison to results from neutron and X-ray structure analyses, it was shown that the correlation of ^{29}Si NMR chemical shifts and T−O−T angles is of comparable quality for experimental as well as for theoretical frameowrk structures.[10] However, since oxygen positions in zeolite frameworks are often dynamically disordered and, therefore, those determined from diffraction studies are averaged positions, the T−O−T angles used for the correlations still contain considerable systematic errors.

In the present work, we have attempted to further confirm and improve the viability of these calculations, to use the results of energy minimization actively for the assignment of NMR signals, and to delineate a number of different applications for them by using the available diffraction and NMR data on the representative zeolite structure types MFI, MEL, and MTT relating to the important catalytic materials ZSM-5, ZSM-11, and ZSM-23, respectively.

Experimental Section

All calculations were carried out using the Metapocs code implemented in the Biosym Catalysis software.[11] The interatomic potentials were derived from empirical fitting to the bulk properties of α-quartz and are described elsewhere.[12] The model included both a "harmonic bond−bending potential" applied to O−Si−O groupings and a "core and shell potential" to account for the polarizability of the framework oxygen as also used in the previous study.[10]

The energy minimization was archived using a modified quasi-Newton method. As starting configurations for our calculations, the experimentally determined structures from diffraction studies of zeolite ZSM-5,[13] zeolite ZSM-23,[14] and ZSM-11[15] were used.

In contrast to the preceding study where constant pressure was applied,[10] the calculations took the form of a constant volume minimization in which the atomic positions were relaxed to their minimum energy configuration within the highly accurate experimentally determined unit cell dimensions and angles. The experimental values of the unit cell parameters were those for the low-symmetry form of the respective zeolite materials, but at temperatures close to room temperature.

The lattice energy minimization does not take the space group symmetry into account and, therefore, was calculated assuming triclinic symmetry. The "find symmetry" operation in the solids adjustment module of the Catalysis software was then used to find the location and nature of the symmetry elements.

The results of the geometrical analysis of the local order obtained from the lattice energy-minimization calculations were correlated with the ^{29}Si 2D MAS NMR chemical shifts using the following general linear equitation:

$$\delta = a[\,\bar{d}(\mathrm{T{-}T})] + b \qquad (1)$$

where δ is the ^{29}Si isotropic chemical shift measured in parts per million (ppm) with respect to TMS taking Q_8M_8 as a secondary reference. The $\bar{d}$(T−T) distance is the mean separation between the target ^{29}Si nucleus and its first nearest neighboring Si atoms, measured in angstroms (Å). Although other correlations of the NMR chemical shift and structural properties have been reported and, for $\bar{d}$(Si−O), also derived theoretically,[16] $\bar{d}$(T−T) distances have been used in this study since the true crystallographic Si−O distances are often obscured by static or dynamic disorder of the oxygen atoms as obvious from the very high displacement parameters of the affected atom. Similar disorder has never been observed for Si atoms in zeolite framework structures.

The measurement error concerning the chemical shift values of the NMR experiment in the present study is estimated to be ±0.05 ppm for resolved peaks and ±0.15 ppm for the deconvolutions of overlapping peaks.

Results and Discussion

The different systems represent different possible applications, and for clarity, the different correlations between the assigned ^{29}Si MAS NMR chemical shifts and the structure related parameters for the zeolite

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(4) Fyfe, C. A.; Feng, Y.; Grondey, H.; Kokotailo, G. T.; Gies, H. *Chem. Rev.* **1991**, *91*, 1, 1525.

(5) Fyfe, C. A.; Feng, Y.; Grondey, H.; Kokotailo, G. T.; Gies, H. *Bruker Report* **1993**, *130*, 29.

(6) Jackson, R. A.; Catlow, C. R. A. *Mol. Simul.* **1988**, *1*, 207.

(7) Tomlinson, S. M.; Jackson, R. A.; Catlow, C. R. A. *J. Chem. Soc., Chem. Commun.* **1990**, 813.

(8) Bell, R. G.; Jackson, R. A.; Catlow, C. R. A. *J. Chem. Soc., Chem. Commun.* **1990**, *1990*, 782.

(9) Morris, R. E.; Weigel, S. C.; Henson, N. J.; Bull, L. M.; Janicke, M. T.; Chmelka, B. F.; Cheetham, A. K. *J. Am. Chem. Soc.* **1994**, *116*, 11849.

(10) Cheetham, A. K.; Bull, L. M.; Henson, N. J. Progress in Zeolite and Microporous Materials Study. In *Surf. Sci. Catal.* **1997**, *105*, 2267.

(11) Catalysis, Release 236; Biosym Technologies: San Diego, 1994.

(12) Sanders, M. J.; Leslie M.; Catlow, C. R. A. *J. Chem. Soc., Chem. Commun.* **1984**, *1984*, 1271.

(13) van Koningsveld, H.; Jansen J. C.; van Bekkum, H. *Zeolites* **1990**, *10*, 235.

(14) Marler, B.; Deroche, C.; Gies, H.; Fyfe, C. A.; Grondey, H.; Kokotailo, G. T.; Feng, Y.; Ernst, S.; Weitkamp J.; Cox, D. E. *J. Appl. Crystallogr.* **1993**, *26*, 636.

(15) Fyfe, C. A.; Gies, H.; Kokotailo, G. T.; Pasztor, C.; Strobl H.; Cox, D. E. *J. Am Chem. Soc.* **1989**, *111* (7), 2470.

(16) (a) Thomas, J. M.; Fyfe, C. A.; S. Ramdas, S.; Klinowski, J.; Gobbi, G. C. *J. Phys. Chem.* **1982**, *86*, 3061. (b) A detailed account is found in ref 3, p 250.

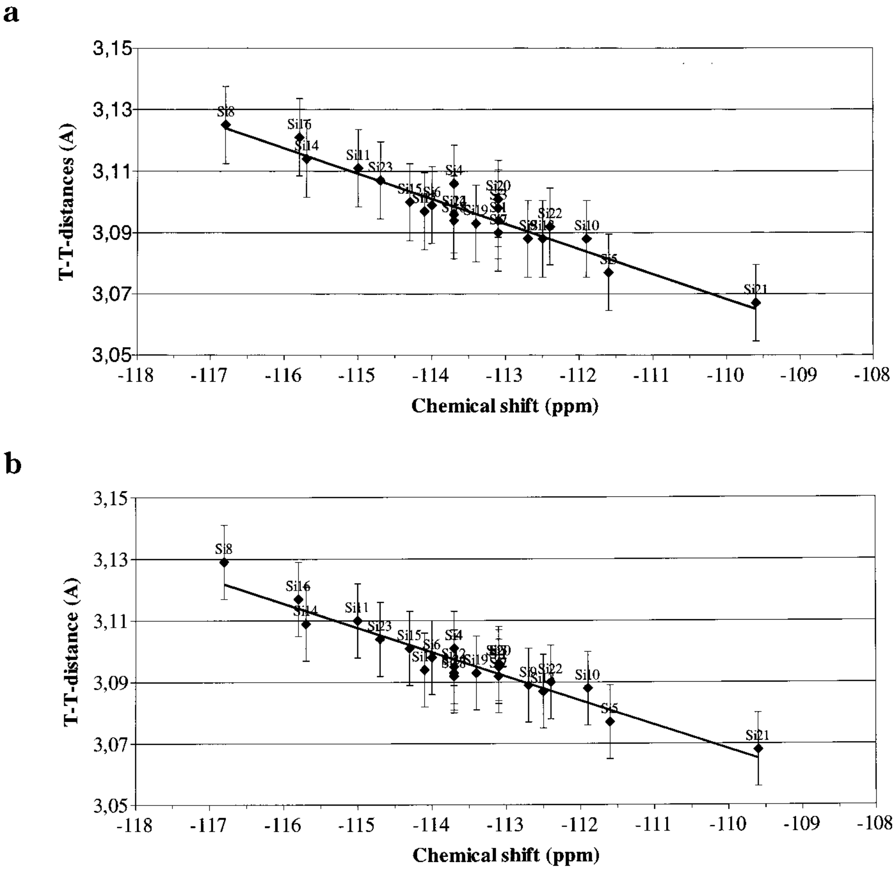

Figure 1. Correlation between T—T distances (Å) (◆: diffraction experiment in a, structure simulation in b) and ^{29}Si chemical shifts (ppm) of zeolite MFI. Part a shows the correlations of T—T distances obtained the results of a singles crystal structure refinement (12), and part b, those from the energy-minimized structure with the ^{29}Si chemical shift data from a high-resolution NMR experiment. The excellent fit of both data set proves the high quality of both experiments, structure analysis from the diffraction experiment, and structure simulation based on energy minimization, respectively.

framework structures of ZSM-5, ZSM-23, and ZSM-11 are described separately.

Zeolite ZSM-5. ZSM-5 was selected as first example for the correlation study between the ^{29}Si 2D MAS NMR chemical shifts and results of the geometrical analysis of the local order obtained from lattice energy-minimization calculations. Several highly accurate single-crystal refinements of various forms of ZSM-5 are available[13,17,18] which provide very accurate and detailed structural information and represent a "best case" for use in structure correlations. Because of this, there is an existing excellent correlation between the NMR data and local geometry parameters, e.g. the average T—T distances as shown in Figure 1a (cf. Table 1) (linear correlation coefficient $T = 0.95$). This situation thus represents a direct test of the assumptions and empirical parameters of the lattice energy-minimization calculations: The resulting correlation should be as good as the one using diffraction data if the calculations are valid.

The energy-minimization calculations have in effect been undertaken at 0 K, and, therefore, it is expected that the minimum energy structure should resemble the low-temperature form. By using the "find symmetry" operation in the solids adjustment module of the Catalysis software, space group $P2_1/n$ was obtained as most probable which is in agreement with the space group symmetry determined from the single-crystal room-

Table 1. Chemical Shifts and T—T Distances Obtained from Structure Simulation Calculations and Structure Refinement of Zeolite Silica-ZSM-5 As Used for the Correlation Calculation in Figure 1a,b

		T—T distance (Å)	
Si atom of ZSM-5	chemical shift (ppm)	structure simulation	structure refinement
1	−113.1	3.095	3.094
2	−113.1	3.092	3.090
3	−113.7	3.096	3.098
4	−113.7	3.101	3.106
5	−111.6	3.077	3.077
6	−114.0	3.098	3.099
7	−113.1	3.092	3.090
8	−116.8	3.129	3.125
9	−112.7	3.089	3.088
10	−111.9	3.088	3.088
11	−115.0	3.110	3.111
12	−113.7	3.095	3.096
13	−112.5	3.087	3.088
14	−115.7	3.109	3.114
15	−114.3	3.101	3.100
16	−115.8	3.117	3.121
17	−114.1	3.094	3.097
18	−113.7	3.092	3.094
19	−113.4	3.093	3.093
20	−113.1	3.096	3.101
21	−109.6	3.068	3.067
22	−112.4	3.090	3.092
23	−114.7	3.104	3.107
24	−113.7	3.093	3.096

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(17) van Koningsveld, H.; Tuinstra, F.; van Bekkum H.; Jansen, J. C. *Acta Crystallogr. Sect. B.* **1989**, *45*, 423.

(18) van Koningsveld, H. *Acta Crystallogr. Sect. B* **1990**, *46*, 731.

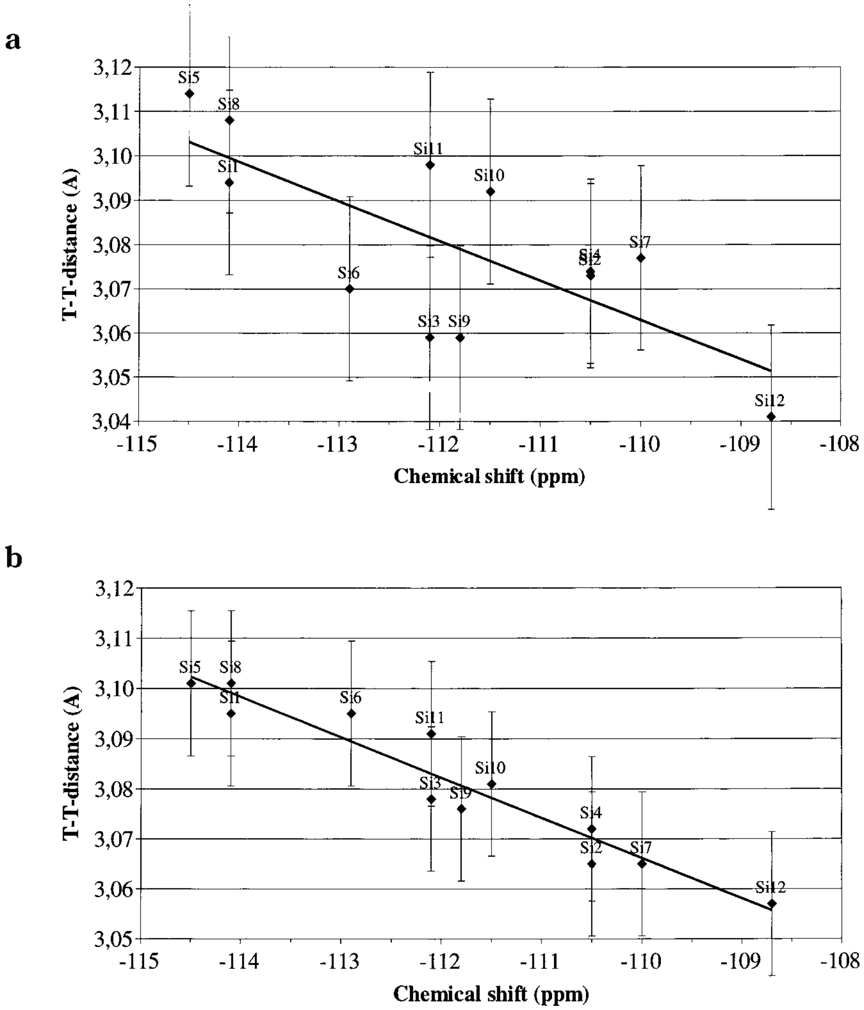

Figure 2. Correlation between T−T distances (Å) (◆: diffraction experiment in a, structure simulation in b) and ^{29}Si chemical shifts (ppm) of zeolite MTT. Part a shows the poor correlation of the experimental data to the assignment II of the 2D NMR experiment, and part b, the superior quality of the fit of the energy-minimized structure to the NMR data of assignment II. The correlation of the data of assignment I failed.

temperature structure refinement of the low-temperature form of ZSM-5.[13]

Figure 1b (cf. Table 1) shows the correlations between the chemical shifts and the mean Si−Si distance derived from the energy-minimization calculations (linear correlation coefficient $T = 0.96$). Both functions describe the variation of $\bar{d}$(Si[4Si]) from H−ZSM-5 quite well, as reflected in the high linear correlation coefficient. This clearly shows the efficiency and accuracy of modeling experiments even for such complicated structures (24 inequivalent T sites). It should, therefore, be possible with the help of energy minimization to discriminate between possible assignments for the NMR chemical shifts of zeolite structures in general.

Zeolite ZSM-23. The structure of zeolite ZSM-23[14] was refined from high-resolution synchrotron X-ray powder data in space group $P12_11$ (no. 4). The use of complementary methods, especially ^{29}Si MAS NMR spectroscopy was essential for the determination of the true space group symmetry, a prerequisite for the successful Rietveld structure refinement.

In 2D INADEQUATE experiments,[19] 17 of the total of 24 expected Si−O−Si connectivities are observed. However, the complete and unambiguous assignment of the individual resonances to T sites in the asymmetric unit of ZSM-23 could not be made from the NMR data alone due to degeneracies of some of the resonances. In principle, additional information which would help to discriminate in favor of one assignment could be gained by combining the NMR data with geometric information from diffraction studies. In general, the resonances of ^{29}Si associated T sites with shorter d(T−T) distances are located to lower field. Unfortunately, the present powder diffraction data is not accurate enough to use for this purpose. None of the possible assignments of individual resonances to T sites yields satisfactory correlations between the chemical shifts and the mean Si−Si distances as shown in Figure 2a for the final assignment as example (cf. Table 2) (linear correlation coefficient $T = 0.74$).

We, therefore, used the geometric data from the energy-minimization calculations for the assignment of the individual resonances to T sites. In the present case, the average T−T distance involving T12 is absolutely the shortest (see Table 1). Thus, the lowest field resonance was assigned to T12. Using this assumption above and the connectivity pattern from the NMR experiment it was possible to find a conclusive assign-

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(19) Fyfe, C. A.; Grondey, H.; Feng, Y.; Kokotailo, G. T.; Ernst, S.; Weitkamp, J. *Zeolites* **1992**, *12*, 50.

Table 2. Chemical Shifts and T−T Distances Obtained from Structure Simulation Calculations and Structure Refinement of Zeolite Silica-ZSM-23 As Used for the Correlation Calculation in Figure 2a,b ZSM-23

Si atom of ZSM-23	chemical shift (ppm)	T−T distance (Å) structure simulation	T−T distance (Å) structure refinement
1	−114.1	3.095	3.094
2	−110.5	3.065	3.073
3	−112.1	3.078	3.059
4	−110.5	3.072	3.074
5	−114.5	3.101	3.114
6	−112.9	3.095	3.070
7	−110.0	3.065	3.077
8	−114.1	3.101	3.108
9	−111.8	3.076	3.059
10	−111.5	3.081	3.092
11	112.1	3.091	3.098
12	−108.6	3.057	3.041

Table 3. Chemical Shifts and T−T Distances Obtained from Structure Simulation Calculations and Structure Refinement of Silica-ZSM-11 As Used for the Correlation Calculation in Figure 3a−d ZSM-11

Si atom of ZSM-11	chemical shift (ppm) assignment I	chemical shift (ppm) assignment II	T−T distance (Å) structure simulation	T−T distance (Å) structure refinement
1	−111.46	−111.46	3.082	3.090
2	−115.56	−116.65	3.114	3.092
3	−111.96	−111.64	3.075	3.109
4	−114.50	−116.52	3.112	3.072
5	−112.49	−114.37	3.095	3.081
6	−113.97	−113.97	3.086	3.076
7	−111.04	−111.84	3.086	3.069
8	−116.65	−115.56	3.109	3.122
9	−111.64	−111.96	3.077	3.090
10	−116.52	−114.50	3.097	3.107
11	−114.37	−112.49	3.087	3.085
12	−111.84	−111.04	3.083	3.085

ment of the resonances to T sites for the asymmetric unit of ZSM-23. Figure 2b (cf. Table 2) shows the resulting correlation diagram between the chemical shifts and the mean Si−Si distances derived from energy-minimization calculations (linear correlation coefficient $T = 0.96$).

The data of Figure 2b thus confirm the reliability of the energy-minimization method and also provide a unique assignment of the ^{29}Si resonances which in this case is not obtainable from the NMR data alone.

Zeolite ZSM-11 (LT Form). ZSM-11 is a microcrystalline highly siliceous zeolite whose crystal structure has been obtained from model building[20] and subsequent Rietveld analysis of synchrotron X-ray powder data.[21] The silica form of zeolite ZSM-11 undergoes a displacive phase transition from the high-temperature form $I\bar{4}m2$ to $I\bar{4}$ at temperatures which depend on the nature and amount of sorbate loaded into the microporous channels. Starting from the high-temperature form of ZSM-11, variable-temperature ^{29}Si NMR and the 2D ^{29}Si MAS NMR experiments, however, led to two possible equally valid assignments of the NMR frequencies to Si sites in the low-temperature form of ZSM-11.[22] In the original work, a decision between the two possible assignments was made on the basis of correlations between the chemical shift values of the low- and high-temperature forms. However, the somewhat subjective nature of this argument is less than satisfactory, and we have attempted to discriminate between the two assignments by chemical shift structure correlations where only one of the assignments should give a linear correlation.

When the plots were made using the structural data from the synchrotron powder XRD refinement of the low-temperature form of ZSM-11[23], neither of the two possible assignments yielded any linear correlation (Figure 3a,b; cf. Table 3) (linear correlation coefficient $T = 0.47$ and 0.11, respectively). As in the previous examples, this is thought to be due to the limited accuracy of the XRD structural parameters. We then took the mean separation values of the theoretically predicted structure for the correlation study. Parts c and d of Figure 3 present the correlation diagrams of the ^{29}Si chemical shifts and the mean Si−Si distances for the two assignments. Comparing the correlations of the geometrical data of the energy-minimized structure with each of the two possible assignments of the ^{29}Si NMR spectrum of ZSM-11 it is evident that only assignment II shown in Figure 3 correlates with the results of the energy-minimization calculation (linear correlation coefficient $T = 0.94$ for assignment II compared to 0.76 for assignment I).

Conclusions

As shown in the excellent linear correlation coefficients, the examples presented clearly demonstrate the improved accuracy of structural parameters derived from lattice energy-minimization calculations on zeolite frameworks. Although the NMR data sets for ZSM-5 and ZSM-23 were measured at room temperature and ZSM-11 at 303 K are compared with the results of the energy minimizations calculated for 0 K, there is clear evidence to justify this assumption.

The NMR experiments were carried out on the low-temperature forms of zeolite ZSM-5, ZSM-23, and ZSM-11. Since the space group symmetry does not change, the geometrical adjustments in the structures of ZSM-5, ZSM-23, and ZSM-11 should only be due to linear changes of the structure caused by thermal expansion. Because of the, in general, linear dependence of the geometrical changes of the structure we concluded that the correlation between NMR and structural data obtained from energy-minimization calculations should be valid. The results of our investigations are also in good agreement with the results of Fyfe et al.,[2i] which suggest that the main limitation in structure chemical shift correlations is the accuracy of the X-ray derived parameters, particularly where refinements of powder diffraction data are involved. Even if the best experimental conditions are chosen, i.e., using high-resolution synchrotron powder diffraction data (ZSM-23, ZSM-11), the method is limited for structural investigations of such complicated structures, and special care must be taken in using positional parameters from such studies for any quantitative calculations.

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(20) Kokotailo, G. T.; Chu, P.; Lawton, S. L.; Meier, W. M. *Nature* **1978**, *275*, 119.

(21) Fyfe, C. A.; Gies, G.; Kokotailo, G. T.; Pasztor, C.; Strobl H.; Cox D. E. *J. Am. Chem. Soc.* **1989**, *111*, 2470.

(22) Fyfe, C. A.; Feng, Y.; Grondey, H.; Kokotailo G. T.; Mar, A. *J. Phys. Chem.* **1991**, *95*, 3747.

(23) Hochgräfe, M.; Marler, B.; Gies, H.; Fyfe, C. A.; Feng, Y.; Grondey, H.; Kokotailo, G. T.; Cox, D. E. *Z. Kristallogr.* **1996**, *211*, 221.

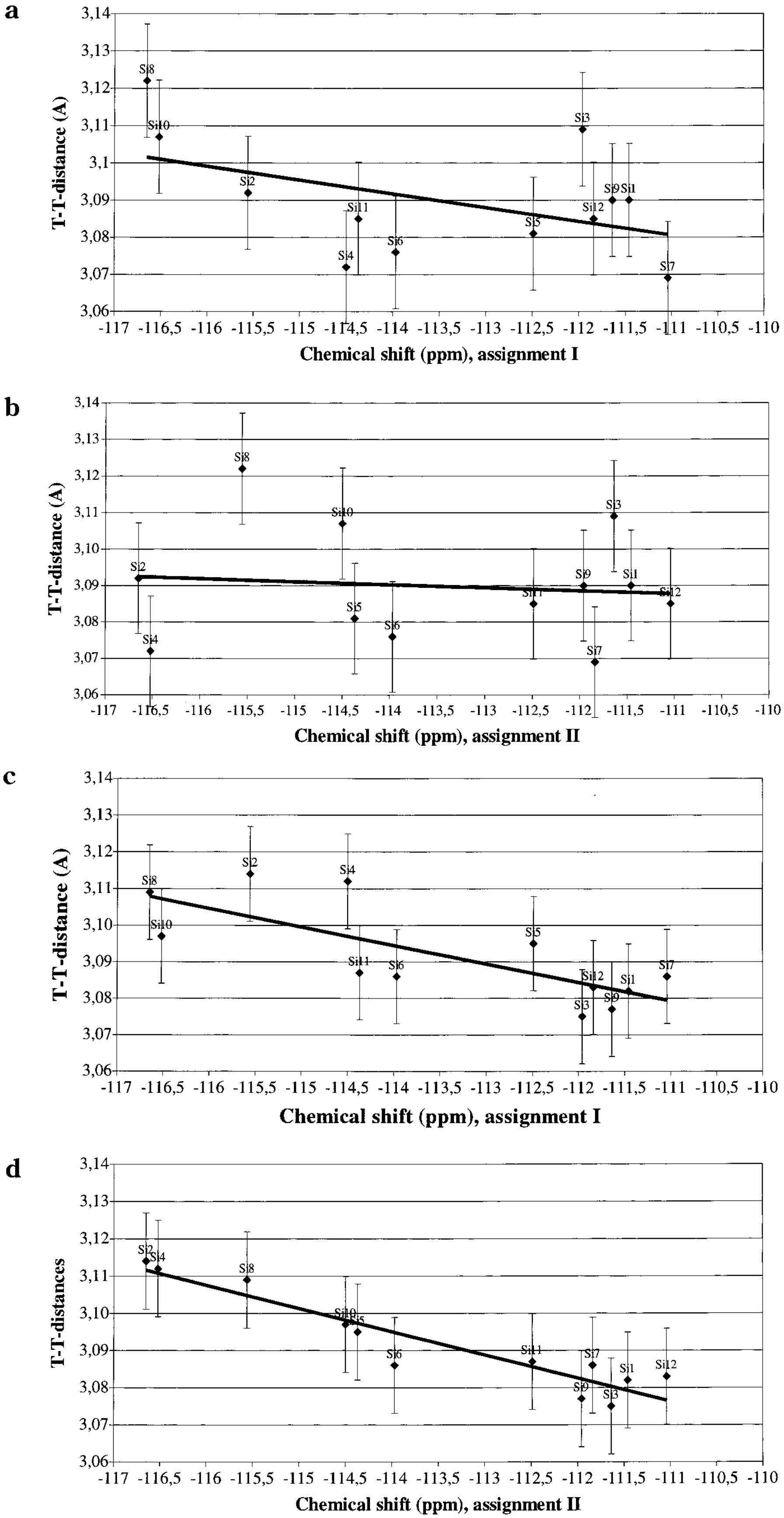

Figure 3. Correlation between T−T distances (Å) and ^{29}Si chemical shifts (ppm) of zeolite MEL. (◆: diffraction experiments in a and b, structure simulations in c and d). Parts a and b show the correlation of the T−T distance data from the crystal structure refinement using assignment I and II obtained from the interpretation of the 2D NMR experiment. In both cases the correlation is poor and not decisive. Parts c and d show the correlation of the energy-minimized structure using again assignment I and II from the 2D NMR experiment. Here, assignment II clearly gives the better correlation and has been used for the interpretation of the structure.

In comparison to the Rietveld structure analysis, modeling experiments are of high accuracy in calculating structural properties for zeolites. For this reason, the possibility of modeling zeolites, with the aid of high-speed computers, is becoming an increasingly important adjunct to experimental studies in solid-state chemistry and they might even substitute for the time-consuming Rietveld analysis of complicated structures, especially for the assignment of the ^{29}Si NMR signals to distinct sites in the crystal structure for zeolite frameworks.

These calculations are an important bridge between the experimental structure determination by X-ray diffraction and NMR chemical shift measurements, making it possible to fully integrate the two techniques. They can be applied to give complete assignments of the ^{29}Si resonances in cases where ambiguity exists as shown in the present examples and now that this reliability is clearly established may be used with confidence in the future to test proposed framework structures if ^{29}Si chemical shift data are available.

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