

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231430404>

Interpretation of the silicon-29 nuclear magnetic resonance spectra of zeolites: Synthetic mazzite

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY · NOVEMBER 1984

Impact Factor: 2.78 · DOI: 10.1021/j150667a057

CITATIONS

32

READS

23

3 AUTHORS, INCLUDING:



[Richard Jarman](#)

College of duPage

58 PUBLICATIONS 668 CITATIONS

SEE PROFILE

for aqueous MgCl_2 . The values of I_{12}/I_{21} and the error δ of this ratio are obtained from eq 21 and 22 of ref 79. (Equation 21 of ref 79 should have F^2 instead of F .) These equations require t_1^h , the Hittorf (or moving boundary) transference number, obtainable from the MB data of Lee and Kay,⁵⁴ and t_1^c , the cell transference number, obtainable from the emf data of Phang and Stokes.³³ Unfortunately, these data do not have a very extensive overlap in concentration. Moreover, the emf data were not done to test the ORR, and thus there are not enough low-concentration points to properly tie down the derivative there. However, we have taken t_1^h from a "best" line through the Lee-Kay points on a w deviation plot (which differs slightly from the "best" line through the combined data) and t_1^c from the fourth-order $E_i(E)$ fit of section IV-A. The errors δt_1^h are as indicated by Lee and Kay, and δt_1^c are the differences between third- and fourth-order fits of $E_i(E)$. The Δ values were taken from Table V, and I_{12}/N from Table VI can be used because I_{12} and I_{21} are very close.

Examination of Table VII shows that the ORR are indeed satisfied, but unfortunately the error limits are relatively large. The verification of the ORR is somewhat better for aqueous AgNO_3 ,⁷⁹ CdCl_2 ,⁷⁵ ZnCl_2 ,⁷⁶ and $\text{Zn}(\text{ClO}_4)_2$ ⁹⁷ because the ex-

periments were designed for that purpose and precision was emphasized.

Acknowledgment. J.A.R. was primarily supported by the National Science Foundation Earth Science Grant No. EAR76-20149 (coprincipal investigators Donald Graf and David Anderson, Geology Department, University of Illinois at Urbana-Champaign). L.B.E. was supported by the Office of Saline Water of the Department of the Interior. The remainder of this work was performed under the auspices of the Office of Basic Energy Science (Geosciences) of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract No. W-7405-ENG-48. We are grateful to George Flatter of Beckman Instruments for invaluable help with the optical realignment.

Registry No. MgCl_2 , 7786-30-3; sucrose, 57-50-1.

Supplementary Material Available: A realignment procedure to optimize the use of a Beckman-Spinco Model H electrophoresis apparatus as a Rayleigh diffusometer (7 pages). Ordering information is given on any current masthead page. Copies may also be obtained from the first two authors.

(96) Miller, D. G. *Chem. Rev.* 1960, 60, 15.

(97) Agnew, A.; Paterson, R. J. *Chem. Soc., Faraday Trans. 1* 1978, 74, 2885.

Interpretation of the Silicon-29 Nuclear Magnetic Resonance Spectra of Zeolites: Synthetic Mazzite

R. H. Jarman, A. J. Jacobson,* and M. T. Melchior

Exxon Research and Engineering Company, Annandale, New Jersey 08801 (Received: April 5, 1984; In Final Form: July 20, 1984)

Interpretation of the ^{29}Si NMR spectrum of synthetic mazzite, which has a structure containing inequivalent crystallographic silicon atoms, has been made using existing information about the sensitivity of ^{29}Si chemical shifts to framework topology and gallium substitution. The assignment of the spectrum has been substantiated by comparison with elemental analysis data and by using a chemical model for the Si-Al distribution to calculate the spectral intensities.

Introduction

In cases where a zeolite structure contains only one crystallographically distinct tetrahedral framework silicon site, high-resolution, ^{29}Si NMR spectroscopy enables a quantitative determination of the relative populations of the five possible chemically distinct silicon environments ($\text{Si}(n\text{Al})$, $4 \geq n \geq 0$).¹ The integrated peak intensities measure the distributions of Si and Al atoms in the framework, which in turn enable inferences about pathways for zeolite crystallization to be drawn. From studies of the zeolites faujasite²⁻⁶ and ZK4⁷⁻⁹ over a wide composition range ($1.0 \leq \text{Si}/\text{Al} \leq 3.0$), it has been concluded that the distributions of Al atoms

in the frameworks are always subject to the constraint of Loewenstein's rule,¹⁰ which forbids the presence of Al-Al nearest neighbors. Superimposed on this is a second, weaker constraint that the number of Al-Al next-nearest neighbors is minimized. The latter has a dependence on framework topology since the Si-Al distributions in faujasite and ZK4 are different over the composition range.⁹ The differences in observed distributions can be interpreted in terms of the pathways to the complete structures from isolated SiO_4 and AlO_4^- tetrahedra. It has been concluded that crystallization of the faujasite lattice probably occurs through a single 6-ring and that of ZK4 probably through a single 4-ring.⁶ Important factors in selecting these systems for detailed treatments are the structural simplicity of the two zeolites, namely, the presence of single crystallographic silicon sites, and the broad range of composition accessible by direct synthesis. For most zeolites,

(1) Lippmaa, E.; Magi, M.; Samoson, A.; Tarmak, M.; Englehardt, G. J. *Am. Chem. Soc.* 1981, 103, 4992.

(2) Ramdas, S.; Thomas, J. M.; Klinowski, J.; Fyfe, C. A.; Hartman, J. S. *Nature (London)* 1981, 292, 229.

(3) Melchior, M. T.; Vaughan, D. E. W.; Jacobson, A. J. *J. Am. Chem. Soc.* 1982, 104, 4859.

(4) Klinowski, J.; Ramdas, S.; Thomas, J. M.; Fyfe, C. A.; Hartman, J. S. *J. Chem. Soc., Faraday Trans.* 1982, 78, 1025.

(5) Englehardt, G.; Lohse, V.; Lippmaa, E.; Tarmak, M.; Magi, M. Z. *Anorg. Allg. Chem.* 1982, 482, 49.

(6) Melchior, M. T. *A.C.S. Symp. Ser.* 1983, 218, 243.

(7) Melchior, M. T.; Vaughan, D. E. W.; Jarman, R. H.; Jacobson, A. J. *Nature (London)* 1982, 298, 455.

(8) Thomas, J. M.; Fyfe, C. A.; Ramdas, S.; Klinowski, J.; Gobbi, G. C. *J. Phys. Chem.* 1982, 86, 3061.

(9) Jarman, R. H.; Melchior, M. T.; Vaughan, D. E. W. *A.C.S. Symp. Ser.* 1983, 218, 267.

(10) Loewenstein, W. *Am. Mineral.* 1954, 39, 92.

unfortunately, these conditions do not obtain.

Measurements on many zeolites have established a strong dependence of the isotropic ²⁹Si chemical shift of a particular silicon environment on framework topology.^{8,9,11-15} Where crystallographically distinct sites are present in one framework, for example, silicalite, a multiplicity of NMR absorptions due to structurally inequivalent silicons are observed.¹¹ The possibility of resolving NMR signals for crystallographically inequivalent silicons was first recognized by Lippmaa et al.¹⁸ in a study of albite. In cases where this structural effect is superimposed on the chemical shift effects due to aluminum substitution, a complex spectrum results. An example is provided by synthetic mazzite,^{13,15} the structure of which is shown in Figure 1.^{16,17} The structure consists of chains of fused gmelinite cages linked into a hexagonal array in an unusual way through the 4-rings. Two crystallographic sites are present: one in the 6-ring (T₆) and the other in the 4-ring (T₄). At a composition Si/Al equal to 3, six resolved peaks are evident in the ²⁹Si NMR spectrum, which implies that some must be composed of overlapping absorptions due to chemically different silicon environments arising from the two crystallographic sites. In such a case, calculations of Si/Al ratios from the ²⁹Si NMR data cannot be made without specifying the partitioning of aluminum atoms between the crystallographically inequivalent sites.

In this paper we describe an approach to the interpretation of the spectra of synthetic mazzites which uses the knowledge of chemical shift effects due to framework topology and gallium substitution,¹⁹ and Si-Al distributions,⁶ available from other well-characterized materials.

Preparation of Mazzite and Gallium-Substituted Mazzite

The preparation of mazzite followed generally the procedures described for ZSM4^{20,21} and omega.²² A gel was prepared by blending together solutions containing tetramethylammonium (TMA) hydroxide (25% aqueous solution, R.S.A. Corp.) and sodium aluminate (Baker); sodium silicate (28.7% SiO₂ aqueous solution, P.Q. Corp.); and aluminum sulfate (Al₂(SO₄)₃·18H₂O, Baker) to give a mixture having the overall composition 1.2TMA₂O:4.8Na₂O:Al₂O₃:15SiO₂:240H₂O. The gel was heated in a sealed teflon bottle for 1 week at 100 °C. The solid product was filtered, washed with distilled water, and dried in air at 100 °C.

A gallium-substituted material was prepared by a similar procedure. A slurry of gallium oxide (Ga₂O₃, K.B.I. Inc.) in a solution of NaOH and TMAOH was mixed with sodium silicate solution. A seeding mixture²³ having the composition 13.3Na₂O:Al₂O₃:12.5SiO₂:267H₂O was added to give 1% Al₂O₃ per mol of Ga₂O₃. A small quantity of sulfuric acid was added to neutralize excess base. The overall composition of the parent gel was 0.7TMA₂O:2.8Na₂O:Ga₂O₃:11SiO₂:240H₂O. After 3 days of heating at 100 °C, the pure solid product was obtained as described previously.

The two products were characterized by elemental analysis using a Jarrel-Ash inductively-coupled plasma spectrometer, powder

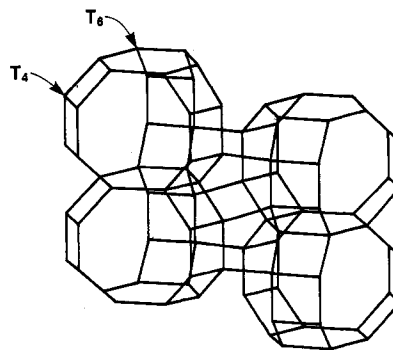


Figure 1. Crystal structure of mazzite.

X-ray diffraction, and scanning electron microscopy. The analytical data are given in Table I. All reflections in the powder X-ray patterns of the two materials could be indexed on the basis of the mazzite hexagonal unit cell. Reflections with hhl ($l = 2n + 1$) were absent, consistent with space group $P6_3/mmc$ proposed by Galli¹⁷ but not with the space group $P6_3/mmm$ for the structure of omega proposed by Barrer and Villiger.²⁴ The refined unit cell dimensions are given in Table I. The unit cell of the gallium-substituted material is slightly larger than its aluminum analogue, consistent with the Ga-O bond being longer than Al-O. The reflections in the X-ray pattern of gallium mazzite were sharp and well-resolved, allowing precise indexing, particularly in regions of closely spaced reflections. The strong reflection with $d = 3.162$ Å was indexed as 500 ($d_{\text{calcd}} = 3.162$ Å) rather than 411 ($d_{\text{calcd}} = 3.146$ Å), contrary to Klinowski et al.²⁵

Scanning electron micrographs showed that gallium mazzite had a well-developed hexagonal-prismatic morphology in contrast to the aluminum material which was in the form of very small spheulitic aggregates, this being consistent with some peak broadening observed in the X-ray pattern of the Al compound. High-resolution ²⁹Si NMR spectra of the materials were obtained on a JEOL FX200 WB spectrometer operating at 4.7 T, using the combined techniques of magic-angle spinning and proton dipolar decoupling. Chemical shift data and integrated intensities are given in Table II.

Chemical Shift Effects

Framework Topology and Gallium Substitution. The work of Smith and Blackwell on silica polymorphs has established a quantitative relationship between the ²⁹Si NMR chemical shift and the structure as described by Si-O-Si angles.²⁶ The linear relationship between chemical shifts and $\sec(\text{SiOSi})$ enables accurate predictions of the former from crystallographic data. For the silicas the structures are accurately determined. For a zeolite, however, a dispersion of chemical environments is present due to the presence of aluminum in the structure, and crystallography measures only an average structure. Therefore, the geometry about any one silicon environment cannot be determined precisely since it is averaged over all the possible aluminum nearest-neighbor distributions. In addition, the chemical shift of a particular absorption shows some compositional dependence⁴ adding a further complication. Nevertheless, by choosing the values of chemical shift for Si(4Si) components of zeolite spectra at compositions close to those for which structural data are available, it is apparent that the correlation determined for pure silicas also applies for zeolites (Figure 2). This idea has been proposed previously^{8,9,12-14} and recently examined in detail by Ramdas and Klinowski.²⁷ The available structural data for mazzite has been used in this work to predict the values of chemical shift for the Si₄(4Si) and Si₆(4Si) components.

(11) Fyfe, C. A.; Gobbi, G. C.; Klinowski, J.; Thomas, J. M.; Ramdas, S. *Nature, (London)* **1982**, 296, 530.

(12) Jarman, R. H. *J. Chem. Soc., Chem. Commun.* **1983**, 512.

(13) Thomas, J. M.; Klinowski, J.; Ramdas, S.; Hunter, B. K.; Tennakoon, D. T. B. *Chem. Phys. Lett.* **1983**, 102, 158.

(14) Fyfe, C. A.; Gobbi, G. C.; Murphy, W. J.; Ozubko, R. S.; Slack, D. A. *Chem. Lett.* **1983**, 1547.

(15) Fyfe, C. A.; Gobbi, G. C.; Kennedy, G. J.; De Schutter, C. T.; Murphy, W. J.; Ozubko, R. S.; Slack, D. A. *Chem. Lett.* **1984**, 163.

(16) Galli, E.; Passaglia, E.; Pongiluppi, D.; Rinaldi, R. *Contrib. Mineral. Petrol.* **1974**, 45, 99.

(17) Galli, E. *Cryst. Struct. Commun.* **1974**, 3, 339.

(18) Lippmaa, E.; Magi, M.; Samoson, A.; Engelhardt, G.; Grimmer, A.-R.; *J. Am. Chem. Soc.* **1980**, 102, 4889.

(19) Vaughan, D. E. W.; Melchior, M. T.; Jacobson, A. J. *A.C.S. Symp. Ser.* **1983**, 218, 231.

(20) Ciric, J. U.K. Patent 1 117 568, 1968; U.S. Patent 3 923 639, 1975.

(21) Rubin, M. K.; Rosinski, E. J. U.S. Patent 4 331 643, 1982.

(22) Flanigen, E. M.; Kellberg, E. R. U.K. Patent 1 178 186, 1970; U.S. Patent 4 241 036, 1980.

(23) Vaughan, D. E. W.; Edwards, G. C.; Barrett, M. G. U.S. Patent 4 340 573, 1982.

(24) Barrer, R. M.; Villiger, H. *J. Chem. Soc., Chem. Commun.* **1969**, 659.

(25) Klinowski, J.; Anderson, M. W.; Thomas, J. M. *J. Chem. Soc., Chem. Commun.* **1983**, 525.

(26) Smith, J. V.; Blackwell, C. S. *Nature (London)* **1983**, 303, 223.

(27) Ramdas, S.; Klinowski, J., private communication.

TABLE I

sample	starting material					product				unit cell dimensions ^a	
	TMA ₂ O	Na ₂ O	T ₂ O ₃	SiO ₂	H ₂ O	TMA ₂ O	Na ₂ O	T ₂ O ₃	SiO ₂	a ₀ /Å	c ₀ /Å
Al-mazzite	1.2	4.8	1	15	240	0.18	0.82	1	6.2	18.143 (7)	7.611 (3)
Ga-mazzite	0.7	2.8	1	11	240	0.22	0.78	1	6.12	18.262 (5)	7.668 (3)

^aHexagonal.TABLE II: Chemical Shifts (ppm vs. Me₄Si) and Relative Intensities of NMR Spectra

k	4	3	2	1	1'	0
Al-Mazzite						
δ	-89.1	-93.7	-98.8	-103.4	-107.0	-112.0
I _k	0.046	0.248	0.408	0.113	0.130	0.056
Si ₆ (nAl)	4	3	2		1	0
Si ₄ (nAl)	3	2	1	0		
Ga-Mazzite						
δ	-84.6	-91.6	-98.2	-105.3		-112.7
I _k	0.048	0.263	0.405	0.224		0.060
Si ₄ (nGa)	4	3	2	1		0
Si ₆ (nGa)	3	2	1	0		
2-Neighbor Distributions for Subunits in Figure 4						
Si(nAl)		2		1		0
T ₆				6		3
T ₄				12		6
Calculated Spectrum for Al-Mazzite at Si/Al = 3.1 (p* = 0.323)						
k	4	3	2	1	1'	0
I _k	0.045	0.235	0.407	0.109	0.150	0.054

In addition, it has been shown previously that in gallium-substituted faujasites the paramagnetic shift of Si in a pure gallium material compared to its aluminum analogue is directly proportional to the number of nearest-neighbor gallium atoms about that silicon.¹⁹ The Si(4Si) absorptions have the same chemical shift in both materials. The gallium shift has been used to identify particular silicon environments by comparing ²⁹Si NMR spectra of corresponding pairs of aluminum and gallium materials.

Assignment of the Mazzite Spectrum. With the structural data for mazzite determined by Galli,¹⁷ the values of chemical shift predicted from Figure 2 are -111.9 and -104.8 ppm for the Si₆(4Si) and Si₄(4Si) absorptions, respectively. The calculated values are in reasonable agreement with those reported by Thomas et al.¹³ for completely dealuminated synthetic mazzite (-114.4 and -106.0 ppm for Si₆(4Si) and Si₄(4Si)). We assign peaks 0 and 1 at -112.0 and -103.4 ppm, respectively, to these two silicon environments (Table II). Using the chemical shift data in Table II and applying the usual Al shift dependence, we accordingly assigned the rest of the spectrum of Al-mazzite (Figure 3). The Ga-mazzite spectrum strongly supports this assignment (Table II and Figure 3). In particular, the paramagnetic shift associated with replacing Si₆(1Al) with Si₆(1Ga) causes the absorption to become merged with that due to Si₄(4Si) which is the same in both spectra. The relative intensity of absorption 1 of Ga-mazzite is nearly equal to the sum of 1 and 1' of Al-mazzite, entirely consistent with the above interpretation. This assignment is in agreement with that determined independently by Fyfe et al.¹⁵ by comparison of the NMR spectra of aluminum-mazzite and its completely dealuminated analogue. The chemical shifts they reported for Si₄(0Al) and Si₆(1Al) of -103.5 and -106.8 ppm¹⁵ are in excellent agreement with the values given in Table II.

Further evidence for the assignment is provided by a comparison of the Si/T ratios determined by chemical analysis and from the ²⁹Si NMR data. In order to determine the ratio from the NMR data, it is assumed that the partitioning of T atoms between the two sites is equal to the site density (T₄:T₆ = 2). Galli¹⁷ found no evidence in the crystallographic data for Al-mazzite that suggested preferential occupation of either site by Al. A recent neutron diffraction determination of the structure of Ga-mazzite also shows no Ga site preference.²⁸ The relation between the Si/T

ratio and the NMR peak intensities for the case of the two inequivalent sites in mazzite, assuming Lowenstein's rule, is given by

$$\text{Si/T} = \frac{4 + (f^A - f_T^A)}{\sum_k I_k - f^A} \quad (1)$$

where A refers to the four-ring site, f^A is the fraction of crystallographic sites of type A, f_T^A is the fraction of T atoms (Al or Ga) in site A, and k and I_k are defined in Table II. Note that for Al-mazzite, the intensity corresponding to $k = 1$ is the sum of the intensities labeled 1 and 1'. For the case of T atoms randomly partitioned between the two sites, eq 1 reduces to

$$\text{Si/T} = \frac{4}{\sum_k I_k - \frac{2}{3}} \quad (2)$$

The derivation of eq 1 for a more general case is given in Appendix 1. The derivation is independent of the details of the Si and T atom distribution within each site.

Analysis of the intensity data given in Table II using eq 2 gives NMR compositions Si/Al = 3.03 and Si/Ga = 2.97 for the two zeolites. These results are in excellent agreement with the chemical analysis values of Si/Al = 3.1 and Si/Ga = 3.06 in support of the spectral assignments. Note that it follows from eq 1 that, once the assignment has been established, the elemental analysis may be used together with the ²⁹Si NMR intensities to determine the T atom partitioning between the two sites provided the material does not contain amorphous or detrital oxide phases. However, the method of determination is less sensitive than direct measurement by ²⁷Al NMR at high field.^{15,25}

With the above assignment a model for the Si-Al(Ga) distribution in mazzite is proposed which is consistent with the crystallographic data¹⁴ and previous studies of Si-Al distributions.³ A set of Si, Al subunits were chosen such that, within the set, Al atoms are arranged subject to Lowenstein's rule and minimization of next-nearest neighbors. At the composition of Si/Al = 3.0 the subunits are as in Figure 4. The two-neighbor distributions for the subunits are given in Table II. The full structure is generated from these units by using statistics and Lowenstein's rule. At this high Si/Al ratio (low Al concentration) topological constraints on the connectivity of the subunits can be ignored, and it may

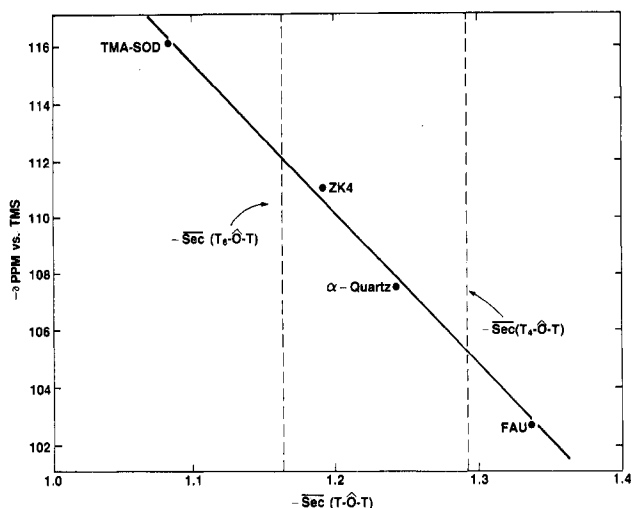


Figure 2. Chemical shift of the Si(4Si) absorption vs. average secant of T-O-T angle for some well-characterized zeolites.

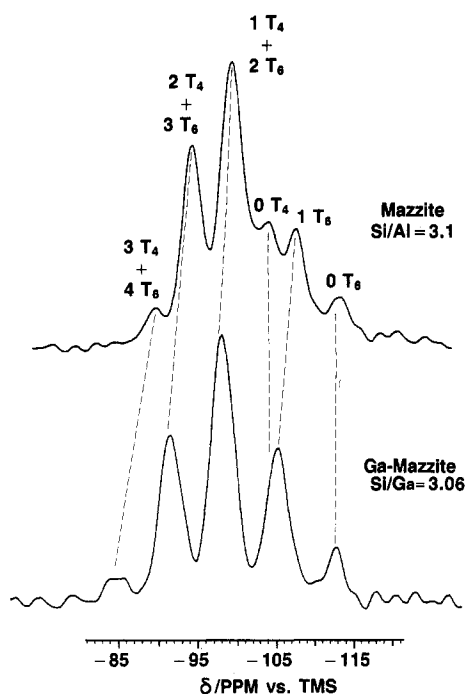


Figure 3. Assignment of spectra for aluminum and gallium mazzites.

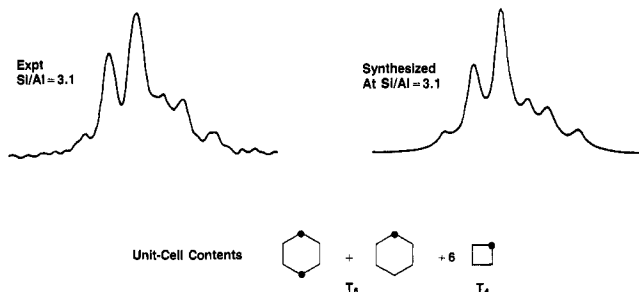


Figure 4. Comparison of the observed ²⁹Si NMR spectrum of aluminum mazzite (Si/Al = 3.1) with a theoretical spectrum synthesized from a model for the Si-Al distribution described in the text.

be assumed that the probability of adding an aluminum atom in each successive step (p^+) is the same for all Si atoms and equal to the ensemble average of $1/(\text{Si}/\text{Al})$. The resulting distribution shown in Table II was calculated for a Si/Al ratio of 3.1, the experimental value. The subunits for this are obtained from the

set for Si/Al = 3.0 by replacing 0.22 Al by Si per unit cell. A spectrum synthesized from these intensity data is compared with the experimental one in Figure 4. The agreement is exceptionally good.

The Al partitioning between the two sites has been taken to be random as discussed above, although the predicted spectral intensities are insensitive to small variations in this partitioning. The spectra are sensitive, however, to introducing next-nearest-neighbor interactions in the subunits, i.e., using 4-rings containing 2Al atoms. Using a set of 4-ring subunits, containing 2, 1, and 0 Al atoms causes significant deviations from the observed intensities. The predicted intensities of the Ga-mazzite spectrum from the same model are obtained by summing components 1 and 1' of Table II; the values are again in good agreement with the observed intensities.

Conclusion

Interpretation of the ²⁹Si NMR spectrum of mazzite, which has a structure containing inequivalent crystallographic silicon atoms, has been achieved by using existing information about the sensitivity of ²⁹Si NMR chemical shifts to framework topology and gallium substitution. The resulting assignment has been substantiated by comparison of the compositions determined by NMR and elemental analysis and by using a chemically plausible model for the Si-Al distribution to calculate the spectral intensities. The model was based on an ordered set of 4-ring and 6-ring units within which Al atoms were divided in the ratio 2:1. The calculated peak intensities are quite insensitive to the exact partitioning of Al atoms between sites but strongly dependent upon the distribution of subunits. This example further demonstrates the subtle dependence of next-nearest-neighbor effects on framework topology. In the case of faujasite the next-nearest-neighbor interactions are fully described by ordering within the 6-ring units, whereas in mazzite the interaction is apparently manifested in the narrow distribution of 4-ring units, each of which contains no intrinsic order.

Acknowledgment. We thank C. F. Pictroski and H. J. Malone for assistance in obtaining the NMR spectra, and Dr. D. E. W. Vaughan for guidance in the synthesis of zeolites.

Appendix

For zeolites containing crystallographically inequivalent silicons the ²⁹Si NMR spectrum can be considered as the superposition of several sets of intensities, each arising from the various Al neighbor environments for Si in a particular crystallographic site. The derivation of the Si/Al ratio from the NMR data is complex. Here we show how the composition can be derived for the case of two inequivalent sites, A and B, when there is a constant offset of the two sets of peaks. That is to say the NMR intensity for Si in site A having n Al neighbors is superimposed on the intensity from Si in site B having n' Al neighbors with a constant integer offset $\delta = n' - n$.

The observed normalized intensities I_k may then be written

$$I_k = I_{k-\delta}^A + I_k^B \quad (\text{A.1})$$

provided we define $I_k^{A(B)} = 0$ unless $0 \leq k \leq 4$. In some cases, it is necessary to combine two observed intensities as, for example, peaks 1 and 1' (Table II) were combined for Al-mazzite. The average number of Al neighbors about silicon, $\overline{\text{Al}}$, is given by

$$\overline{\text{Al}} = \sum_{j=0}^4 j I_j^A + \sum_{j=0}^4 j I_j^B \quad (\text{A.2})$$

which can be rewritten as a single sum.

$$\begin{aligned} \overline{\text{Al}} &= \sum_{k=0}^{4+\delta} \{(k-\delta) I_{k-\delta}^A + k I_k^B\} \\ &= \sum_k k I_k - \delta f_{\text{Si}}^A \end{aligned} \quad (\text{A.3})$$

where $f_{\text{Si}}^{\text{A}} = \sum_k I_{k-\delta}^{\text{A}}$ is the fraction of the total Si in site A. For the general case in which the partitioning of Al and Si between sites A and B is different we can write

$$f_{\text{Si}}^{\text{A}} = f^{\text{A}} + 1/R(f^{\text{A}} - f_{\text{Al}}^{\text{A}}) \quad (\text{A.4})$$

where f^{A} is the fraction of crystallographic sites of type A, f_{Al}^{A} is the fraction of total aluminum in site A, and R is the Si/Al ratio.

Assuming that Lowenstein's rule is obeyed we have the relation³

$$\overline{\text{Al}} = 4/R \quad (\text{A.5})$$

which combined with (A.3) and (A.4) gives the silicon to aluminum ratio.

$$R = \frac{4 + \delta(f^{\text{A}} - f_{\text{Al}}^{\text{A}})}{\sum_k k I_k - \delta f^{\text{A}}} \quad (\text{A.6})$$

Note that the sum over I_k is known from the ^{29}Si NMR data, f^{A} from the crystal structure, and f_{Al}^{A} may, in principle, be determined from high-field ^{27}Al NMR.

Registry No. ^{29}Si , 14304-87-1.

Interaction of Surface Hydroxyls with Adsorbed Molecules. A Quantum-Chemical Study

Paul Geerlings,

Vrije Universiteit Brussel, Eenheid Algemene Chemie, Pleinlaan 2, B-1050 Brussel, Belgium

Nicolas Tariel, Alain Botrel, Roland Lissillour,

Laboratoire de Chimie Theorique—L.A. CNRS 254, Université de Rennes, Campus de Beaulieu, F-35042 Rennes-Cedex, France

and Wilfried J. Mortier*

K.U. Leuven, Laboratorium voor Oppervlaktischeikunde, Kard. Mercierlaan 92, B-3030 Leuven (Heverlee), Belgium (Received: April 3, 1984; In Final Form: June 1, 1984)

An attempt has been made to rationalize the interaction mechanisms of (bridging and terminal) surface hydroxyl groups with molecules, using ab initio, EHT, and CNDO/2-FA quantum-chemical calculations. Bond strength variations and charge shifts were found to be in complete agreement with Gutmann's rules, and provide a basis for the understanding of the Brønsted acid properties of zeolites and amorphous silica-alumina. A quantitative measure of the interaction strength is possible by referring to the experimentally determined donor number (Gutmann) following many molecules, but care should be taken for those molecules for which the donor strength was determined by indirect methods. Only a few exceptions to Gutmann's rules should exist, e.g., in those cases where the atom interacting with the proton is not the most electronegative of the donor molecule (such as for CO). Individual bonds in a given complex are more susceptible to perturbations (changes in composition and interactions with adsorbing molecules) if the coordination number increases. These rules are in agreement with the observations and apply to all reactions (inter- or intramolecular) involving a change in coordination.

Introduction

Insight into the properties of the surface hydroxyls of amorphous silica-alumina and of zeolites forms the basis of the scientific understanding of surface reactions and of catalytic processes. Apart from the intrinsic properties of these hydroxyls, which are more or less easily estimated, a prediction of their reactivity is far more complex. The intrinsic properties are being probed by a variety of physicochemical techniques and among the most important the following may be cited: IR spectroscopy (most recent publications on zeolites, silica gel, and aluminosilicates: Kustov et al.;¹ on amorphous silica-alumina: Borovkov et al.²

and Bremer et al.³) and NMR (most recent work on amorphous aluminosilicates: Freude et al.;⁴ and for silica gel, aluminum oxides, and zeolites: Freude et al.⁵). A consistent picture of the fundamental difference between hydroxyls of high and low acidity has emerged from both experiments and theoretical calculations, i.e., the structural distinction between "bridging" and "terminal" hydroxyls.⁶ Incompletely polymerized silicic acid ($\text{Si}(\text{OH})_4$), for

(2) Borovkov, V. Yu.; Alexeev, A. A.; Kazansky, V. B. *J. Catal.* **1983**, *80*, 462.

(3) Bremer, H.; Jank, M.; Fahlke, B.; Starke, P.; Wendlandt, K. P. *Z. Anorg. Allg. Chem.* **1983**, *500*, 51.

(4) Freude, D.; Pfeiffer, H.; Bremer, H.; Jank, M.; Wendlandt, K. P. *Chem. Phys. Lett.*, in press.

(5) Freude, D.; Hunger, M.; Pfeiffer, H. *Chem. Phys. Lett.* **1982**, *91*, 307.

(1) Kustov, L. M.; Borovkov, V. Yu.; Kazansky, V. B. *J. Catal.* **1981**, *72*, 149.