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Applications of NMR Spectroscopy to the Study of Zeolite Synthesis

A.T. Bell

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Applications of NMR Spectroscopy
to the Study of Zeolite Synthesis

by

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APPLICATIONS OF NMR SPECTROSCOPY TO THE STUDY OF ZEOLITE SYNTHESIS

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NMR spectroscopy is a powerful technique for identifying the structure and concentration of silicate and aluminosilicate anions in gels and solutions used for zeolite synthesis. A review is presented of the types species that have been observed and the dependence of the distribution of these species on pH and the nature of the cations present.

Introduction

The synthesis of zeolites occurs from solutions or gels containing a broad spectrum of silicate and aluminosilicate anions. Since some of these species resemble secondary building units, it has been postulated that zeolite formation is nucleated by the condensation-polymerization of SBU's and that subsequent crystal growth proceeds via the addition of SBU's to the surface of the growing crystallites [1]. Because the growth of a given zeolite involves only one SBU, or at most a small number of SBU's, there has been a strong interest in identifying the conditions which maximize the concentration of a desired SBU.

NMR spectroscopy is ideally suited for characterizing the silicate and aluminosilicate species present in the media from which zeolites are formed. The nuclei observable include ^{29}Si , ^{27}Al , and all of the alkali metal cations. The largest amount of information has come from ^{29}Si spectra [1-3]. This nucleus has a spin of 1/2, no quadrupole moment, and a chemical shift range of about 60 ppm. As a consequence, it is possible to identify silicon atoms in specific chemical structures. ^{27}Al , on the other hand, is a spin 3/2 nucleus and has a sizeable quadrupole moment. This results in broad lines and limits the amount of information that can be extracted from ^{27}Al spectra.

In this paper we shall summarize our recent findings concerning the nature and distribution of species present in silicate and aluminosilicate solutions and gels. Particular attention will be focused on establishing the effects of pH, cation composition, Si/Al ratio, and solvent composition.

Silicate Solutions

Figure 1 illustrates a high resolution ^{29}Si spectrum for a sodium silicate solution [4,5]. The individual resonances comprising this spectrum are grouped into bands each of

which is designated as Q^n . In this notation, Q represents a silicon bonded to four oxygen atoms forming a tetrahedron. The superscript n indicates the connectivity of the designated tetrahedron to nearest-neighbor tetrahedra. Thus, Q^0 denotes the monomeric anion SiO_4^{4-} , Q^1 end-groups of chains, Q^2 middle groups in chains or cycles, Q^3 chain branching sites, and Q^4 three-dimensionally cross-linked groups. The degree of protonation is ignored in this description.

Many of the individual lines observed in spectra such as those shown in Figure 1 can be assigned to specific silicate structures based on spectra of well defined silicate species and detailed NMR studies of the homonuclear spin-spin coupling of ^{29}Si nuclei in ^{29}Si -enriched silicate solutions [6-8]. Such studies have revealed that the chemical shift of a given silicon atom depends on its connectivity, the length of the Si-O bonds, and the angle of Si-O-Si bonds, as well as the pH of the medium and the cation type. As a consequence the transference of assignments made for one silicate solution to another must be carried out with caution.

Approximately 85% of the of the peak area shown in Figure 1 can be assigned to 19 specific silicate structures [4,5]. A schematic of these structures is presented in Table I, together with the chemical shift for each distinct silicon atom. It is evident from this table that silicate oligomers tend to occur as single and multiple ring structures, rather than as linear chains.

If proper care is taken in the acquisition of Si NMR spectra, then all of the dissolved silicon will be expressed in the spectrum. In this case, the peak integral is directly related to the fraction of Si present as that spin, and the molar concentration of the anion is given by the ratio of the peak integral and the number of such identical spins in an anion.

The distribution of silicon amongst the different structures listed in Table I is a strong function of the silicate ratio, R, where $R = [SiO_2]/[Na_2O]$. The dependence of anion mole percentages on silicate ratio is given in Table II. The response of the anion distribution to the silicate ratio falls into one of three general classes. For monomer (1), dimer (2), linear trimer (3), cyclic trimer (4), branched cyclic trimer (7), bridged cyclic trimer (9), and pentacyclic heptamer (16), the anion percentages decrease monotonically with increasing silicate ratio. The linear tetramer (5), cyclic tetramer (6), branched cyclic tetramer (8), bicyclic pentamer (10), tricyclic hexamer (11), cis- and trans-tricyclic hexamers (12,13), and hexacyclic octamer (18) each exhibit a maximum mole percentage as the silicate ratio increases. Only the cubic octamer (17) and the double hexamer (19) show monotonic increase in mole percentage.

From Table II it is apparent that there are distinct ranges of the silicate ratio in which particular anions are maximized. These ranges are not governed by anion size alone. For example, the large pentacyclic heptamer is present only at silicate ratios typically characterized by high concentrations of monomer and dimer. The connectivity distribution suggests that anions with higher average connectivity tend to achieve maximum concentration at high silicate ratio. For example, the pentacyclic heptamer level is maximum at lower R than the hexacyclic octamer. Furthermore, for anions with the same number of Si atoms, a linear structure will establish maximum level at lower R than will a cyclic structure; this relationship is evidenced by the behavior of the linear and cyclic trimers and tetramers. Finally, structures with only trimeric cyclic units peak at lower R than structures with both cyclic trimeric and larger cyclic units. As the number of three-membered rings decreases or the the number of other rings increases, so does the value of R at the maximum level. This trend may be the result of

Table 1 Assignment of ^{29}Si NMR Peaks

No.	Structure	R = 1.0	1.5	2.0	2.5	3.0
1		18.0	6.0	-5.0	6.0	5.0
2		5.2	1.5	1.2	0.9	1.1
3		2.4	1.0	1.2	0.7	0.7
4		2.8	1.6	0.6	0.3	-0
5		1.0	1.1	0.5	-0	-0
6		-0	0.3	1.2	0.6	n.o.
7		2.0	1.0	0.9	0.2	-0
8		2.0	2.1	3.3	1.8	1.7
9		0.5	0.5	0.5	-0	-0
10		1.0	1.7	-0	-0	-0
11		-0	0.8	1.8	0.8	0.6
12		-0	0.4	0.3	-0	-0
13		-0	0.4	0.3	-0	-0
14		0.3	0.5	0.7	-0	-0
15		0.4	0.6	1.4	0.3	0.3
16		0.4	-0	-0	-0	-0
17		0	0	0.1	n.o.	n.o.
18		0.2	0.3	0.2	n.o.	n.o.
19		0	0.1	0.2	0.2	0.3

n.o. - not observable

Table 2 Effect of Silicate Ratio on the Percentage of SiO_2 in a Given Silicate Ion

No. (1)	Structure	$ \delta_{\text{Si}} $ (ppm)			
		Peak 1A	Peak 1B	Peak 1C	Peak 1D
1		0	0	-	-
2		8.20-8.70	-	-	-
3		7.90-8.20	16.80-16.83	-	-
4		10.02-10.12	-	-	-
5		7.95-8.28	a	-	-
6		16.01-16.19	-	-	-
7		7.80-8.10	9.70-9.80	18.09	-
8		a	15.66-15.96	a	24.02-24.10
9		14.06-14.28	21.90-22.05	-	-
10		9.79-9.89	16.31-16.53	16.95-17.25	-
11		15.94-16.11	16.42-16.59	17.48-17.75	24.77-24.92
12		10.38-10.43	a	-	-
13		10.55-10.57	18.12	-	-
14		14.45-14.68	21.29-21.53	-	-
15		17.11-17.43	-	-	-
16		a	17.22	18.79	-
17		27.50	-	-	-
18		a	20.62	26.82	-
19		25.41-25.48	-	-	-

a Not positively identified

b Capital letter identifies specific Si spin environments

bond-angle stability. Higher R solutions may encourage the predominance of larger Si-O-Si bond angles.

At a fixed silicate ratio, the distribution of silicate structures is affected by the nature of the cation. An illustration of this effect is shown in Figure 2 for the alkali metal cations [9]. As the size of the cation increases, the extent of oligomerization increases. This trend is clearly seen in Figure 3, which represents the distribution of Si among different connectivity states. Since the pH of silicate solutions is unaffected by the nature of the cation, the influence of cation size on the extent of oligomerization has been ascribed to the formation of cation-anion pairs. Results from alkali metal cation NMR spectroscopy provide direct evidence for the presence of cation-silicate anion pairs and indicate that the extent of pair formation increases with increasing cation size [10]. It has been proposed that the formation of such pairs stabilizes the anionic species to hydrolysis and explains the increase in oligomerization with increasing pair formation.

When organic cations are used instead of alkali metal cations, the distribution of silicate species observed at a given silicate ratio is narrower. Figure 4 shows a series of spectra for tetraalkylammonium (TAA) silicate solutions. The solution prepared with tetramethylammonium hydroxide (TMAOH) exhibits four dominant features which in order of increasing shielding are due to monomer, dimer, cyclic trimer, bicyclic hexamer (D3R), and cubic octamer (D4R). As the length of the alkyl branches increases, the D4R structure rapidly disappears and the spectrum is dominated by the smaller silicate oligomers. The strong dependence of the concentration of D4R on the structure of the TAA cation is observed when only one of the four methyl groups in TMA^+ is substituted, as can be seen in Figure 5. Since TAA^+ cations are large compared to alkali metal cations, extensive cation-anion pairing is not expected. As a consequence the observed effect of cation structure on the distribution of silicate species must be ascribed to other causes. One hypothesis is that the hydrophobic surface of TAA^+ cations plays a role in organizing monomeric silicate anions into larger structures. The exact means by which this occurs is not understood and is a subject of current research.

The reactivity of silicate anions can be determined from the rate of Si exchange between anions. Attempts to estimate Si exchange rates from an analysis of ^{29}Si NMR lineshapes have been made, but the accuracy of this technique has been limited by the current understanding of ^{29}Si spin relaxation mechanisms [11-13]. Accurate determinations of the rate of Si exchange between anions can be obtained, however, from an analysis of selective spin inversion experiments [14-16]. Figure 6 illustrates the spectra resulting from the selective spin inversion of the monomer peak in a potassium silicate solution containing only monomer, dimer, and cyclic trimer anions [16]. These spectra are interpreted on the assumption that Si exchange occurs via the following two reactions:

1. $\text{M} + \text{M} = \text{D}$
2. $\text{M} + \text{D} = \text{c-T}$

where M = monomer, D = dimer, and c-T = cyclic trimer. The rate coefficients for reactions 1 and 2 can be determined from simulations of the time evolution of inverted spins. Of significant interest is the recent observation that these rate coefficients are a function of the nature of the cation. As can be seen in Figure 7, the rate coefficient for reaction 1 is greatest for K^+ and the rate coefficient for reaction 2 is greatest for Na^+ . The effects of cations on the dynamics of Si exchange have been attributed to the formation of cation-anion pairs.

Aluminosilicate Solutions

The silicate species discussed in the preceding section can react with aluminate anions, $\text{Al}(\text{OH})_4^-$ to produce aluminosilicate anions. ^{29}Si NMR spectra of solid silicates and aluminosilicates indicate that the replacement of Si by Al in the second coordination sphere of a given Si causes a low-field shift of about 5 ppm. Since each Si atom can have up to four metal atoms in its second coordination sphere, fifteen possible $\text{Q}^n(\text{mAl})$ structural units can be envisioned. The estimated chemical shift ranges for these units are given in Table 3. It is apparent from this table that the ^{29}Si spectrum of an aluminosilicate solution in which Al and Si atoms were statistically distributed would be much more complex than that of an analogous solution containing only silicate species.

Because of the quadrupolar nature of Al, ^{27}Al NMR spectra of aluminosilicate solutions exhibit broad lines from which it is possible to determine the coordination of Al and its connectivity with Si, but the precise environment of each Al atom cannot be defined. A peak for $\text{Al}(\text{OH})_4^-$ is observed at 75 - 79 ppm, and up to three peaks in the range 58 - 72 ppm which have been assigned to various $\text{Al}(\text{OSi})_n(\text{O}^-)_{4-n}$ building units.

The structure of aluminosilicate species formed upon mixing silicate and aluminate solutions is a strong function of the compositions of both solutions and the nature of the cation. Figure 8 shows a series of ^{29}Si and ^{27}Al spectra taken after addition of sodium aluminate to a silicate solution containing only monomeric silicate anions [17]. The presence of aluminate anions results in no new features in the ^{29}Si spectrum, but only an upfield shift in the one observable peak. The ^{27}Al spectrum shows a weak feature upfield of the strong peak for $\text{Al}(\text{OH})_4^-$. The observation of only a single ^{29}Si peak suggests that the Si atoms are in rapid exchange between isolated $[\text{Si}(\text{OH})_{4-x}\text{O}_x]^{x-}$ species and aluminosilicate structures. Based on the position of the ^{29}Si peak in the solution prepared with a Si/Al ratio of 2, the aluminosilicate species is proposed to be an aluminodisilicate anion.

^{29}Si and ^{27}Al spectra obtained upon addition of sodium aluminate to a solution containing monomer, dimer, and cyclic trimer silicate anions is shown in Figure 9 [17]. The ^{29}Si spectrum of the aluminosilicate solution shows a preferential attenuation of the peak associated with the cyclic trimer, while the ^{27}Al spectrum shows the appearance of features attributable to Al atoms attached to one and two silicate tetrahedra. The higher reactivity of the cyclic trimer may be due to the strained character of the three membered ring.

Studies of aluminate reaction with TAA silicate solutions have also yielded interesting results. For example, Englehardt and Michel [2] have shown convincing evidence for a D3R structure containing one Al atom in a TEA aluminosilicate solution. In other studies, Englehardt et al. [18] have found that TMA silicate solutions containing primarily D4R units do not react with TMA aluminate solutions at room temperature. Upon heating, though, the DAR silicate structure decomposes to produce a variety of aluminosilicate species.

Aluminosilicate Gels

At the concentration levels characteristic of zeolite synthesis, highly viscous gels are formed upon mixing silicate and aluminate solutions. The use of liquid-line NMR techniques to observe such gels results in very broad spectral features due to the fact

Table 3 Estimated ^{29}Si Chemical Shift Ranges of Q^n and $\text{Q}^n(\text{mAl})$
Structural units of Silicate and Aluminosilicate Anions in Solutions (18)

Q unit	Structure	$-\delta(\text{ppm})^a$	Q unit	Structure	$-\delta(\text{ppm})^a$
Q^0	$\begin{array}{c} \text{O} \\ \text{OSiO} \\ \text{O} \end{array}$	66–73	$\text{Q}^3(3\text{Al})$	$\begin{array}{c} \text{O} \\ \text{AlOSiOAl} \\ \text{O} \\ \text{Al} \end{array}$	ca 85
Q^1	$\begin{array}{c} \text{O} \\ \text{OSiOSi} \\ \text{O} \end{array}$	76–83	Q^4	$\begin{array}{c} \text{Si} \\ \text{O} \\ \text{SiOSiOSi} \\ \text{O} \\ \text{Si} \end{array}$	103–120
$\text{Q}^1(1\text{Al})$	$\begin{array}{c} \text{O} \\ \text{OSiOAl} \\ \text{O} \end{array}$	ca 75			
Q^2	$\begin{array}{c} \text{O} \\ \text{SiOSiOSi} \\ \text{O} \end{array}$	86–91	$\text{Q}^4(1\text{Al})$	$\begin{array}{c} \text{Si} \\ \text{O} \\ \text{SiOSiOAl} \\ \text{O} \\ \text{Si} \end{array}$	97–105
$\text{Q}^2(1\text{Al})$	$\begin{array}{c} \text{O} \\ \text{SiOSiOAl} \\ \text{O} \end{array}$	ca 85			
$\text{Q}^2(2\text{Al})$	$\begin{array}{c} \text{O} \\ \text{AlOSiOAl} \\ \text{O} \end{array}$	ca 80	$\text{Q}^4(2\text{Al})$	$\begin{array}{c} \text{Si} \\ \text{O} \\ \text{AlOSiOAl} \\ \text{O} \\ \text{Si} \end{array}$	92–99
Q^3	$\begin{array}{c} \text{O} \\ \text{SiOSiOSi} \\ \text{O} \\ \text{Si} \end{array}$	95–101	$\text{Q}^4(3\text{Al})$	$\begin{array}{c} \text{Al} \\ \text{O} \\ \text{AlOSiOAl} \\ \text{O} \\ \text{Si} \end{array}$	88–94
$\text{Q}^3(1\text{Al})$	$\begin{array}{c} \text{O} \\ \text{SiOSiOAl} \\ \text{O} \\ \text{Si} \end{array}$	ca 95	$\text{Q}^4(4\text{Al})$	$\begin{array}{c} \text{Al} \\ \text{O} \\ \text{AlOSiOAl} \\ \text{O} \\ \text{Al} \end{array}$	83–87
$\text{Q}^3(2\text{Al})$	$\begin{array}{c} \text{O} \\ \text{AlOSiOAl} \\ \text{O} \\ \text{Si} \end{array}$	ca 90			

^aShift ranges of the central Si atom referenced relative to TMS

that dipolar and quadrupolar interactions and CSA are not fully averaged out. It has been shown recently that these limitations can be overcome by use of MAS-NMR [19]. Figure 10 shows a series of ^{29}Si spectra of gels used to synthesize NaY zeolite. The synthesis mixture has a nominal composition of 4.1 Na₂O: 1.0 Al₂O₃: 13.1 SiO₂: 189 H₂O and is made from silica sol, sodium aluminate solution, sodium hydroxide solution, and demineralized water. The freshly prepared mixture is homogenized using a turbine mixer and then aged at room temperature. The broad peak at -40 ppm, which is characteristic of Q⁴ Si atoms appears to be unaffected by mixing of the reagents. Upon aging of the freshly prepared gel at room temperature, the silica sol dissolves, resulting in a decrease in the intensity of the Q⁴ peak and the progressive appearance of peaks indicative of silicon in Q⁰, Q¹, Q², and Q³ environments. The time evolution of these peaks, which is shown in Figure 10, suggests that dissolution of the sol produces monomeric silicate anions which then undergo condensation-polymerization to form oligomeric silicate and aluminosilicate structures. Further changes in the spectra occur upon heating of the gel to 100 C, as may be seen from Figure 10. The shift in the distribution of peak intensities is indicative of further polymerization of the dissolved anions. X-ray diffraction of the recovered solids shows that crystalline zeolite begins to appear after 48 h of heating and that crystallization is completed after 112 h. During this period the composition of the gel changes very little, but the NMR spectra do show progressive evidence for NaY zeolite.

Conclusions

High resolution ^{29}Si NMR spectroscopy can provide considerable insights into the structure and distribution of silicate and aluminosilicate anions present in solutions and gels from which zeolites are synthesized. The narrowness of individual lines and the sensitivity of the chemical shift to details of the local chemical environment make it possible in many instances to identify exact chemical structures. Studies using ^{29}Si NMR have shown that the distribution of anionic structures is sensitive to pH and the nature of the cations in solution. Alkali metal cation NMR has demonstrated the formation of cation-anion pairs the formation of which is postulated to affect the dynamics of silicate and aluminosilicate formation and the equilibrium distribution of these species. ^{27}Al NMR has proven useful in identifying the connectivity of Al to Si, but because of quadrupolar broadening cannot be used to define the precise environment of Al atoms.

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Fig. 1 ^{29}Si NMR spectrum of a 3.0 mol% SiO_2 , $R = 1.5$ sodium silicate solution.

Fig. 2 ^{29}Si NMR spectra of 3.0 mol% SiO_2 , $R = 2.0$ alkali metal silicate solutions.

Fig. 3 The influence of the cation on the distribution of Si among the connectivity states at the composition 3.0 mol% SiO_2 , $R = 2.0$.

Fig. 4 ^{29}Si NMR spectra of 1.0 mol% SiO_2 , $R = 2.0$ TAA silicate solutions prepared with TMAOH, TEAOH, TPAOH, and TBAOH.

Fig. 5 ^{29}Si NMR spectra of 1.0 mol% SiO_2 , $R = 2.0$ TAA silicate solutions prepared with Me_4NOH , EtMe_3NOH , and PrMe_3NOH .

Fig. 6 The fraction of inverted spins in Q^0 , Q^1 , and Q^2_{Δ} environments as a function of time following selective or nonselective spin inversion of a potassium silicate solution.

Fig. 7 The dependence of k_1 and k_2 on cation radius.

Fig. 8 (a) A ^{29}Si NMR spectrum of a monomeric Na silicate solution of the composition 1.0 mol% SiO_2 , $R = 0.1$ and an ^{27}Al spectrum of a monomeric Na aluminate solution of the composition 1 M NaAlO_2 ; (b)-(d) ^{29}Si and ^{27}Al spectra of aluminosilicate solutions with increasing Al concentration. ^{29}Si spectral frequencies are referenced to $\text{Si}(\text{OH})_4$ and Al spectral frequencies are referenced to the octahedral Al^{3+} ion in an aqueous solution of AlCl_3 .

Fig. 9 (a) ^{29}Si spectrum of a Na silicate solution of the composition 3.0 mol% SiO_2 , $R = 0.4$, $[\text{SiO}_2]/[\text{Al}_2\text{O}_3] = 10.0$.

Fig. 10 ^{29}Si MAS-NMR spectra of a sodium silicate gel (nominal composition 4.1 Na_2O : 1.0 Al_2O_3 : 13.1 SiO_2 : 189 H_2O) taken after aging the gel at 20 C and heating for 1 h at 100 C.

XBL 866-2139

XBL 881-138

XBL 8810-3605

XBL 8810-3604

XBL 886-2234

XBL 881-291

a

3 mol% SiO₂
 SiO₂/Na₂O = 0.4

SiO₂/Al₂O₃ = 10

b

XBL 886-2215

XBL 8810-3606

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