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High Resolution ^{29}Si Nuclear Magnetic Resonance Study on Gallosilicates with Zeolitic Structures

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High resolution ^{29}Si nuclear magnetic resonance spectra have been measured using magic angle sample spinning technique for several gallosilicates and aluminosilicates with zeolitic structures. The number of gallium atoms coordinating to the SiO_4 tetrahedron was determined by the technique in the same manner as established for aluminium in aluminosilicates. The resonance lines were observed to shift to lower field by the substitution of silicon atoms with gallium as well as aluminium. The magnitudes of lower-field shifts were larger for the substitution by gallium than aluminium. The chemical shift ranges of ^{29}Si nuclei are discussed for gallosilicates with the values for aluminosilicates compared.

High resolution ^{29}Si nuclear magnetic resonance (NMR) spectroscopy in solids has recently become a powerful tool to study the structure of various silicates[1] and aluminosilicates.[2] In silicates the chemical shift of ^{29}Si nuclei depends on the degree of condensation of silicon-oxygen tetrahedra. On the other hand, aluminosilicates are composed of two kinds of tetrahedra, SiO_4 and AlO_4, and the ^{29}Si chemical shift correlates well with the degree of substitution of silicon by aluminium.

A zeolite is a crystalline aluminosilicate with many pores inside it. The pore size is an important factor in determining the selectivity of the catalytic reaction and of the molecular sieving. Various modifications have been carried out to change the pore size: for example, the substitution of silicon and aluminium by other elements, cation exchange, and modification of the surface. In some zeolites aluminium atoms can be replaced by gallium atoms, resulting in zeolitic gallosilicates.[3—6]

Vaughan *et al.*[7] have recently measured high resolution ^{29}Si NMR spectra of gallium faujasites and sodalite to study the effect of gallium substitution for aluminium on the ^{29}Si spectra, but no other works have been reported so far on gallosilicates. In the present work we have carried out an extensive study of high resolution ^{29}Si NMR spectra of various gallosilicates. The ^{29}Si chemical shift has been observed to change depending on the number of gallium atoms coordinating to the silicon-oxygen tetrahedron in the same manner as established for aluminosilicates. In addition to the one caused by the gallium atom, the ^{29}Si resonance line shifts by a crystallographical inequivalence. The range of the chemical shift in ^{29}Si spectra has been discussed, taking into consideration the effects of the substitution by gallium and of the crystallographical inequivalence, and the values for gallosilicates have been compared with those for aluminosilicates.

Experimental

Several gallosilicates were synthesized by the procedures described in Refs. 3—6. Aluminosilicates which have similar compositions and structures were synthesized for comparison. The structures of the synthesized zeolitic materials were checked by measuring powder X-ray diffraction patterns, and the compositions were determined by X-ray fluorescence (XRF) method.

High resolution ^{29}Si NMR spectra were measured by a Bruker CXP-100 pulsed spectrometer which was equipped with a probe for magic angle spinning of the sample and was operated at a resonance frequency of 17.9 MHz. An Andrew-type rotor[8] made of Delrin (polyoxymethylene) was spun at a rate of about 3.5 kHz. The angle of the rotation axis was determined by optimizing the ^{127}I spectrum of KI, using a procedure similar to that described in Ref. 9. Free induction decay signals observed after single pulse excitations were accumulated before Fourier transformation. The repetition times of the pulse excitations were between 2 and 10 s. Silicone rubber was used as an internal second reference, whose chemical shift is −22.0 ppm with respect to tetramethylsilane (TMS).[10] All the chemical shifts in this paper are referred to TMS.

The spectra were deconvoluted into several components with Lorentzian or Gaussian line shapes by a nonlinear least squares method using a FACOM M-380 computer.

Results and Discussion

NMR measurements have been performed for four kinds of zeolitic materials which were reported that aluminium can be substituted by gallium. Figures 1—4 show high resolution ^{29}Si spectra of gallosilicates as well as aluminosilicates in the increasing order of the Si/M ratio (M=Ga or Al). All the silicon atoms are equivalent crystallographically in the frameworks of hydroxysodalite and faujasite, while inequivalencies are present in offretite and ZSM-5.[11] The assignment of each peak observed in gallosilicates has been performed by analogy with aluminosilicates having similar composition and structure, as described below. Si(nM) used in this work means the silicon atom in an SiO_4 tetrahedron coordinated by n Al atoms.

Hydroxysodalite. The spectra for hydroxysodalites are shown in Fig. 1, and the results are summarized in Table 1. Spectra have been measured for three gallosilicates with different Si/Ga ratios,

TABLE 1. ^{29}Si CHEMICAL SHIFT, RELATIVE INTENSITY OF THE RESONANCE LINE, AND Si/M RATIO IN HYDROXYSODALITES[a)]

Sample		Chemical shift (ppm) and relative intensity (%)					Si/M (NMR)	Si/M (XRF)
	$n^{b)}$ =	4	3	2	1	0		
Gallium-containing (M=Ga)								
Hydroxysodalite	(A)	−74.9(81)	−82.8(19)				1.05	1.15
	(B)	−74.9(86)	−82.9(14)				1.04	1.14
	(C)	−75.1(98)	−84(2)				1.005	0.2
Sodalite[c)]		−76.0	−82.4	−89.0	−94.9	−101.3	1.26	
Aluminium-containing (M=Al)								
Hydroxysodalite		−84(65)	−88(35)				1.10	

a) Lorentzian line shapes are assumed. b) n in Si(nM). c) From Ref. 7.

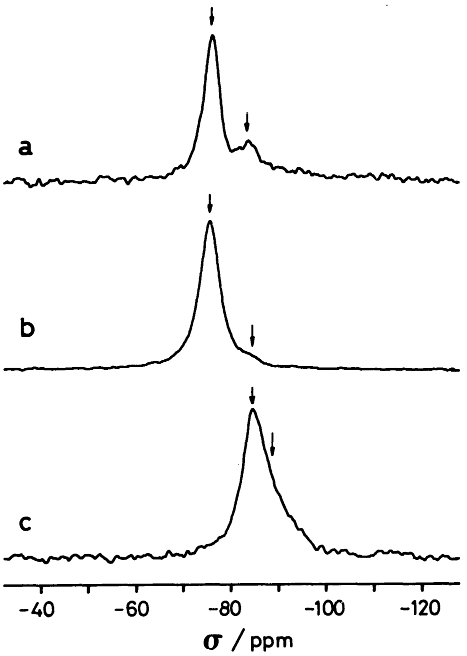

Fig. 1. High resolution ^{29}Si spectra of gallium-containing hydroxysodalite A (a) and C (b), and aluminium-containing hydroxysodalite (c). Arrows in the figure indicate the line positions.

and for one aluminosilicate. The observed peaks can be assigned to silicon atoms in Si(nM) configurations as shown in Table 1. The spectrum of the aluminosilicate has a line shape with a large asymmetry, which might be due to two overlapping lines attributed to Si(4Al) and Si(3Al). The chemical shifts of the two lines are determined to be −84 and −88 ppm. In gallosilicates the spectra are composed of two lines with chemical shifts, −75 and −83 ppm. By comparing the spectra with that of the aluminosilicate, the lines in the gallosilicates can be assigned to Si(4Ga) (−75 ppm) and Si(3Ga) (−83 ppm). The observed line shapes have been well fitted by using Lorentzian line shapes. The Si(nGa) line in gallosilicates shifts to lower field compared with the corresponding Si(nAl) line in aluminosilicate. The chemical shift values in Ref. 7 are also listed in Table 1, and the values obtained in the present work are in good agreement to the reported values.

The ratio of the number of silicon atoms to that of gallium or aluminium atoms (Si/M ratio) has been determined by the XRF method as well as the NMR method. The Si/M ratio from the NMR spectra was calculated assuming Loewenstein's rule,[12)] that is, by using the following equation:

$$(\mathrm{Si/M}) = (\sum_{n=1}^{4} nI_n/4)^{-1}, \qquad (1)$$

where I_n is a normalized intensity of the Si(nM) resonance line. Good agreements between the ratios obtained from the XRF and NMR methods are found in the cases of gallium-containing hydroxysodalite A and B within the experimental errors of the two methods. However, the discrepancy observed in gallium-containing hydroxysodalite C is too large to be explained by the experimental errors. Since the sample was found to be too rich in gallium atoms, it was considered to violate the Loewenstein's rule, as reported in Ref. 4, and hence Eq. 1 cannot be applied to this sample.

Faujasite. Figure 2 shows the spectra of faujasites containing Na ions. Four resonance lines are clearly observed in the aluminium-containing compound. Their chemical shifts are determined to be −83.6, −88.4, −93.8, and −99.2 ppm, which can be attributed to Si(4Al), Si(3Al), Si(2Al), and Si(1Al), respectively. A peak around −102 ppm is not clearly resolved but observed as a shoulder, which can be assigned to Si(0Al). The gallium-containing faujasite has also four clearly resolved lines. Their chemical shifts are −76.7, −83.3, −90.8, and −98.8 ppm, which can be assigned to Si(4Ga), Si(3Ga), Si(2Ga), and Si(1Ga), respectively, by analogy with the aluminium-containing compound. In both faujasites the spectra can be simulated well when a Lorentzian line shape is assumed for each line. The results are summarized in Table 2, together with the values in Ref. 7. The differences in the chemical shift between the neighboring

Table 2. ^{29}Si Chemical shift, relative intensity of the resonance line, and Si/M ratio in faujasites[a)]

Sample	Chemical shift (ppm) and relative intensity (%)					Si/M (NMR)	Si/M (XRF)
	$n^{b)}=$ 4	3	2	1	0		
Gallium-containing (M=Ga)							
NaX	−76.7(19)	−83.3(41)	−90.8(32)	−98.8(9)		1.47	1.58
NaX[c)]	−77.7	−84.2	−90.3	−96.4	−102.8	1.11	
NaX[c)]	−78.0	−84.2	−90.9	−97.4	−104.2	1.39	
NaY[c)]	−78.3	−84.6	−91.4	−98.2	−105.8	2.06	
Aluminium-containing (M=Al)							
NaX	−83.6(10)	−88.4(40)	−93.8(37)	−99.2(11)	−102(2)	1.63	1.75

a) Lorentzian line shapes are assumed. b) n in Si(nM). c) From Ref. 7.

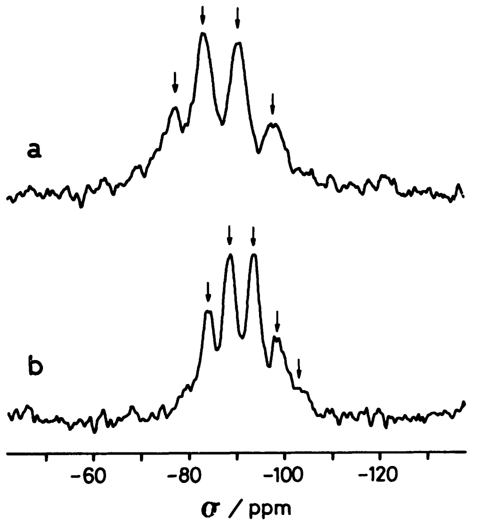

Fig. 2. High resolution ^{29}Si spectra of NaX-type faujasites containing gallium (a) and aluminium (b) atoms.

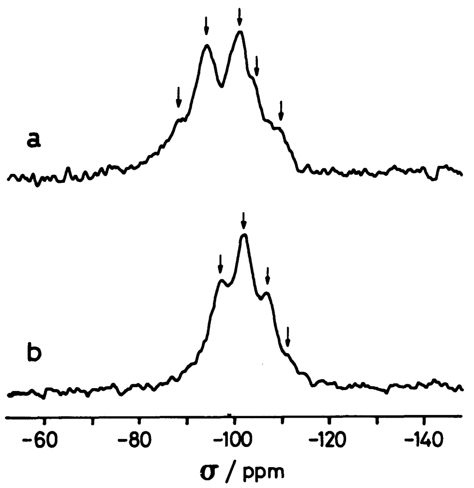

Fig. 3. High resolution ^{29}Si spectra of offretites containing gallium (a) and aluminium (b) atoms. Tetramethylammonium ion is included as the cation.

lines are 6—8 ppm for gallosilicates and 5—6 ppm for aluminosilicates. In gallosilicates the shift differences are a little larger in the present work than in Ref. 7. It can be concluded that a gallium atom deshields the silicon nucleus more than an aluminium atom.

Offretite. Figure 3 shows the spectra of offretites containing tetramethylammonium ion. Four lines are observed in the aluminum-containing compound, whose chemical shifts are −96.5, −101.7, −107.0, and −110.9 ppm. Nagy *et al.*[13)] have measured the spectra of offretite with an Si/Al ratio of 3.8, and have made assignment as follows; −92 ppm to Si(3Al), −97 ppm to Si(2Al), −102 ppm to Si(1Al), and −107 and −112 ppm to Si(0Al). Two inequivalent sites however are present with the ratio of 2:1 in the framework of offretite, in contrast to hydroxysodalite and faujasite. Fyfe *et al.*[14)] have reassigned the spectra of offretite by taking into consideration the effect of crystallographical inequivalence on the ^{29}Si chemical shift. The chemical shift dispersion for the two structurally inequivalent sites was reported to be about 5 ppm,[14)] which is comparable in magnitude to the effect of the first nearest neighboring aluminium. According to the assignment of Fyfe *et al.*,[14)] the lines observed in the present work are assigned as follows; −96.5 ppm to Si(2Al), −101.7 ppm to a mixture of Si(2Al) and Si(1Al), −107.0 ppm to a mixture of Si(1Al) and Si(0Al), and −110.9 ppm to Si(0Al). The fraction of each component is estimated as shown in Table 3, assuming that each Si(nAl) line consists of two lines with the intensity ratio of 2:1. Excellent agreement is obtained between the observed and estimated fractions, and the Si/M ratios obtained from the two methods are considered to agree within the experimental error.

In the spectra of gallium-containing offretite four resonance lines can be clearly observed, whose chemical shifts are −88.2, −94.6, −101.4, and −110.7 ppm. In addition to the four lines, there seems to exist at least one line between −101.4 and −110.7 ppm, whose chemical shift is calculated to be −104.5 ppm. They are tentatively assigned as shown in Table 3 by analogy with the aluminium-containing offretite, taking into

Table 3. ^{29}Si Chemical shift, relative intensity of the resonance line, and Si/M ratio in TMA-containing offretites$^{a)}$

Chemical shift (ppm) and Obsd. intensity (%)	Estimated intensity (%) of Si(nM) $n^{b)}$ = 3	2	1	0	total	Si/M (NMR)	Si/M (XRF)
Aluminosilicates (M=Al)							
−96.5 (40)		40			40		
−101.7 (36)		20	16		36		
−107.0 (18)			8	10	18		
−110.9 (6)				5	5		
total (100)		60	24	15	99	2.75	3.2
Gallosilicates (M=Ga)							
−88.2 (10)	10				10		
−94.6 (29)	5	24			29		
−101.4 (25)		12	13		25		
−104.5 (31)			7	20	27		
−110.7 (5)				10	10		
total (100)	15	36	20	30	101	2.92	2.8

a) Lorentzian line shapes are assumed. b) n in Si(nM).

Table 4. ^{29}Si Chemical shift, relative intensity of the resonance line, and Si/M ratio in H-type ZSM-5$^{a)}$

Sample	Chemical shift (ppm) and relative intensity (%) $n^{b)}$ = 1	0			Si/M (NMR)	Si/M (XRF)
Gallium-containing (M=Ga)						
(A)	−103.7 (13)	−112.3 (62)	−115.7 (25)		31	30
(B)		−110.6 (7)	−113.7 (82)	−116.9 (10)	—	194
Aluminium-containing (M=Al)						
(A)	−105.6 (9)	−112.3 (58)	−115.6 (33)		44	65
(B)	−104.5 (1)	−110.3 (13)	−113.2 (75)	−116.2 (11)	400	620

a) Gaussian line shapes are assumed. b) n in Si(nM).

consideration the effects of the first nearest neighboring gallium and the crystallographical inequivalence. The agreement between the observed and estimated fractions is not very good for the lines at −104.5 and −110.7 ppm. The discrepancy is considered to have its origin in the procedure of the deconvolution of the spectra. Since the three lines between −101 and −111 ppm overlap markedly, the observed fractions are considered to include appreciable errors. Furthermore, the line shape in the higher field appears to be different from a Lorentzian line shape, as shown in Fig. 3a, although Lorentzian line shapes are assumed for all lines. If the line shape can be assumed differently for each line based on a theoretical consideration, the observed spectra should be simulated very well, which is impossible at the present stage.

ZSM-5. ZSM-5 has a very high Si/M ratio compared with the materials described above, and has several sites which are inequivalent crystallographically. Figure 4 shows the spectra of H-type ZSM-5 with different Si/M ratios, and Table 4 summarizes the results. The observed spectra can be well simulated by assuming a Gaussian line shape for each component.

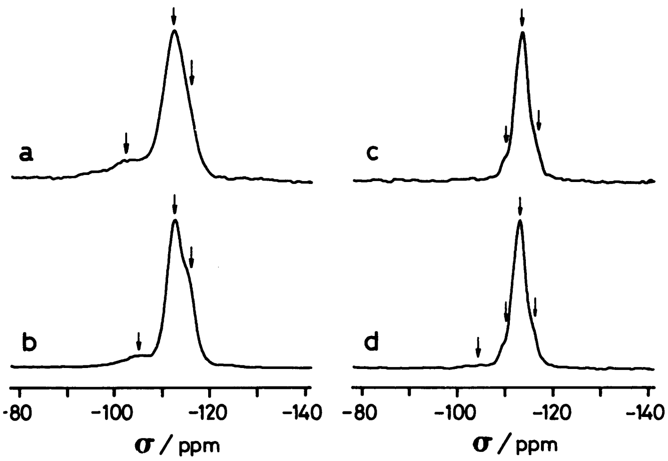

Fig. 4. High resolution ^{29}Si spectra of H-type ZSM-5. Gallium-containing A (a) and B (c), and aluminium-containing A (b) and B (d).

In aluminium-containing compounds with a lower Si/Al ratio, three lines are observed, whose chemical shifts are −105.6, −112.3, and −115.6 ppm. For the

ZSM-5 with a higher Si/Al ratio four lines are observed, whose chemical shifts are −104.5, −110.3, −113.2, and −116.2 ppm. The lines at about −105 ppm are attributed to Si(1Al), from the consideration of the Si/Al ratio obtained by the XRF method. The other lines are all assigned to Si(0Al), whose chemical shifts are dispersed because of the crystallographical inequivalence, as pointed out by Fyfe *et al.*[15)]

The spectral shapes of the gallium-containing ZSM-5 are similar to those of the aluminium-containing ones with similar Si/M ratios. Three lines are observed in the sample with a lower Si/Ga ratio whose chemical shifts are −103.7, −112.3, and −115.7 ppm, while the sample with a higher Si/Ga ratio has three lines with chemical shifts of −110.6, −113.7, and −116.9 ppm. The line around −104 ppm is attributed to Si(1Ga), and the other lines are all attributed to Si(0Ga). It is reasonable that the Si(0Al) and Si(0Ga) lines have almost the same chemical shift.

Chemical Shift. The ranges of the chemical shift of Si(*n*M) lines in gallosilicates are summarized in Table 5, together with the values in aluminosilicates. The ranges of the chemical shifts of Si(*n*Ga) lines cover lower field than the corresponding Si(*n*Al). In other words, gallium deshields ^{29}Si nucleus more than aluminium. The deshielding effects are 6—8 ppm per gallium atom and 5—6 ppm per aluminium atom when a nearest neighboring silicon atom is substituted by gallium or aluminium. In addition to the deshielding effect, the crystallographical inequivalence affects the chemical shift, which broadens the range of the chemical shift of each Si(*n*M) line.

Line Shape. In the procedure of the deconvolution a Lorentzian line shape was used for hydroxysodalite, faujasite, and offretite, while a Gaussian line shape was used for ZSM-5. In offretite, a Loretzian line shape is not suitable for the higher-field line. In other words, a Lorentzian line shape is suitable for the Si(*n*M) lines with *n* between 1 and 4, while a Gaussian line shape for Si(0M) line. There are two mechanisms of the line broadening: dipolar interaction between ^{29}Si and ^{27}Al or between ^{29}Si and ^{69,71}Ga, and distribution of aluminium and gallium in second and further nearest coordination spheres. The origin of the linewidth in aluminosilicates at high magnetic fields has been discussed by Fyfe *et al*,[17)] and they concluded that the aluminium atoms in the second and further nearest coordination spheres produce the chemical shift dispersion of silicon nuclei. At the magnetic field used in the present work the dipolar interaction works in addition to the above mechanism, since the quadrupole interactions in ^{27}Al nuclei becomes larger at lower magnetic fields.[18)] The mechanisms of the line broadening in gallosilicates are considered to be the same as those in aluminosilicates. The shape and width of each Si(*n*M) line reflect the contribution of the two mechanisms. In this work the linewidths of the ^{29}Si lines are found to be broader for gallosilicates than those for aluminosilicates. The gallium atoms in the second and further nearest coordination spheres may be one of the causes of the broader linewidth in gallosilicates, since the deshielding character is stronger in a gallium atom than in an aluminium atom.

TABLE 5. RANGES OF THE CHEMICAL SHIFTS (ppm) OF ^{29}Si NUCLEI IN GALLOSILICATES AS WELL AS ALUMINOSILICATES

n in Si(*n*M)	Gallosilicates (M=Ga)	Aluminosilicates (M=Al)	
		this work	Ref. 16
4	−74.9∼ −78.3	−84	−80∼ −87
3	−82.4∼ −94.6	−88	−88∼ −95
2	−89.0∼−101.4	−93.8∼−101.7	−93∼−100
1	−94.9∼−104.5	−99.0∼−107.0	−97∼−106
0	−101.3∼−116.9	−102∼−116.2	−102∼−113

In addition to the above mechanisms of the line broadening the site inequivalence makes the spectra very complex, sometimes producing the overlap of the resonance lines, as shown in offretite. The deconvolution of the ^{29}Si NMR spectrum is difficult when lines are heavily overlapped. The error in the fraction of each line produces a larger error in the calculated Si/Al ratio as the ratio becomes higher. The value obtained from the XRF method may have the experimental error of ±10%. Consequently, the Si/M ratios obtained from NMR and XRF methods are considered to agree well within the experimental errors in most cases.

Spin-lattice Relaxation Time. Spin-lattice relaxation times (T_1) of ^{29}Si nuclei in gallosilicates studied in this work range between 1 and 3 s at a resonance frequency of 17.9 MHz, which are the same order of magnitude as the T_1 values in aluminosilicates with similar structures. These results indicate that either a gallium atom as well as an aluminium atom have little contribution to the ^{29}Si spin-lattice relaxation, or the two atoms have the similar contribution to it if exists. Barron *et al.*[19)] and Watanabe *et al.*[20)] have measured the T_1 values of ^{29}Si nuclei in several layer aluminosilicates, and have correlated the T_1 value with paramagnetic impurities. In the case of the relaxation due to paramagnetic impurities all of the ^{29}Si nuclei should have the same T_1 value. independent of the number of coordinating aluminium atoms. In the present work however differences in the T_1 values are found among the peaks in the two NaX samples studied. There is a trend that the T_1 value of the Si(*n*M) line with higher *n* value becomes shorter. From the dependence of the T_1 value on the *n* value it can be concluded that aluminium and gallium nuclei contribute to the spin-lattice relaxation of ^{29}Si nuclei in gallosilicates and aluminosilicates.

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