Synthesis and Characterization of Gallosilicate Molecular Sieves with High Gallium Contents: Examples of Structure Direction Exerted by Gallium

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Hydrothermal syntheses of the microporous gallosilicates TNU-1 (CGS topology), TNU-2 (GIS topology), TNU-3 (a synthetic counterpart of the natural zeolite gonnardite, NAT topology), and TNU-4 (a synthetic counterpart of the natural zeolite natrolite, NAT topology) are presented. In the range of synthesis conditions studied here, the presence of Ga itself is found to be the critical factor directing the crystallization of microporous gallosilicate materials with topologies different from those of the aluminosilicate zeolites obtained when Ga is replaced by Al. This suggests that the introduction of Ga into silicate synthesis mixtures may be a viable route for the synthesis of novel low-silica zeolite structures. The Si, Ga ordering in TNU-3 and TNU-4 materials is investigated in an attempt to understand why the crystallization of the same synthesis mixture at different temperatures results in two materials with the same topology and chemical composition but with different symmetries. A high degree of Si, Ga ordering is observed in TNU-4 by ^{29}Si MAS NMR, and possibly as a consequence, its ^{71}Ga MAS NMR spectrum clearly shows a line shape affected by second-order quadrupolar interactions rarely found in these kinds of materials.

Introduction

Zeolites and related materials are crystalline, microporous solids that have found a broad spectrum of commercial applications as catalysts and separation media in the petrochemical industry.[1] Since many important properties of zeolitic materials are closely related to the size, shape, and dimensionality of the pore systems that are primarily determined by their framework structures, the discovery of novel materials has been a matter of primary concern in zeolite science and technology. Over the past several decades, as a direct result, a number of zeolite structures have been synthesized in the presence of the inorganic and/or organic species generally known as structure-directing agents (SDAs) in the synthesis mixture.[2] On the other hand, recent advances in the synthesis of zeolites and molecular sieves have revealed that the introduction of heteroatoms such as Be or Zn into silica frameworks during the crystallization process is one of the most effective ways to synthesize microporous solids with novel topologies, which has been attributed to the relatively low ratio of nonbonded radius to T−O distance for these heteroatoms, possibly favoring the formation of structures with acute T−O−T angles.[3,4] These new structures frequently display an ordered distribution of the heteroatoms over the crystallographically distinct tetrahedral sites.[3]

Ga is right below Al in the periodic table and has chemical properties similar to those of Al. Thus, isomorphous substitution of Ga for Al in the zeolite framework during the crystallization process has been extensively attempted in order to synthesize materials isostructural to known aluminosilicate zeolites.[5,6] Until a recent date, however, no new silicate-type zeolite structures have been produced as a result of the presence of Ga^{3+} in the synthesis mixture. Very recently, we have reported the synthesis and the structure of TNU-1 (Taejon National University No. 1), a novel gallosilicate material having no counterpart among aluminosilicates.[7] This gallosilicate molecular sieve, which apparently had a precedent denoted as TsG-1 in the Russian literature,[8] comprises a three-dimensional pore system consisting of 10-ring channels in the [100] direction that

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intersect two 8-ring channels in the [010] and [011] directions, respectively. The latter 8-ring channels are sinusoidal in character, having the 8-ring windows offset from one to the next. TNU-1 is isostructural to the MeGaPO-6 (Me = Co or Zn) materials, whose topology has been recently assigned the IZA structure code CGS.[9,10] Of particular interest is the fact that TNU-1 formation requires the presence of Ga in the synthesis mixture since replacement of Ga by Al in the TNU-1 synthesis medium yields a MER-type zeolite. This has led us to believe that the structure-directing effect exerted by Ga could be quite different from that of Al in certain low-silica synthesis conditions.

The purpose of our work is to further understand the structure-directing ability of Ga that is essential to synthesize microporous gallosilicate materials with topologies different from those of the aluminosilicate zeolites obtained when Ga is replaced by Al. Here we have synthesized a series of low-silica zeolitic materials with different framework structures by varying the type of alkali metal cations in the synthesis mixture and the crystallization temperature. Among them are included a gallosilicate version of gismondine-type materials (GIS topology, with a symmetry different from those of the natural gismondine, amicite, garronite, and gobbinsite and the synthetic Na−P1 aluminosilicates), gonnardite (NAT topology), and natrolite (NAT topology) that are respectively denoted as TNU-2, TNU-3, and TNU-4 (Taejon National University Nos. 2−4, respectively). To the best of our knowledge, no synthetic counterparts of the mineral gonnardite have been reported and the crystal symmetry of TNU-2 is unique among GIS materials. To date, on the other hand, several papers on the synthesis of gallosilicate materials with the same structure and crystal symmetry as TNU-4 have already been published in the literature.[11−13] For the sake of clarity and distinction from TNU-3, however, we will refer to the gallosilicate version of the mineral natrolite by our laboratory code TNU-4 in this paper. The four gallosilicate materials including TNU-1 are characterized by powder X-ray diffraction, elemental and thermal analyses, scanning electron microscopy, IR, and ^{29}Si and ^{71}Ga MAS NMR spectroscopies.

Experimental Section

Synthesis. The following reagents were used for the synthesis of microporous gallosilicate and aluminosilicate materials: NaOH (50% aqueous solution, Aldrich), KOH (45% aqueous solution, Aldrich), gallium oxide (Ga_2O_3, 99.99+%, Aldrich), aluminum hydroxide ($Al(OH)_3 \cdot 0.5H_2O$, Aldrich), and colloidal silica (Ludox AS-40, DuPont). In a typical synthesis of gallosilicate molecular sieves, Ga_2O_3 was mixed with a solution of either KOH or NaOH in water and heated overnight at 100 °C. To the resulting clear solution, after cooling to room temperature, a given amount of colloidal silica was added. The oxide composition of the resulting mixture was fixed to $6.0M_2O \cdot 1.0Ga_2O_3 \cdot 10.0SiO_2 \cdot 150H_2O$, where M is K or Na. For the synthesis of aluminosilicate materials, Ga_2O_3 was replaced by the equivalent amount of $Al(OH)_3 \cdot 0.5H_2O$ under the conditions described above. The final synthesis mixture (pH > 13.5) was stirred at room temperature for 24 h, charged into Teflon-lined 45-mL autoclaves, and heated at 100 or 150 °C for the required crystallization time. The solid products were recovered by filtration, washed repeatedly with water, and then dried overnight at room temperature.

Characterization. Powder X-ray diffraction (XRD) patterns were measured on a Rigaku Miniflex or a Philips PW 1820 diffractometer with Cu Kα radiation. For the identification of phases, the samples were analyzed in the 2θ range 5−40° in steps of 0.03°. For the calculation of the unit-cell parameters, long-step scans were taken in the 2θ range 3−50° with a step size of 0.02° and a count time of 23 s/step. Indexing of the XRD patterns obtained was carried out using the program VISSER.[14]

Chemical analysis was carried out by a Jarrell-Ash Polyscan 61E inductively coupled plasma (ICP) spectrometer in combination with a Perkin-Elmer 5000 atomic absorption spectrophotometer. Thermogravimetric and differential thermal analyses (TGA/DTA) were performed in air on a TA Instruments SDT 2960 thermal analyzer. Approximately 15 mg of sample was used at a heating rate of 10 °C min^{-1}. Crystal morphology and size were determined by a JEOL JSM-6300 scanning electron microscope. The IR spectra of the structural region for all materials prepared here were recorded on a Nicolet 710 FT-IR spectrometer using the KBr pellet technique.

The ^{29}Si MAS NMR spectra were measured on a Bruker DSX 400 spectrometer at a spinning rate of 12.0 kHz using 4 mm rotors at a ^{29}Si frequency of 79.490 MHz with a $\pi/5$ rad pulse length of 2.0 μs. The recycle delay for ^{29}Si NMR spectra was varied between 40 and 60 s to avoid relaxation effects in the signal intensities. Typically, 1000 scans were accumulated and the ^{29}Si chemical shifts are referenced to TMS. Spectral deconvolution and simulation were performed using mixed Gaussian−Lorentzian curves with the PEAKSOLV curve-fitting software. The ^{71}Ga MAS NMR spectra were obtained on the same spectrometer at a ^{71}Ga frequency of 122.040 MHz in 4 mm rotors at a spinning rate of 10.0 kHz. The spectra were obtained with an acquisition of ca. 15 000 pulse transients, which was repeated with a $\pi/4$ rad pulse length of 1.0 μs and a recycle delay of 0.1 s. The ^{71}Ga chemical shifts are reported relative to a $Ga(H_2O)_6^{3+}$ solution. Simulation of the ^{71}Ga MAS NMR spectra obtained was carried out using the program WINFIT (Buker).

Results and Discussion

Figure 1 shows the typical XRD patterns of all gallosilicate materials prepared here: TNU-1, TNU-2, TNU-3, and TNU-4. Comparison of the XRD patterns in Figure 1 with those in the literature reveals that all the materials prepared here are highly crystalline and no reflections other than those from each zeolite structure are observed.[7,15] Table 1 lists the representative synthesis conditions and results. It can be seen that four different gallosilicate materials were obtained, depending on the crystallization temperature and the type of the alkali metal cations added to in the gallosilicate synthesis mixture. TNU-1 was produced in the presence of K, for example, when the crystallization was performed at 150 °C for 7 days. We note here that TNU-1

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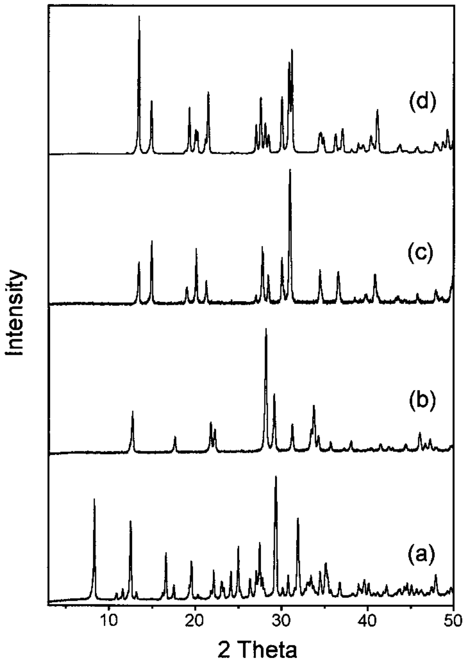

Figure 1. Powder X-ray diffraction patterns of gallosilicate molecular sieves prepared in this study: (a) TNU-1; (b) TNU-2; (c) TNU-3; (d) TNU-4.

Table 1. Representative Synthesis Conditions and Results[a]

M	Me	temp (°C)	time (days)	product[b]
K	Ga	150	7	gallosilicate TNU-1 (CGS)
Na	Ga	150	10	gallosilicate TNU-4 (NAT)
K	Ga	100	5	gallosilicate TNU-2 (GIS)
K	Ga	100	21	gallosilicate TNU-1(CGS) + gallosilicate TNU-2 (GIS)
Na	Ga	100	10	gallosilicate TNU-3 (NAT)
K	Al	150	7	aluminosilicate merlinoite (MER)
Na	Al	150	10	aluminosilicate analcime (ANA)
K	Al	100	10	aluminosilicate merlinoite (MER)
Na	Al	100	7	aluminosilicate Na−P1 (GIS) + aluminosilicate analcime (ANA)

[a] Composition of the synthesis mixture: $6.0M_2O{\cdot}1{\cdot}0Me_2O_3{\cdot}10SiO_2{\cdot}150H_2O$, where M is K or Na and Me is Ga or Al. [b] If more than one phase is obtained, the phase in the highest concentration is first listed.

is stable for at least additional 2 weeks of heating in the crystallization medium. When Na instead of K is added to the synthesis mixture, on the other hand, TNU-4 was obtained. This is not unexpected because the strong influence of the type of alkali cations on the crystallization product is frequently observed in zeolite syntheses in the absence of organic additives.[16] There are several published synthesis routes to the gallosilicate version of natrolite.[11−13] However, all these synthesis procedures are significantly different from the synthesis method shown here in that they include the use of organic SDAs such as tetramethylammonium (TMA) or benzyltrimethylammonium (BTMA) cation, with stirring during the crystallization process, or alternatively require a small amount of Na−Y to be added to the synthesis mixture (and hence the resulting materials may actually be galloaluminosilicates).

An interesting observation obtained from Table 1 is that the synthesis at 100 °C resulted in the formation of gallosilicate materials completely different from those produced at 150 °C, although both syntheses were carried out using reaction mixtures with the same oxide composition. As seen in Table 1, at 100 °C TNU-2 (GIS) is the phase formed in the presence of K (instead of TNU-1, obtained at 150 °C). In contrast, the use of Na as an inorganic SDA yielded TNU-3 (instead of TNU-4 at 150 °C, both with NAT topology but different symmetry). This clearly shows that the crystallization temperature, as well as the type of alkali metal cations added to the synthesis mixture, is a critical factor governing the phase selectivity of the crystallization. The fact that TNU-2, a gallosilicate possessing the GIS topology, crystallizes in the presence of K rather than Na is somehow surprising, since the conventional synthesis of GIS-type zeolites such as Na−P1 normally includes the use of aluminosilicate gels rich in Na.[2] We also note that the extended period (3 weeks) of heating in the TNU-2 synthesis medium yielded a considerable amount of TNU-1 as an impurity phase, together with TNU-2. This clearly shows that TNU-2 is thermodynamically less stable than TNU-1 in the crystallization medium.

Most interestingly, when gallium oxide is replaced by the equivalent amount of $Al(OH)_3$, the obtained products are zeolites with topologies different from those of the microporous gallosilicates synthesized under otherwise identical conditions. A merlinoite (MER) zeolite crystallizes at 100 or 150 °C in the presence of K, for example, while the synthesis at 150 °C in the presence of Na results in the formation of an analcime (ANA) zeolite (a mixture of aluminosilicates ANA and GIS being obtained at 100 °C). These results again show that the structure-directing ability of Ga is quite different from that of Al. We are investigating the synthesis of gallosilicate molecular sieves in crystallization conditions other than those described above in order to find new silicate-type microporous materials, and the results will be described in our future paper.

Table 2 lists the chemical composition and crystallographic data for TNU gallosilicate materials together with those for the corresponding synthetic or natural analogues reported in the literature.[7,17−19] These data reveal that the bulk Si/Ga ratios of all the gallosilicate materials except TNU-1 are lower than 2.0, revealing their low-silica nature. An unexpected observation obtained from the crystallographic data in Table 2 is that the unit cell volume of TNU-2 is smaller by ca. 4% than that of its closest natural counterpart (i.e., the mineral garronite), despite the similarity in the extent of heteroatom substitution. This is in contrast with the general conjecture that isomorphous substitution of Al by Ga in the zeolite framework causes an increase in unit cell parameters because of the Ga−O bond distance (1.83 Å) being longer than the Al−O bond distance (1.75 Å). If the metal cations balancing the negatively charged zeolite framework are in a dehydrated state, they could have a relatively high polarizing power and thus lead to a unit cell contraction with a reduction in T−O−T angles.[20] However, this is not the case of TNU-2 since the unit cell parameters of TNU-2 in Table 2 have been obtained from the hydrated sample.

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Table 2. Chemical Composition and Crystallographic Data for Gallosilicate TNU Molecular Sieves and Related Materials

material	IZA code	unit cell composn	Si/Me^a ratio	cryst system and space group	unit cell params (Å) and volume (Å^3)	ref
TNU-1	CGS	$K_{10.3}Ga_{10.3}Si_{21.7}O_{64}\cdot 11.6H_2O$	2.11	orthorhombic, *Pnma*	$a = 8.659$, $b = 14.717$, $c = 16.328$, $V = 2003.6$	7
CoGaPO-6	CGS	$4(C_7NH_{14})Co_{4.0}Ga_{12.0}P_{16.0}O_{64}\cdot xH_2O$	1.00^b	monoclinic, $P2_1/c$	$a = 14.365$, $b = 16.305$, $c = 8.734$, $\beta = 90°24'$, $V = 2045.7$	9
TNU-2	GIS	$K_{6.1}Ga_{6.1}Si_{9.9}O_{32}\cdot 8.2H_2O$	1.62	tetragonal, $I\bar{4}_1$	$a = 10.055$, $c = 9.646$, $V = 975.2$	this work
garronite	GIS	$Na_{0.8}Ca_{2.8}Al_{5.6}Si_{10.4}O_{32}\cdot 12.1H_2O$	1.86	tetragonal, $I\bar{4}m2$	$a = 9.927$, $c = 10.303$, $V = 1015.2$	17
TNU-3	NAT	$Na_{7.9}Ga_{7.9}Si_{12.1}O_{40}\cdot 10.2H_2O$	1.53	tetragonal, $I\bar{4}2d$	$a = 13.220$, $c = 6.668$, $V = 1165.4$	this work
gonnardite	NAT	$Na_{6.4}\ Ca_{1.5}Al_{9.2}Si_{10.7}O_{40}\cdot 12.4H_2O$	1.16	tetragonal, $I42d$	$a = 13.210$, $c = 6.622$, $V = 1155.6$	18
TNU-4	NAT	$Na_{15.6}Ga_{15.6}Si_{24.4}O_{80}\cdot 17.6H_2O$	1.56	orthorhombic, *Fdd*2	$a = 18.405$, $b = 18.882$, $c = 6.661$, $V = 2314.9$	this work
natrolite	NAT	$Na_{16.0}Al_{16.0}Si_{24.0}O_{80}\cdot 16.0H_2O$	1.50	orthorhombic, *Fdd*2	$a = 18.30$, $b = 18.63$, $c = 6.60$, $V = 2250.1$	19

[a] Determined from chemical analysis. Me is Ga or Al. [b] (Co + Ga)/P ratio.

Since the unit cell volume is not merely related to the T−O distances but also to the T−O−T angles, we have tried to investigate the differences in Si−O−Ga angles in TNU-2 and the known aluminosilicates with GIS topology. As no high-resolution XRD data are available for TNU-2, we made use of the ^{29}Si MAS NMR data (vide infra) since it is known that the chemical shift of a given $Si(OGa)_n(OSi)_{4-n}$ tetrahedral species is related to the average T−O−T angles over that species. However, while several experimental correlations exist for aluminosilicate zeolites that enable to extract average Si−O−T angles (T = Si, Al), up to our knowledge not such a correlation has been published to date for gallosilicates (the experimental correlation by Newsam and Vaughan[5] allows to determine expected chemical shifts from individual Si−O−T angles (T = Si, Ga) determined by crystallography rather than the opposite). Hence, we have derived our own correlation using the data reported by Newsam and Vaughan plus our data for TNU-1 (vide infra) and applying the approach of Radeglia and Engelhardt.[21] The approach is based on a simple quantum-chemical model: the known dependence between ^{29}Si chemical shift and the electronegativity of the four oxygen atoms surrounding Si, which in turn depends on the degree of *s*-hybridization of the oxygen orbitals, allows one to represent the ^{29}Si chemical shift as a linear function of $\cos\alpha/(\cos\alpha - 1)$ for each $Si(OGa)_n(OSi)_{4-n}$ species. A regression analysis of 31 data for 8 gallosilicate materials including 6 different framework topologies (i.e., ABW, SOD, FAU, LTL, MAZ, and CGS) yields (correlation factor: 0.98)

$$\delta = -50.5 + 6.7n - 126.7 \cos\alpha/(\cos\alpha - 1) \quad (1)$$

where α is the average Si−O−T angle over a Si species surrounded by *n*Ga in its second neighbor coordination sphere. The reasonable agreement between experimental and predicted chemicals shifts is shown in Figure 2.

Using this correlation the calculated Si−O−T angles in TNU-2 (weighted average: 140.4°, range 135.7−143.8°, using the ^{29}Si MAS NMR data shown below) are significantly smaller than those of the natural GIS materials gismondine (145.7°), amicite (145.1°), gobbinsite (146.9°), and garronite (147.9°) and also slightly smaller than that of the synthetic Na−P1 (142.2°). The average angles for all these aluminosilicate GIS materials were determined from the available structural data obtained from either single-crystal or powder XRD refinement.[15] Thus, the relatively small Si−O−T angles in TNU-2 gives this material a unit cell volume considerably smaller than expected and smaller than those found for aluminosilicate materials with the same topology (see Figure 3). The data for aluminosilicate materials in Figure 3, which span over a range of Si/T ratios well below and above that of TNU-2, are close to a linear trend and are always above 1004 Å^3. However, the effect of differences in the type of main countercations on the unit cell volume of these GIS-type materials cannot be completely ruled out on the basis of the data in Figure 3, yielding some uncertainty about whether the smaller unit cell volume found for TNU-2 is mainly due to the decrease in Si−O−T angles or to the presence of K as a unique countercation or both. It is interesting in this respect that Newsam and Vaughan[5] also found a contraction of the unit cell of gallosilicate sodalite (SOD) materials compared to aluminosilicate ones and in that case there was not uncertainty about the cause of the contraction, since both materials were synthesized with Na$^+$ as a unique countercation. We then agree with their opinion that gallium incorporation does not simply produce an expansion of the cell but may produce changes on the Si−O−T angles and on the relative orientation of tetrahedra that may eventually result in

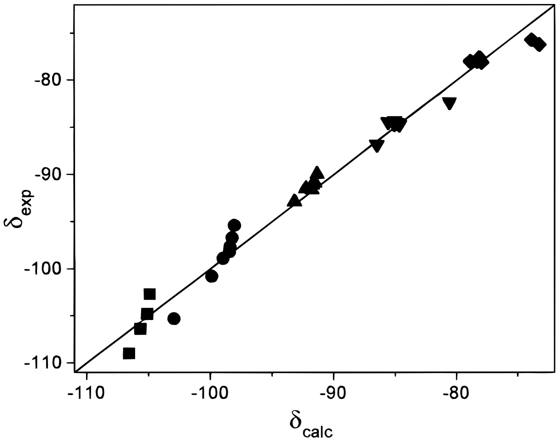

Figure 2. Experimental ^{29}Si MAS NMR chemical shifts of gallosilicate zeolites vs the shifts calculated using eq 1. $Si(OGa)_n(OSi)_{4-n}$ species are designated by ■, ●, ▲, ▼, and ◆ for n = 0, 1, 2, 3, and 4, respectively.

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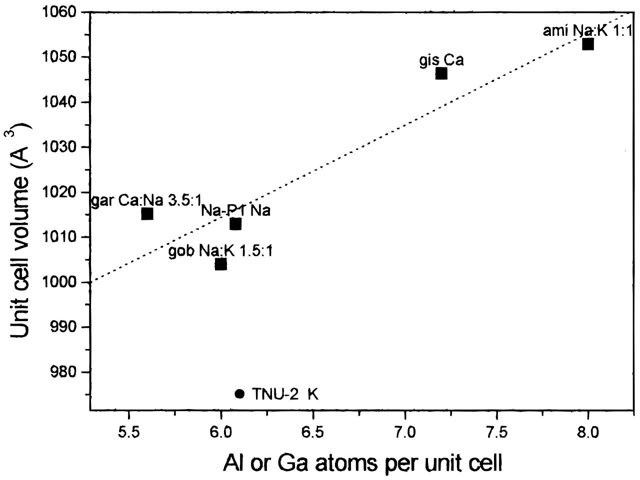

Figure 3. Unit cell volumes of aluminosilicate (■) and gallosilicate (●) zeolites with GIS topology as a function of the Al or Ga content. The countercations in each material (as well as their relative concentration when more than one is present) are shown next to each data point. The natural aluminosilicate zeolite materials are denoted as gar (garronite), gob (gobbinsite), ami (amicite), and gis (gismondine).

contractions rather than expansions of the cell. Both cases (contraction of the cell in gallosilicate SOD and GIS materials) added to the case of aluminosilicate SOD materials[20] support the warning in ref 20 that changes in the unit cell size cannot be solely taken as a proof for the isomorphous substitutions in zeolites.

Unlike the case of TNU-2, on the other hand, the unit cell parameters of the Ga materials with NAT topologies were found to be larger than those of gonnardite and natrolite, which is more consistent with the results commonly found in known gallosilicate materials. However, the expansion is only around 0.8% for TNU-3/gonnardite while it is 2.9% for TNU-4/natrolite. Newsam and Vaughan[5] already advanced that the changes in unit cell size upon isomorphous substitution of Al by Ga is apparently framework-specific: it sometimes produces an expansion of the cell (like in our NAT materials or in the ABW, THO, FAU, MAZ, and LTL materials reported by them) while in other cases a contraction is found (like in our GIS and their SOD materials). Given the differences in expansion for our two NAT materials, the changes appear to be not only framework-specific but also depend on the symmetry or degree of order of materials with the same topology (vide infra).

Figure 4 shows the scanning electron micrographs of the four gallosilicate materials prepared in this study. TNU-1 consists of needlelike crystals of approximately 15−20 μm in length. TNU-2 typically appears as agglomerates of very small (1 μm), heavily overlapped cuboids. TNU-3 has spherical aggregates of 20−25 μm that are in turn made of very small spheres. TNU-4 is composed of orthorhombic prisms of approximately 20 μm in length bound at both ends by pyramids, which is similar to the crystal morphology reported by Occelli et al. for the gallosilicate natrolite.[12]

The TGA/DTA curves for each gallosilicate material in its as-synthesized form are given in Figure 5. TNU-1 exhibits a large weight loss (ca. 9.5%) at temperatures up to 400 °C, which can be attributed to the desorption of occluded water. Also, this material gives no noticeable DTA peaks associated with a phase change in the temperature region studied here, revealing that it has a good thermal stability. In fact, in situ XRD experiments in static air have shown that TNU-1 normally synthesized as the K form maintains its structural integrity even after heating at 900 °C. A quite similar result is also observed for the as-synthesized K form of TNU-2. Thus, the thermal stability of K-TNU-2 appears to be comparable to that of K-TNU-1. After NH_4^+ exchange, however, these two materials began losing crystallinity around 350 °C, suggesting a poor stability for their acid form. Possibly, decomposition of NH_4^+ (occurring in the 300−400 °C range, according to TGA analysis) to yield H^+ may be followed by the attack of the dehydrated proton on the gallosilicate framework. As seen in Figure 5, on the other hand, the DTA/TGA curves for both TNU-3 and TNU-4 (as-made samples) are characterized by a sharp endothermic peak and a significant weight loss around 300 °C. The weight loss must be ascribed to dehydration and the materials become amorphous during this process. This reflects that the thermal stability of the two NAT-type gallosilicate materials prepared in the Na form is much poorer than that of TNU-1 or TNU-2.

Figure 6 shows the IR spectra of the framework vibration region for a series of gallosilicate molecular sieves. Due to the featureless nature of the IR bands for TNU-1, together with no existence of an aluminosilicate CGS analogue, a reliable interpretation and assignment of every band in the spectrum for this gallosilicate material cannot be made at this time. However, TNU-1 gave the most intense asymmetric T−O stretching band around 970 cm^{-1}, revealing its high Ga content. Despite considerable differences in the framework structure, no noticeable differences in the IR spectra of TNU-1 and TNU-2 are observed. On the other hand, TNU-3 and TNU-4 can be distinguished from the first two materials, due to their well-resolved IR spectra. As seen in Figure 6, in particular, the splitting of the structural vibration bands found in the 900−1300 cm^{-1} region is more explicit for the low-symmetry phase TNU-4, giving a fingerprint feature for this gallosilicate material. Thus, six asymmetric T−O stretching bands at 935, 950, 975, 1030, 1050, and 1075 cm^{-1} are clearly distinguished from the IR spectrum of TNU-4. This can be attributed to the ordering of Si and Ga much higher in TNU-4 than in TNU-3 (vide infra) and the concomitant decrease in crystal symmetry, together with a possible contribution of differences in the crystal size. Comparison of the IR spectra of these two NAT-type gallosilicate materials with those of the natural aluminosilicate counterparts reveals that most of the structural vibration bands shift to lower wavenumber regions in the gallosilicates,[22] which again shows the isomorphous substitution of Al by heavier Ga in the zeolite framework.

Figure 7 shows the ^{29}Si MAS NMR spectra of TNU gallosilicate materials together with the simulated spectra and their deconvoluted components. Here we deconvoluted the spectra using mixed Lorentzian−Gaussian functions and assigned each resonance to $Si(OGa)_n(OSi)_{4-n}$ species with $n = 0-4$ on the basis of

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(22) Gottardi, G.; Galli, E. *Natural Zeolites*; Springer-Verlarg: Heidelberg, Germany, 1985; pp 347−349.

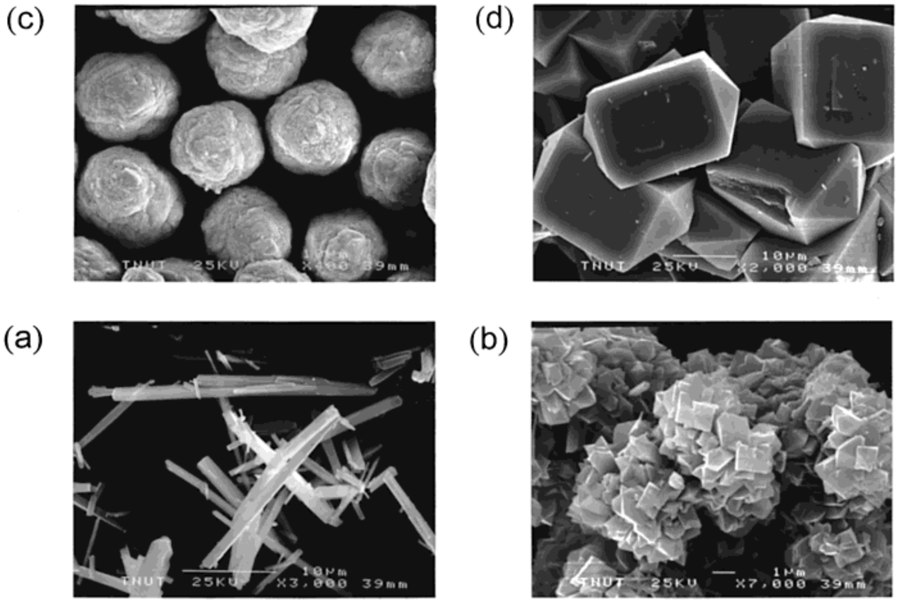

Figure 4. Scanning electron micrographs of (a) TNU-1, (b) TNU-2, (c) TNU-3, and (d) TNU-4.

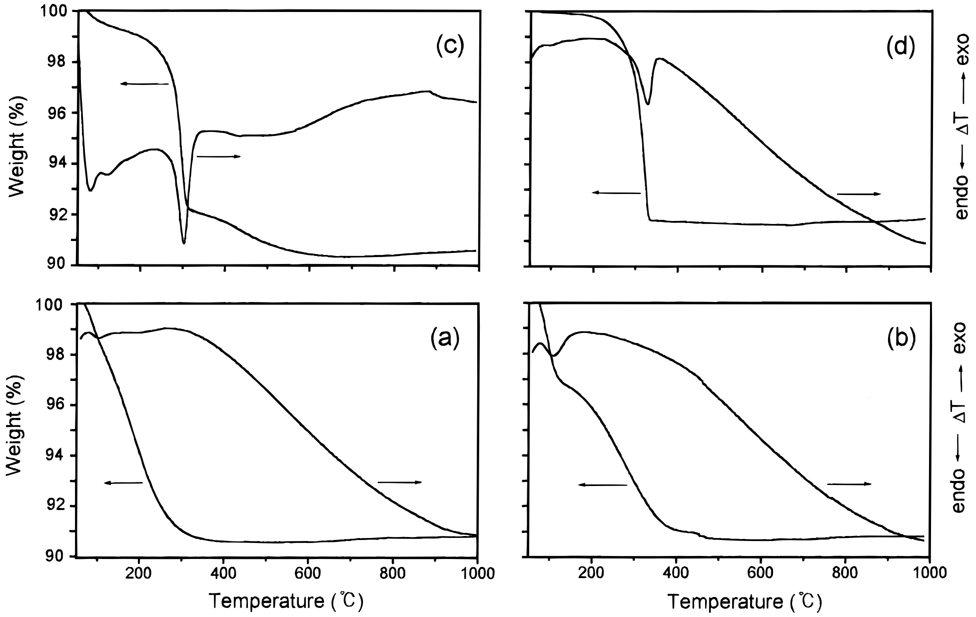

Figure 5. TGA/DTA curves of as-made (a) TNU-1, (b) TNU-2, (c) TNU-3, and (d) TNU-4.

the known ranges of chemical shifts for such species in the already known gallosilicate materials with Si/Ga < 3.0.[23] As seen in Figure 8, however, this does not lead to unambiguous assignments, not only due to the severe overlapping of ranges for different Si species but also due to the frequent splitting of species with the same *n*. In addition, comparison of Figure 8 and the equivalent figure for aluminosilicate materials given in ref 23 shows a more severe overlapping of chemical shift ranges, despite the wider range of chemical shifts for gallosilicates and greater deshielding of Si atoms for gallosilicate than for aluminosilicate materials. Thus, for the proposed assignment of ^{29}Si resonances, we took into account the experimental values of Si/Ga ratios, in such a way that the Si/Ga ratios calculated from the ^{29}Si MAS NMR intensities were in reasonable agreement with the values obtained by chemical analysis. For the calculation of the Si/Ga ratios by NMR, we assumed also that the Loewenstein rule of avoidance of Al−O−Al species, generally encountered in aluminosilicate zeolites synthesized hydrothermally at low temperatures, also holds for gallosilicate materials (avoidance of Ga−O−Ga species). This assumption is in agreement with previous findings on the low-temperature hydrothermal crystallization of gallosilicates.[5,23]

The chemical shifts, relative intensities, and proposed assignments of the ^{29}Si MAS NMR resonances for our TNU gallosilicate materials are summarized in Table 3. Among the results presented, those of TNU-3 and TNU-4 are the most interesting. As stated earlier, these two materials have the same framework topology (NAT) but different symmetries. In addition, both materials have essentially the same chemical composition. An

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(23) Engelhardt, G.; Michel, D. *High-Resolution Solid-State NMR of Silicates and Zeolites*; John Wiley & Sons: New York, 1987; and references sited therein.

Table 3. ^{29}Si MAS NMR Resonances for TNU Gallosilicates and Proposed Assignment[a]

TNU-1			TNU-2			TNU-3			TNU-4		
chem shift (ppm)	*I* (%)	*n*Ga	chem shift (ppm)	*I* (%)	*n*Ga	chem shift (ppm)	*I* (%)	*n*Ga	chem shift (ppm)	*I* (%)	*n*Ga
−77.6	2.5	4	−79.8	11.2	4	−78.1	8.4	4	−79.5	4.1	3
−83.8	22.7	3	−85.4	33.5	3	−81.3	6.6	3	−83.7	60.9	3
−87.1	3.0	3	−92.2	41.7	2	−83.7	41.4	3	−93.7	27.4	2
−90.3	47.5	2	−98.0	6.0	1	−87.4	12.1	2	−96.2	7.6	1
−95.9	11.8	1	−100.4	5.7	1	−90.9	6.2	2			
−98.9	10.9	1	−103.6	1.8	0	−93.6	15.8	2			
−103.7	1.6	0				−98.1	9.5	1			
$Si/Ga_{nmr} = 1.96$ (2.1)[b]			$Si/Ga_{nmr} = 1.66$ (1.6)[b]			$Si/Ga_{nmr} = 1.57$ (1.5)[b]			$Si/Ga_{nmr} = 1.55$ (1.6)[b]		

[a] *n*Ga refers to the number of Ga atoms in $Si(OGa)_n(OSi)_{(4-n)}$ species. [b] Si/Ga_{nmr} is the Si/Ga ratio calculated according to the proposed assignments and assuming the avoidance of Ga−O−Ga bonds (extended Loewenstein rule). The Si/Ga ratio determined by chemical analysis is given in parentheses.

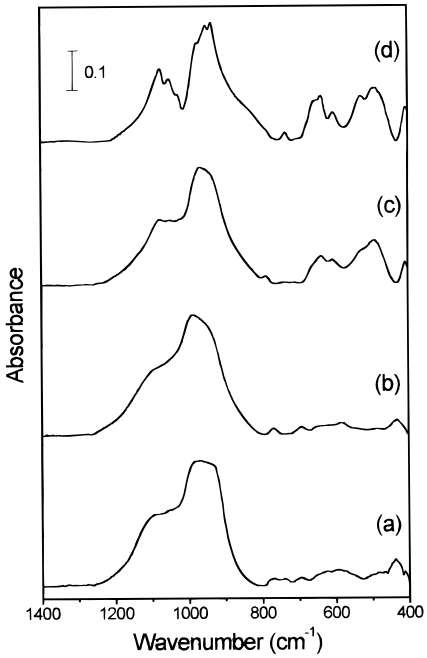

Figure 6. IR spectra of as-made (a) TNU-1, (b) TNU-2, (c) TNU-3, and (d) TNU-4 in the structural region.

inspection of their ^{29}Si MAS NMR results immediately evidences a large difference in the intensities of various $Si(OGa)_n(OSi)_{4-n}$ resonances, suggesting a difference in the Si, Ga ordering among the different T-sites. Thus, we will consider first the issue of Si, Ga ordering in TNU-3 and TNU-4 materials and then their crystal symmetries.

For a material with a bulk Si/Ga ratio of 1.5, a random distribution of Ga and Si over different T-sites subject only to the "extended" Loewenstein rule will lead to the following relative populations of $Si(OGa)_n(OSi)_{4-n}$ species with $n = 0$, 1, 2, 3, and 4: 1.6, 11.5, 31.5, 38.1, and 17.3%, respectively. Comparison with the observed intensities for TNU-3 and TNU-4 (Table 3) shows that while TNU-3 has intensities reasonably similar to those expected for a random but Loewensteinian distribution, TNU-4 is sharply distinct, presenting two prominent resonances at −83.7 and −93.7 ppm with an intensity ratio of 2:1 that must be assigned to $Si(OGa)_3(OSi)_1$ and $Si(OGa)_2(OSi)_2$ species. It should be noted here that the ^{29}Si MAS NMR spectrum of TNU-4 is quite similar to that of the corresponding aluminosilicate counterpart, i.e., natrolite.[24] According to the single X-ray structure determination study on this mineral,[19] natrolite consists of $Si(OAl)_3(OSi)$ and $Si(OAl)_2(OSi)_2$ units in a 2:1 ratio, in accordance with its Si/Al ratio (1.5). Therefore, it is clear that a high degree of local order exists also in TNU-4 as opposed to TNU-3. However, Figure 7 shows that some broad resonances which should be assigned

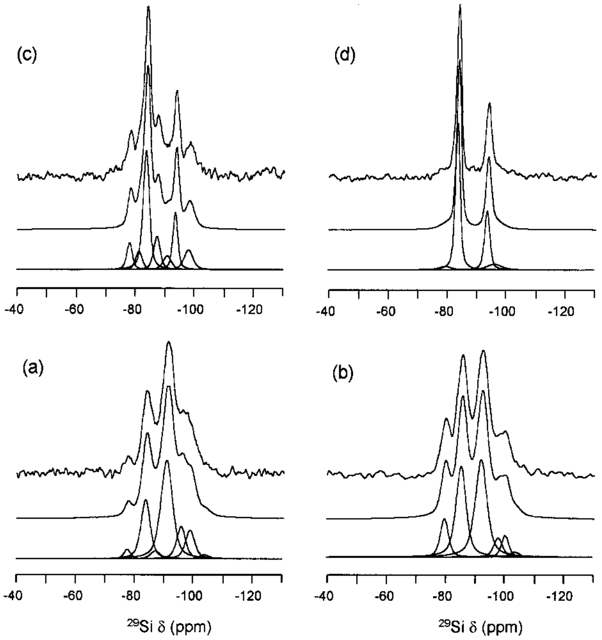

Figure 7. Curve deconvolution of the ^{29}Si MAS NMR spectra of (a) TNU-1, (b) TNU-2, (c) TNU-3, and (d) TNU-4: experimental (top); simulated (middle); deconvoluted components (bottom).

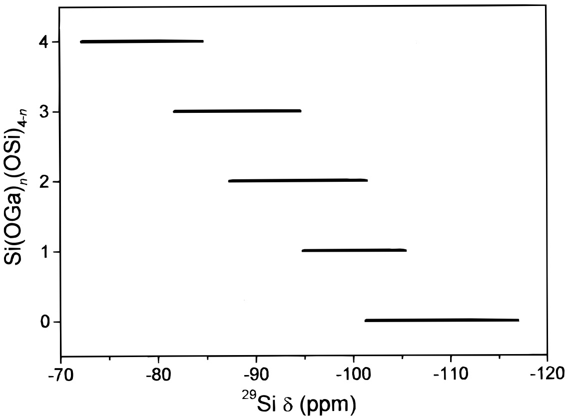

Figure 8. ^{29}Si chemical shift ranges of $Si(OGa)_n(OSi)_{4-n}$ species with $n = 0-4$ in gallosilicate molecular sieves.

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

to $Si(OGa)_n(OSi)_{4-n}$ species in different environments exist in the ^{29}Si NMR spectrum for TNU-4. This is in apparent contradiction with the ordering and symmetry of this NAT-type gallosilicate material. Such broad bands could just be due to a minor portion of “disordered” TNU-3 in the “ordered” TNU-4 sample. We note that, most likely, the presence of a TNU-3 impurity in TNU-4 would not be noticeable by a simple inspection of the powder XRD data, given the structural relationship between both types of samples and the essentially identical chemical composition. The scanning electron micrographs, however, show different morphologies for each type of samples, without a hint for the presence in TNU-4 of impurities of TNU-3 (Figure 4). Alternatively, the possibility for the existence in TNU-4 of mixed ordered and disordered domains should be considered (see discussion on the ^{71}Ga MAS NMR results below). We also note that the Si/Ga ratio (1.48) of TNU-4 calculated by ^{29}Si MAS NMR is almost the same as that (1.56) from chemical analysis, if only the two prominent bands are taken into account.

In space group *Fdd*2, the NAT topology has three different T-sites with multiplicities 8:16:16. To achieve a Si/Ga ratio of around 1.5 with Si, Ga ordering to give only $Si(OGa)_3(OSi)_1$ and $Si(OGa)_2(OSi)_2$ species, one of the sites with high multiplicity should be fully occupied by Ga, while the other sites should be fully occupied by Si. A previous powder neutron diffraction study[11] by Newsam and co-workers showed that the T3 site, one of the high multiplicity sites in the gallosilicate version of natrolite, has significant Ga occupancy. This result is consistent with that obtained from the ^{29}Si MAS NMR spectrum of TNU-4, although the ^{29}Si NMR result itself does not give direct information on which of the high-multiplicity sites is occupied by Ga, due to their topological equivalence. In the high-symmetry NAT material (TNU-3, space group $I\bar{4}2d$), on the other hand, only two different T-sites with multiplicities 4:16 exist. Thus, a complete ordering of Si and Ga cannot be achieved for a Si/Ga ratio of about 1.5. This led us to conclude that a different distribution of Si and Ga over the tetrahedral sites of the NAT topology may be responsible for the different symmetries of TNU-3 and TNU-4. However, it is still unclear what causes such a different distribution of tetrahedral atoms. Clearly and very interestingly, in the synthesis of TNU-3 and TNU-4, the crystallization temperature is a main factor that may cause such a different distribution of heteroatoms other than Si. Possibly, the more ordered material is thermodynamically more stable but has a higher activation energy for nucleation and/or crystallization, favoring its crystallization at a higher temperature. The details are, however, beyond the scope of this article.

Figure 9 shows the ^{71}Ga MAS NMR spectra of all gallosilicate molecular sieves prepared here. Although all the spectra exhibit no noticeable ^{71}Ga resonances attributable to octahedrally coordinated Ga species, the absence of extraframework Ga in our gallosilicate molecular sieves cannot be ruled out. This is because resonances of these sites may be broadened beyond detection by strong second-order quadrupolar interactions. TNU-1, TNU-2, and TNU-3 show only one broad asymmetric resonance in the range 145–165 ppm, which is very similar to the results observed for other gallosilicate materials and corresponds to tetrahedral Ga in the zeolite framework.[13,25,26]

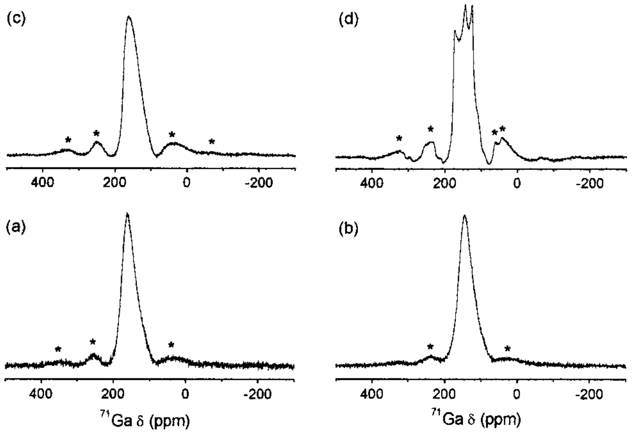

Figure 9. ^{71}Ga MAS NMR spectra of (a) TNU-1, (b) TNU-2, (c) TNU-3, and (d) TNU-4. Spinning sidebands are marked by asterisks.

Of particular interest is the ^{71}Ga NMR spectrum of TNU-4, because of two observations: First, it clearly shows a line shape which is dominated by second-order quadrupolar interaction. This line shape is lacking in the spectra of the other materials. Actually, it is very uncommon that the powder ^{27}Al or ^{71}Ga MAS NMR spectra of zeolites show quadrupolar line shapes as those in the spectrum in Figure 9d. We believe that the high degree of local order due to a nonrandom distribution of Si and Ga (see above) may be responsible for this observation because of a smaller distribution of electric field gradients. Since Si, Ga ordering appears to be the main difference between TNU-3 and TNU-4, this hypothesis looks reasonable. On the other hand, there is one published ^{71}Ga NMR spectrum of a gallosilicate with the NAT topology synthesized in the presence of Na, K, and BTMA cations,[12] which is similar to that observed for TNU-4. The field strength (7.0 T) applied for obtaining this spectrum was weaker than that (9.4 T) used in this work. However, the ^{71}Ga MAS NMR line shape observed in ref 12 was found to pronounce second-order quadrupole effects much less clearly than observed in our TNU-4 materials. This can be attributed to the higher degree of Si, Ga ordering in TNU-4 and/or to differences in the cationic composition of the materials studied.

The second observation is that the spectrum in Figure 9d reveals the existence in TNU-4 of at least two different environments for Ga, which is in apparent contradiction with the symmetry and Si, Ga ordering discussed above. One possible explanation is that the true or local symmetry in TNU-4 is lower than observed by XRD and that the high multiplicity site occupied by Ga is actually split in two (at least at the short-range scale). This would still give rise to just two types of $Si(OGa)_n(OSi)_{4-n}$ species with $n = 2$ and 3, respectively. Alternatively, and as already suggested above, it is also possible that there are crystalline domains in TNU-4

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(25) Bellussi, G.; Millini, R.; Carati, A.; Maddinelli, G.; Gervasini, A. *Zeolites* **1990**, *10*, 642.

(26) Bayense, C. R.; Kentgens, A. P. M.; De Haan, J. W.; Van de Ven, L. J. M.; van Hoof, J. H. C. *J. Phys. Chem.* **1992**, *96*, 775.

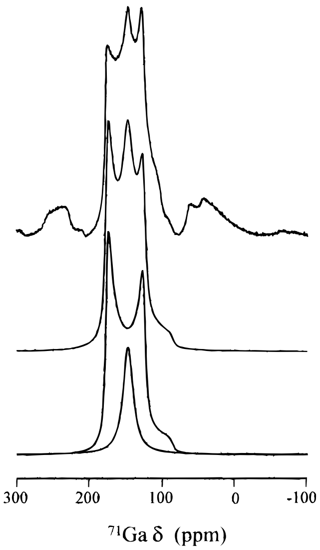

Figure 10. Simulation of the ^{71}Ga MAS NMR spectrum of TNU-4: experimental (top); simulated (middle); deconvoluted components (bottom).

with different degrees of Si, Ga ordering, which would explain not only the presence of at least two types of Ga species in the ^{71}Ga MAS NMR but also the existence of additional species in the ^{29}Si MAS NMR spectrum (see Figure 7d and Table 3). Given that the differences between TNU-3 and TNU-4 are just due to a different crystallization temperature, this looks as a sensible hypothesis. Figure 10 shows a simulation of the ^{71}Ga MAS NMR spectrum of TNU-4 consisting of two components, one Gaussian component at a chemical shift similar to that of TNU-3 plus a quadrupolar component significantly shifted to lower field ($\delta = 191$ ppm, $C_Q = 5.0$ MHz, $\eta = 0$). In our interpretation, the Gaussian resonance corresponds to Ga in the more disordered domains while the quadrupolar resonance in due to Ga in ordered domains.

Conclusions

A series of gallosilicate molecular sieves with different framework topologies have been hydrothermally synthesized from wholly inorganic systems and characterized by XRD, elemental and thermal analyses, scanning electron microscopy, IR, and ^{29}Si and ^{71}Ga MAS NMR measurements. It is observed that the presence of Ga in the synthesis mixture is the critical factor directing the crystallization of microporous gallosilicate materials with topologies different from those of the aluminosilicate zeolites prepared under otherwise identical conditions. Also, the type of alkali metal cations added to the gallosilicate synthesis mixture and the crystallization temperature were found to govern the phase selectivity of the zeolitic products obtained. A GIS-type material has been prepared using K^+, rather than Na^+, as a countercation. On the other hand, two NAT zeolites where prepared with different degrees of order in the distribution of Si and Ga atoms over the available tetrahedral sites in the framework, as a function of the crystallization temperature. The overall results of this study demonstrate large differences in the hydrothermal chemistry of aluminosilicate and gallosilicate systems and suggest that the introduction of Ga into silicate frameworks could lead to the discovery of novel low-silica zeolite structures.

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