Synthesis and Properties of Gallium Tetramethylammonium Sodalite, $NMe_4GaSi_5O_{12}$

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A tetramethylammonium gallosilicate zeolite with the sodalite structure was synthesized. Its chemical analysis showed a Si/Ga ratio of 5:1. *X*-Ray powder diffractograms and i.r. spectra of the new zeolite were also recorded and its thermal stability studied by differential thermal analysis. A formula of $NMe_4GaSi_5O_{12}$ is indicated.

Tetramethylammonium sodalite in pure form was first synthesized by Baerlocher and Meier[1] in 1969. Barrer *et al.*[2] reported that the ideal chemical formula of the unit cell of hydrosodalite is $Na_6Al_6Si_6O_{24}\cdot8H_2O$. Unlike the synthesis of most other zeolites, the synthesis of a hydrosodalite, which is richer in silicon, is possible only by means of the tetramethylammonium cation. During this synthesis only the NMe_4^+ cations are available as monovalent cations and because of its size only one NMe_4^+ is incorporated in one sodalite cage. Further, this means that only one silicon ion of the cage framework can be substituted by an aluminium ion, as every further substitution would create a negative charge which would require an additional cation to compensate it. As the unit cell contains two sodalite cages (so called β cages), an Si/Al ratio of 5:1 results for the tetramethylammonium sodalite.

Suzuki *et al.*[3] described a synthesis of a pure gallium hydrosodalite in 1985 in which all aluminium atoms were replaced by gallium. Accordingly a Si/Ga ratio of 1:1 was found. Our synthesized gallosilicate zeolite can be interpreted as a Ga-substituted homologous form of the tetramethylammonium sodalite. Similar to the hydrothermal synthesis of the tetramethylammonium sodalite, the gallium tetramethylammonium sodalite was prepared in an autoclave at 180 °C under the corresponding water-vapour pressure. Its synthesis and properties are now presented.

Experimental

Synthesis.—As starting materials we used tetramethylammonium hydroxide [25% (w/w) in water] and tetramethoxosilane from Fluka Feinchemikalien and Ga_2O_3 [99.99% (w/w)] from Morton Thiokol. Tetramethoxosilane (9.15 g) was added dropwise to NMe_4OH (50.6 g) solution and water (18.7 g) and stirred intensively. After the saponification of the tetramethoxosilane, the clear solution was boiled for 15 min to evaporate all the methanol formed. Co-evaporated water was subsequently replaced. Powdered Ga_2O_3 (0.428 g) was added to this solution, and was completely dissolved during the synthesis. The hydrothermal crystallization took place in a stainless-steel autoclave with poly(tetrafluoroethylene) insert to avoid contamination of the autoclave body. Its utilizable volume was *ca.* 120 cm^3, designed as a borehole with a cylindrical diameter of 30 mm.

The charge was aged for 5 d without stirring at 100 °C to dissolve all the Ga_2O_3. The temperature of crystallization was 180 °C and the duration was 5 d. After quenching of the hot autoclave in cold water, a white product could be separated from the mother-liquor on sintered glass at a bank of suction filters. The product was washed thoroughly with distilled water and was dried at 100 °C. A yield of about 70% based on the Ga_2O_3 used was obtained.

The tetramethylammonium sodalite was synthesized according to Baerlocher and Meier,[1] but we substituted aluminium tri-isopropoxide with Al metal. The aluminium (p.a. from Merck) was directly dissolved in the tetramethylammonium hydroxide solution.

Characterization and Discussion

The zeolite was stored over saturated aqueous $Ca(NO_3)_2$ (56% relative humidity at room temperature) for 7 d before analysis. The analytical results are shown in Table 1. The determination of Si and Ga was carried out in the classical gravimetric manner, Si as SiO_2 and Ga as gallium quinolin-8-olate. The contents of C, H, and N determined by microanalysis are uncertain as the residue was not white after combustion and presumably the combustion was not complete. The addition of V_2O_5 resulted in only a slight improvement. The excess of H was due to a small water content of the zeolite visible in the i.r. spectra and differential thermal analysis curves as explained below. The analytical results showed that we had synthesized a gallosilicate with a Si/Ga ratio of 5:1.

The identification of the product was carried out by *X*-ray powder diffractometry. A Siemens D 500 diffractometer was employed at a scan rate of 1° min^{-1} with nickel-filtered Cu-K_α radiation over a 2θ range of 2—80°. A comparison of the diffractograms for tetramethylammonium sodalite[1] and our gallosilicate (see Table 2) showed that both zeolites have a sodalite structure. The cubic lattice parameter was calculated from 26 identifiable reflections using silicon as an internal standard. Our sodalite, $NMe_4GaSi_5O_{12}$, is cubic body-centered with a lattice parameter of a = 0.8925 nm, slightly less than that of tetramethylammonium sodalite[1] (a = 0.8975 nm). A similar difference was found by comparison of the lattice parameters of hydroxysodalite (a = 0.8866 nm) and gallium hydroxysodalite (a = 0.8856 nm).[3] The felspathoids bromosodalite, $Na_6Al_6Si_6O_{24}\cdot2NaBr$ (a = 0.8934 nm),[4] and gallium bromosodalite (a = 0.8854 nm)[5] also showed a noticeable lattice contraction.

We recorded the i.r. spectra of both zeolites [see Figure 1(*a*) and (*b*)] in the range 200—4 000 cm^{-1} on a Perkin-Elmer 283B

Table 1. Chemical composition of gallium tetramethylammonium sodalite

Component	Content/% (w/w) Theoretical	Content/% (w/w) Analytical	Analytical method
Si	29.5	29.2	Gravimetry (SiO_2)
Ga	14.65	14.85	Gravimetry (quinolin-8-olate)
C	10.1	7.45	Microanalysis
H	2.55	2.65	Microanalysis
N	2.95	2.00	Microanalysis

Table 2. *X*-Ray diffraction data

d/nm	hkl	I/I_0	d/nm	hkl	I/I_0
0.6303	110	1.3	0.1628	521	6.3
0.4450	200	36	0.1579	440	8.3
0.4035	210	2.7	0.1532	433, 530	3.5
0.3641	211	100	0.1488	442, 600	7.5
0.3159	220	15	0.1448	532, 611	5.1
0.2823	310	16	0.1414	620	0.9
0.2574	222	28	0.1379	541	1.9
0.2383	321	6.3	0.1345	622	9.7
0.2227	400	6.3	0.1318	631	3.9
0.2104	330, 411	5.6	0.1290	444	4.5
0.1998	420	2.5	0.1263	543, 550, 710	2.5
0.1903	332	8.4	0.1238	640	0.6
0.1819	422	2.5	0.1215	552, 633, 721	2.9
0.1752	431, 510	15			

Table 3. Infrared absorption bands (cm^{-1})

Assignment	Tetramethylammonium sodalite	Gallium tetramethylammonium sodalite
H_2O	3 430	3 430
NMe_4^+	—	3 040
H_2O	1 650	1 650
NMe_4^+	1 490	1 490
NMe_4^+	1 420	1 420
	1 080	1 020
NMe_4^+	960	—
	760	760
	720	670
	600	595
	460	450
	—	330

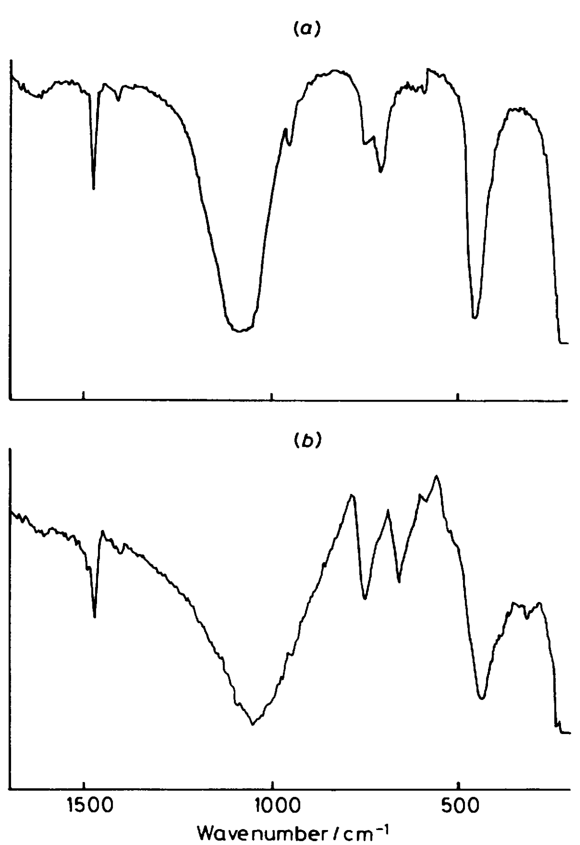

Figure 1. Infrared spectra of tetramethylammonium sodalite (*a*) and gallium tetramethylammonium sodalite (*b*)

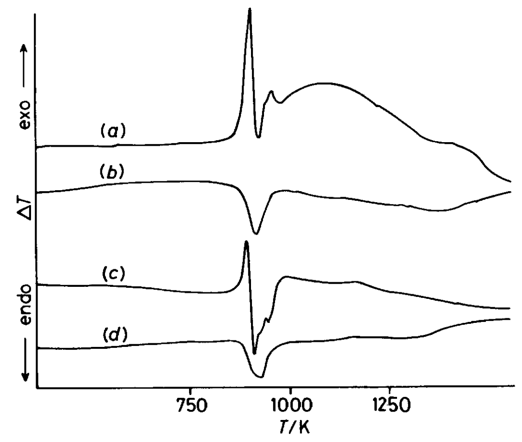

Figure 2. D.t.a. curves for the tetramethylammonium sodalite, (*a*) in air, (*b*) in a nitrogen atmosphere, and for the gallium tetramethylammonium sodalite, (*c*) in air, (*d*) in a nitrogen atmosphere

using the KBr disc technique. The sodalites (each 3 mg) were ground with ultrapure KBr (300 mg) in a vibration mill, then compressed at 7 500 bar (7.5 × 10^8 Pa) to obtain discs of 13 mm in diameter. The following structures or 'compounds' could be identified (see Table 3): (1) weak and broad bands at 3 430 and 1 650 cm^{-1} due to a small water content of both zeolites,[5,6] even though this is not expressed in the ideal summation formula; (2) by comparison with the spectrum of tetramethylammonium iodide,[7] bands at 960, 1 420, 1 490, and 3 040 cm^{-1} assigned to the NMe_4^+ cation; and (3) remaining bands attributed to the aluminosilicate and gallosilicate lattices; only some of these show differences.

Taking into account the work of previous investigators,[4,6,8,9] our assignments of the remaining bands are as follows. The bands at 1 080 and 1 020 cm^{-1} for the tetramethylammonium and present sodalites respectively must be assigned to an Si–O stretching mode with some contribution from Al–O motion and Ga–O motion, respectively. The band at 760 cm^{-1} appears for both zeolites and can be assigned to an Si–O mode. The bands at 720 and 670 cm^{-1} respectively for the two sodalites are most interesting because they are regarded as an Al–O mode and a Ga–O mode, respectively.

Differential thermal analysis (d.t.a.) was carried out with Linseis L 62 equipment and a computer (for a detailed description of the hard- and soft-ware see refs. 10, 11). The rate of heating was 10 K min^{-1} and *ca.* 30 mg of sample were used. The d.t.a. curves in air for the tetramethylammonium and present sodalites [see Figure 2(*a*) and (*c*)] showed exothermic peaks at 893 and 897 K, respectively, corresponding to the oxidation of the organic cation. The exothermic peak of the tetramethylammonium sodalite was followed by a very broad peak, corresponding to the slow oxidation of residual carbon. The exothermic peak of the gallium tetramethylammonium sodalite was rapidly followed by an endothermic peak at 924 K.

Solid-state reactions which are accompanied by a gas exchange reveal that the packing density of the sample is of great importance because it substantially influences the gas diffusion. A scanning electron microscopic study (with a Leitz REM 1200) of the tetramethylammonium sodalite only shows crystallites smaller than 1 µm. Our sodalite shows well developed cubic crystallites with an average edge length of 5 µm

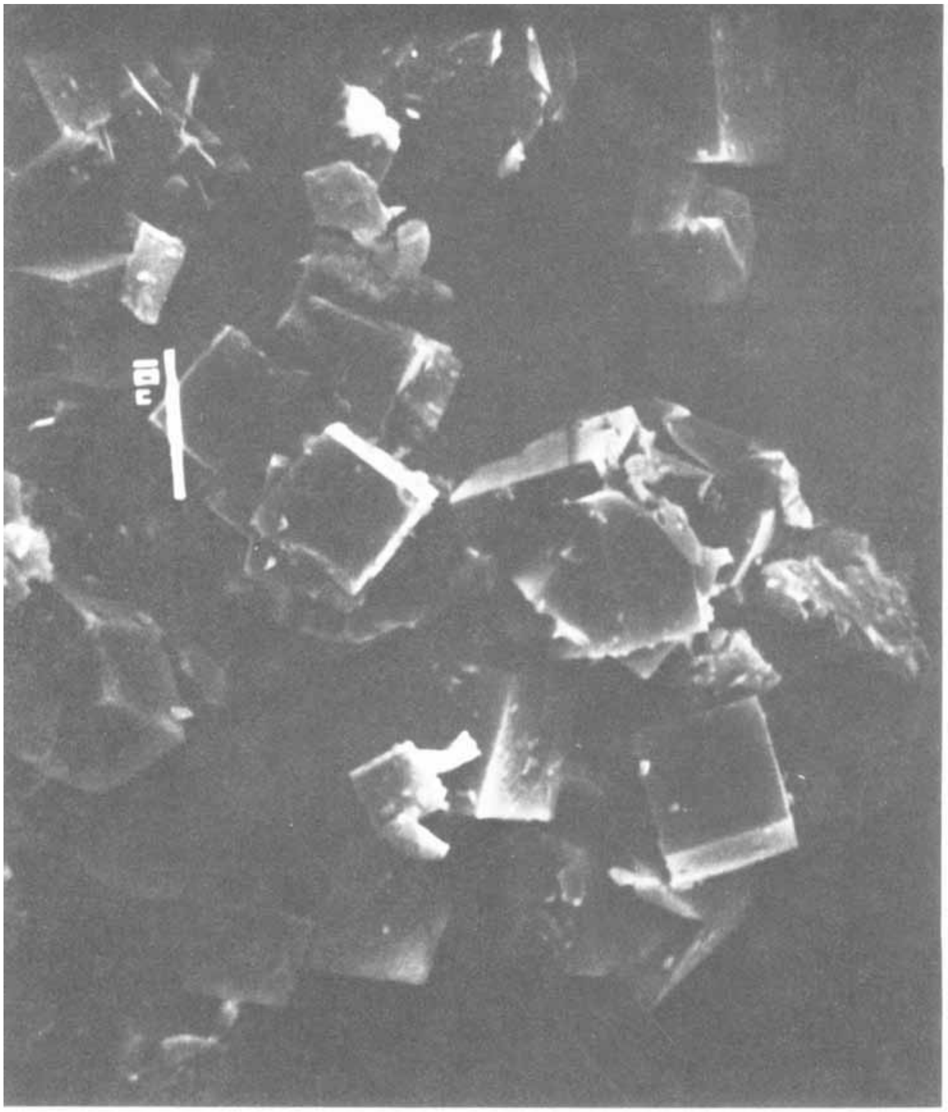

Figure 3. Scanning electron micrograph of the gallium tetramethylammonium sodalite

(see Figure 3). For this reason the endothermic peak of this sodalite can be interpreted as the decomposition of NMe_4^+ because the decomposition is endothermic in the absence of oxygen. Such a situation occurs in the centres of the large crystallites of our sodalite and in compact agglomerates. Also the carbon formed is located inside the large crystallites and cannot be oxidized. The same behaviour was observed during the d.t.a. of the two sodalites in a nitrogen atmosphere [see Figure 2(*b*) and (*d*)]. The curves only show endothermic peaks at 905 and at 928 K, respectively. Powder diffractograms of the two sodalites upon heating at 923 K in nitrogen for 3 h verify that the discussed reactions relate exclusively to the NMe_4^+ and are not related to a collapse of the silicate framework. Beside the above reactions, no other thermal effects can be observed. The high thermal stability of these zeolites was expected due to their high silicon content.

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