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Synthesis of gallosilicates — MTW- type structure zeolites: Evidence of Ga-substituted T atoms

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Gallosilicates with the ZSM-12 structure have been synthesized from the reaction mixture of sodium silicate, gallium nitrate, and methyl triethylammonium bromide at 353 K in an autoclave. XRD results associated with an i.r. study of the lattice vibrations indicated that highly crystalline materials with the ZSM-12 structure were obtained. ⁷¹Ga MAS n.m.r. studies along with ²⁹Si measurements showed that Ga is in tetrahedral positions and the Si/Ga atomic ratio = 70. T.p.d. of ammonia adsorbed on H-GaZSM-12 clearly showed the acid nature of the material, which supports strongly the presence of Ga³⁺ in the zeolite framework.

Keywords: Ga-ZSM-12 synthesis; Ga-ZSM-12 acidity; ⁷¹Ga MAS n.m.r.

INTRODUCTION

The synthesis of zeolite ZSM-12, the structure of which contains noninterconnecting 12-ring (0.57 × 0.61 nm) channels, has been described in the patent literature.¹⁻³ It has been shown that among various tetraalkylammonium cations, methyl triethylammonium cation (MTEA)⁺ is the most appropriate to direct the structure of ZSM-12. More recently, a crystallization kinetic study has allowed the synthesis of ZSM-12 to be optimized in the presence of MTEA as organic template.⁴ Isomorphous substitutions of Al in the framework of zeolites have been of considerable interest and several papers report the synthesis of gallium analog zeolites.⁵⁻¹⁰ In this paper, we report the synthesis of a gallosilicate with the ZSM-12 structure in the presence of MTEA bromide as organic template. X-ray diffraction, infrared spectroscopy, ⁷¹Ga MAS n.m.r. and t.p.d. of ammonia provided good evidence of the highly crystalline nature of the gallium analog ZSM-12 material.

EXPERIMENTAL

Materials

Ga-ZSM-12 samples were prepared from a sodium silicate solution (Prolabo Na₂O = 8 wt%; SiO₂ = 26 wt%), Ga(NO₃)₃ · x H₂O, and methyl triethylammonium bromide (MTEA Br), both purchased from Aldrich-Chemistry.

Characterization

The synthesized samples were characterized by

(i) X-ray powder diffraction. The X-ray diffractograms were recorded with a Philips PW 1710 diffractometer using CuK α radiation.

(ii) Framework infrared spectra in the region 1200–300 cm⁻¹ were recorded with a Perkin-Elmer 580 spectrometer. The zeolite samples were ground with KBr powder (1% by weight of zeolite) and pressed into thin wafers.

(iii) Solid-state ²⁹Si and ⁷¹Ga-state MAS n.m.r. experiments were performed on a Bruker MSL 300 spectrometer. The rotor was spun at a rate of 4 kHz. Ga(NO₃)₃ was used as an external standard reference for the samples containing gallium, and TMS was the reference for ²⁹Si n.m.r. spectra.

(iv) The acidity of the zeolites was estimated from the temperature-programmed desorption t.p.d. of ammonia. The sample (0.3 g) was activated at 833 K for several hours in flowing oxygen. It was then cooled at 353 K and exposed to a NH₃-N₂ gas flow for 1 h. The t.p.d. experiment was carried out in the temperature range 353–853 K at a heating rate of 5 K/min. Quantitative measurements of desorbed ammonia were made with a gas chromatograph equipped with a Delsi GC 121 MB catharometer.

Chemical analysis by atomic emission spectrophotometry for Ga and atomic absorption for Si gave 2.0 wt% Ga₂O₃ and 97.6 wt% SiO₂, which corresponds to a Si/Ga atomic ratio of 60.

RESULTS AND DISCUSSION

Synthesis

The standard procedure was as follows: The solu-

Table 1 Mole ratios of the different reagents for Ga-ZSM-12 synthesis

SiO ₂ /Ga ₂ O ₃	Na ⁺ /SiO ₂	R ₄ N ⁺ /SiO ₂	OH ⁻ /SiO ₂	H ₂ O/SiO ₂	Na ⁺ /R ₄ N ⁺
120	0.60	0.40	0.30	125	1.5

tions were prepared in polypropylene flask; 0.33 g of Ga(NO₃)₃ × H₂O and 3.9 g of MTEA Br were dissolved in 25 cm³ of distilled water (solution A); and 11.5 g of sodium silicate were added to solution A under stirring, at ambient temperature. The required [OH]⁻ concentration was adjusted by adding a calculated amount of H₂SO₄ solution (0.52 g of concentrated sulfuric acid per cm³ H₂O) to the reagent mixture. For the above zeolite preparation, 1, 2 cm³ of the diluted H₂SO₄ solution was added. Crystallization was carried out in a Teflon bottle introduced into the autoclave and heated at 428 K under autogeneous pressure. The crystallization time was 135 h. The solid recovered was washed with distilled water and dried in air at 353 K. The gel solution composition is shown in *Table 1*.

The X-ray diffraction pattern of the as-synthesized material is shown in *Figure 1*. In *Table 2* are reported the interplanar spacing *d* values and the corresponding relative peak intensities.

The data presented in *Figure 1* and *Table 2* showed that the as-synthesized sample was highly crystalline: it has the ZSM-12 structure free of other crystalline impurities. The X-ray diffraction pattern shown in *Figure 1* is comparable to those given in Refs 1, 2, and 11 and is assigned to the ZSM-12 structure.

Infrared study

Midinfrared spectroscopic studies of the zeolite framework vibrations in the region 1200–300 cm⁻¹ have been widely used to characterize and to differentiate various zeolite structures.^{12–13} This technique was used to identify the gallium analog ZSM-12 sample synthesized in the present work. *Figure 2* shows the i.r. spectrum in the 1200–300 cm⁻¹ range of the as-synthesized Ga sample. Several i.r. bands are observed at 1220, 1080, 780, 640, 580, 545, and 480 cm⁻¹. Shoulders at 800 and 440 cm⁻¹ are also observed. The intense i.r. band at 1220 cm⁻¹ was previously assigned to the external asymmetric stretching vibrations of zeolite framework containing four chains of five-membered rings (pentasil family)

Table 2 XRD interplanar spacings and peak relative intensities

Peak	2θ (CuKα)	<i>d</i> (Å)	<i>I</i> / <i>I</i> ⁰
1	7.4	11.9	50
2	7.6	11.57	31
3	8.87	9.95	27
4	20.90	4.24	100
5	21.01	4.22	70
6	22.95	3.87	44
8	23.24	3.82	36
10	26.28	3.38	13
11	27.90	3.19	8
12	35.58	2.52	12

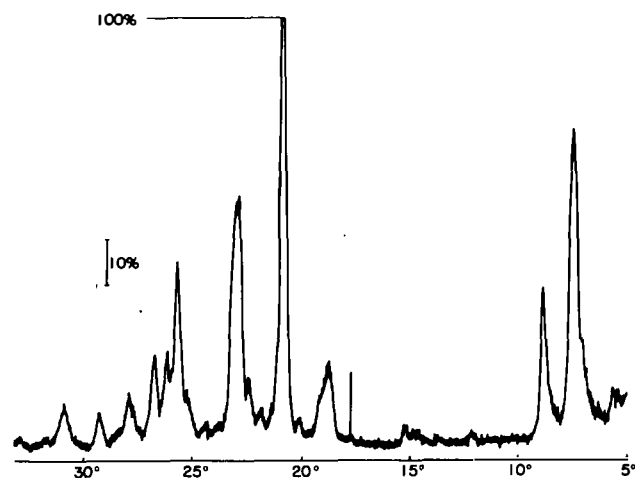
or one chain of five-membered rings (mordenite family).¹³

Zeolites that contain five-membered rings usually present i.r. bands at 1220 and 560 cm⁻¹. The intense i.r. band at 1220 cm⁻¹ was assigned to the external asymmetric stretching vibrations of the framework (four chains of five-membered rings for the pentasil family or one chain of five-membered rings for the mordenite family)¹³, while the i.r. band at 550 cm⁻¹ was attributed to the double five-membered-ring blocks.¹² It was argued that the frequency of the double five-membered-ring blocks is sensitive to the topology and building units of the zeolite frameworks.^{12, 13} In mordenite, the i.r. stretching vibration of these building units was found at 580 cm⁻¹. Since zeolites with MTW framework topology belong structurally to the mordenite group, one should expect that they will show identical i.r. features, in particular, intense i.r. bands at 1220 and 580 cm⁻¹. The i.r. spectrum reported in *Figure 2* strongly suggests that the gallium-substituted T-atom zeolite synthesized in this work belongs to the MTW-type-structure zeolite.¹ From the i.r. optical density ratio of 580–550/450 cm⁻¹ bands (which is close to 1 for the Ga sample), one can conclude, as suggested in Refs. 14 and 15, that the sample is well crystallized.

The i.r. results along with the X-ray diffraction study strongly suggest that the gallium analog material discussed in this work has the ZSM-12 structure.

MAS n.m.r. study

Figure 3 shows the ⁷¹Ga MAS n.m.r. spectrum of the Ga analog MTW calcined in air at 773 K and contacted with acetylacetone (acac). Indeed, it has been reported that ⁷¹Ga n.m.r. peak of octahedral Ga

**Figure 1** Experimental X-ray diffraction powder pattern of as-synthesized Ga-MTW zeolite

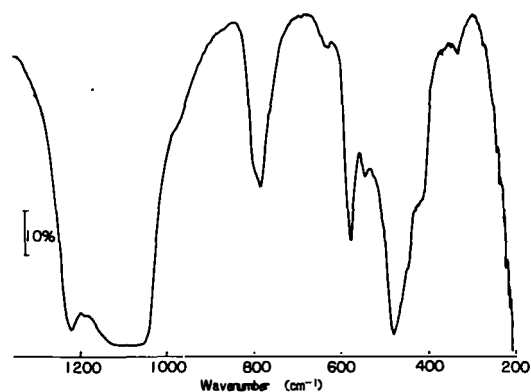


Figure 2 Midinfrared absorption spectrum of as-synthesized Ga-MTW zeolite (KBr wafer)

species in zeolites could be observed only after equilibration of the system with acac.¹⁶

The important feature shown in this figure is that the peak at 117 ppm with respect to $\text{Ga}(\text{H}_2\text{O})_6^{3+}$ can be assigned unambiguously to tetrahedral Ga species. Indeed, ^{71}Ga chemical shifts in the range 150–180 ppm were previously observed on compounds containing tetrahedral Ga species.^{5–7}

By comparing the intensities of the ^{71}Ga n.m.r. signals of the as-synthesized and calcined samples, we could conclude that less than 5% extraframework Ga species was formed upon calcination. This result is strongly supported by the absence of a signal at 0 ppm on the ^{71}Ga n.m.r. spectrum reported on *Figure 3*.

Figure 4 illustrates the ^{29}Si MAS n.m.r. spectrum of the calcined zeolite. A peak at -112.1 and a shoulder at ~ -109.5 ppm with respect to TMS are observed. These peaks can be assigned to $^{29}\text{Si}(4\text{Si})$ atoms

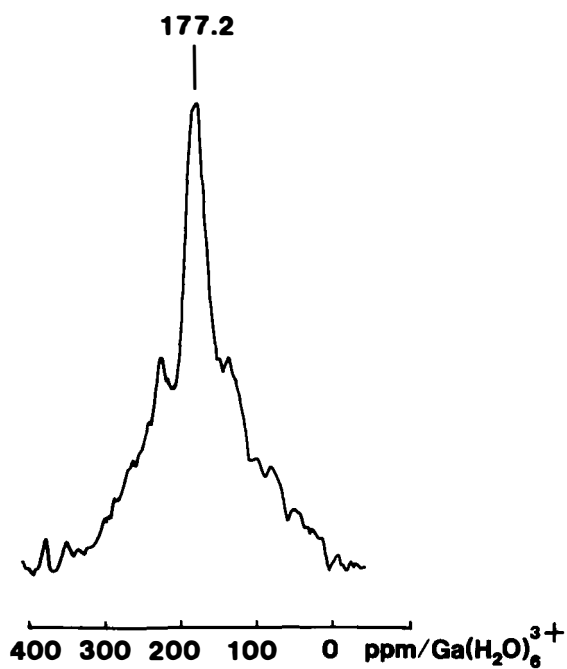


Figure 3 ^{71}Ga MAS n.m.r. spectrum of calcined Ga-MTW zeolite

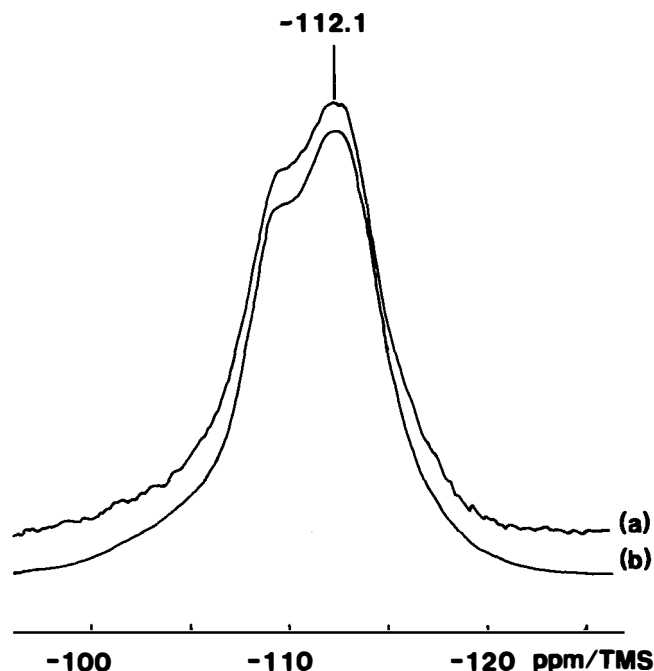


Figure 4 ^{29}Si MAS n.m.r. spectrum of calcined Ga-MTW zeolite (a) and simulated spectrum (b)

located in different individual crystallographic sites.¹⁷ Indeed, the ^{29}Si MAS n.m.r. spectrum of a highly siliceous ZSM-12 exhibits three peaks at -109.2 , -111.5 , and -112.9 ppm with respective intensities in the ratio 3:2:2.

After deconvolution of the experimental ^{29}Si MAS spectrum of *Figure 4*, an additional line is observed at -104.8 ppm. This small line, whose intensity corresponds to 5.6% of the total intensity, can be assigned to the Si (1 Ga) species by analogy to chemical shifts observed on Ga-ZSM5.¹⁸

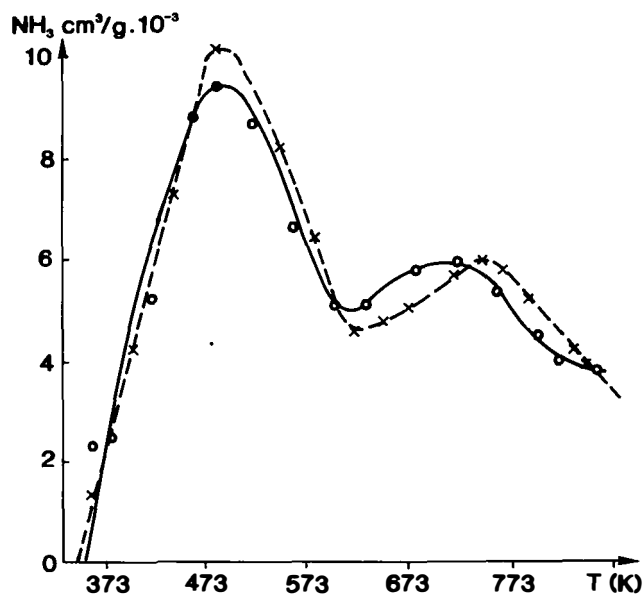


Figure 5 T.p.d. of NH_3 on (O) H-Ga-MTW and (X) H-Al-ZSM-12

Integration of the deconvoluted spectrum leads to a value of 71.4 for the atomic ratio Si/Ga. This value is in relative good agreement with the Si/Ga value in the precursor gel and with the value determined by chemical analysis on the crystallized zeolite (Si/Ga = 60).

T.p.d. of ammonia

The effect of substitution of Si by Ga in the ZSM-12 zeolite structure is to produce cationic sites exchangeable by protons. The calcined Ga-ZSM-12 was exchanged with NH_4^+ and converted to its H-form upon calcination. Figure 5 represents the NH_3 t.p.d. curve for Ga-HZSM-12. This curve shows two maxima at 473 and 723 K, the peak at 723 K corresponding to strong acid sites. From the amount of NH_3 molecules desorbed from the solid during the t.p.d. experiment, and with the hypothesis that only the high-temperature t.p.d. peak is related to the zeolite acid sites, a value of 2.8×10^{-4} mole NH_3 per gram of zeolite was calculated. Since the one unit cell of ZSM-12 contains 28 T atoms, and using a Si/Ga value of 70, one calculates 2.5×10^{-4} Ga atom per gram of zeolite. Since every framework Ga atom develops one acid site, one should expect 2.5×10^{-4} equivalent acid sites per gram of zeolite. The calculated acidity is close to that determined by t.p.d. of ammonia. These experiments provide additional evidence that the gallium analog MTW zeolite has been synthesized. Further, this clearly confirms that tetrahedral Ga atoms were not extracted from the lattice upon calcination at 773 K.

In Figure 5, the NH_3 t.p.d. curve for H-Al-ZSM-12 with an Si/Al ratio equal to 60 is also shown. It is remarkable that the two curves are almost similar with a positive shift of the high-temperature peak of about 20 K for the Al-ZSM-12 sample. These results are those expected since it has already been shown that Ga-substituted zeolites exhibit acid strength slightly less than that of Al-substituted zeolites.¹⁹

CONCLUSION

The most relevant results from this work are the following:

Gallium analog MTW zeolite can be prepared with the Si/Ga ratio in the range 60–120 using the method

reported for Al-ZSM-12 in the presence of methyl triethyl ammonium template.

The thermal stability of tetrahedral Ga is good since *no extra framework octahedral* Ga was detected after activation at 823 K.

Ga analog MTW zeolite shows acidic properties comparable to those of the Al analog. The NH_3 t.p.d. curve exhibits a strong peak with a maximum at 723 K. The acid strength of HZSM-12 (Ga or Al) is comparable to that developed by HZSM-5.

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