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collision complex undergoes a curve crossing to the ($a^3\Sigma^+$) state,³⁴ which then dissociates to $O(^3P) + N_2(X^1\Sigma_g^+)$. We must emphasize, however, that the presence of this channel is only inferred in our experiments by the excess of the CO yield over the N_2O yield and the lack of any likely secondary reactions for CO formation. Direct detection of oxygen atoms formed in this product channel would be a useful complement to our studies.

Conclusions

We have directly detected the products of the $NCO + NO$ reaction in a time-resolved experiment using infrared absorption

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spectroscopy. On the basis of product yields, we have determined the branching ratios for this reaction. Three product channels are active, with $CO_2 + N_2$ the most important. Further experiments, especially at the higher temperatures more relevant to combustion chemistry, as well as theoretical calculations are clearly necessary in order to gain a better understanding of this important reaction.

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Determination of Gallium in H(Ga)ZSM5 Zeolites by ^{71}Ga MAS NMR Spectroscopy

Cees R. Bayense,[†] Arno P. M. Kentgens,[‡] Jan W. de Haan,^{*†} Leo J. M. van de Ven,[†] and Jan H. C. van Hooff[†]

Eindhoven University of Technology, Laboratories of Inorganic Chemistry and Catalysis and of Instrumental Analysis, P.O. Box 513, 5600 MB Eindhoven, The Netherlands, and University of Nijmegen, Faculty of Science, SON/NWO HF-NMR Facility, Toernooiveld, 6525 ED Nijmegen, The Netherlands
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^{71}Ga and ^{29}Si magic angle spinning (MAS) NMR and some ^1H NMR (CRAMPS) investigations have been carried out on H(Ga)ZSM5 zeolites. Quantification of the ^{71}Ga NMR responses, obtained for the acid form of the zeolite, showed that about $70 \pm 2\%$ of the theoretical signal intensity was measured, based on the total gallium content of the samples. Only signals from tetrahedral gallium were observed in a reproducible manner. The lack of gallium NMR response, which is ascribed to the presence of large electric field gradients on part of the gallium nuclei, has been found to depend on the nature of the counterion in the zeolite. Maximum NMR signal intensities were obtained for Rb^+ - and Cs^+ -exchanged zeolites. A model to explain these phenomena is presented. The gallosilicates were found to be thermally stable up to a temperature of 600°C , but in the presence of steam a loss of framework gallium was observed above 550°C .

Introduction

Zeolites are microporous aluminosilicates that can act as shape-selective catalysts. If, in addition to the acidic properties of the zeolite, a catalytically active species is introduced in the pore system, e.g., in the form of a highly dispersed metal, bifunctional catalysts are obtained.^{1,2} Upon introduction of gallium in H(Al)ZSM5 zeolites, very suitable catalysts for the aromatization of small alkanes can be prepared.^{3,4} Due to the shape-selective properties of the HZSM5 framework, mainly small aromatics are formed (benzene, toluene, and xylenes), and deactivation by coke formation is relatively slow, as no polyaromatics can be formed.

The gallium can be introduced by physically mixing Ga_2O_3 powder (specific surface area $5\text{ m}^2/\text{g}$) with the zeolite or by impregnation of the zeolite with a solution of a gallium salt, followed by calcination. Both physical mixing and the impregnation method, however, yield deposition of the gallium oxide on the outer surface of the zeolite particles, as for the latter method the large size of the hydrated gallium ion hinders penetration into the zeolite pores. As a consequence, shape-selective restrictions for the reaction exist to a much lesser extent on these catalysts, and the formation of polyaromatics is facilitated. As such compounds can act as coke precursors, strongly enhanced deactivation occurs.

Another way to introduce trivalent ions like gallium is isomorphous substitution in the framework, replacing the aluminum by gallium in the stage of zeolite synthesis.^{5,6} This method has also been applied to other trivalent ions such as boron, iron, etc.⁷

From NH_3 temperature-programmed desorption and IR measurements, it has been shown that replacement of aluminum by gallium in H(Al)ZSM5 gives zeolites with a reduced framework acidity.⁷ In this way, zeolites with varying acidities can be prepared, changing the activities for acid-catalyzed reactions.

The catalytic properties of the gallosilicates have been extensively studied, but there is a paucity of data regarding the physical characterization of the materials, notably with respect to the thermal and hydrothermal stabilities. Application of techniques such as XRD, IR, and chemical analysis (AAS) can provide information about changes in structure and composition of the catalyst after certain treatments but do not offer the possibility of distinguishing between framework gallium and extraframework gallium. One of the techniques that can give important information about the surroundings and coordination of different atoms in the framework is MAS NMR spectroscopy.

In the field of MAS NMR spectroscopy for the characterization of zeolites and related materials, much work has been done ap-

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[†]Eindhoven University of Technology.

[‡]University of Nijmegen.

plying ^{27}Al and ^{29}Si solid-state MAS NMR spectroscopy.⁸⁻¹² In principle, Si/Ga ratios of zeolites can be determined from ^{29}Si MAS NMR spectra.^{12,13} In practice, this method is limited to cases where Si/Ga ≤ 50 .¹³ Another complication is that lattice defects in the form of silanol groups (e.g., nests¹⁴) interfere (see also the Discussion). For these reasons, the emphasis in the present paper is very much on gallium NMR, in order to estimate the amounts of framework gallium.

With ^{27}Al MAS NMR of dealuminated H(Al)ZSM5 zeolites, tetrahedrally coordinated (framework) Al can be distinguished from octahedrally coordinated Al, present as extraframework species. Also pentacoordinated aluminum atoms have been proposed to occur in dealuminated zeolites.¹⁵

For the physical characterization of solids, application of the ^{69}Ga or ^{71}Ga MAS NMR technique still remains in a relatively early stage of development. Application of ^{69}Ga and ^{71}Ga MAS NMR spectroscopy for the characterization of cesium gallate glasses was described by Zhong and Bray.¹⁶ In their work, they showed that different Ga NMR lines are detected for tetrahedrally and octahedrally coordinated gallium atoms in these structures, indicating that Ga NMR may be an effective tool for the characterization of solid materials.

The possibility of ^{69}Ga MAS NMR spectroscopy on zeolitic materials (gallosilicates) was first shown by Ione et al.¹⁷ Other work, applying both ^{69}Ga and ^{71}Ga MAS NMR spectroscopy, was done by Timken et al.,¹⁸ who showed the importance of high magnetic field strengths in order to minimize the average second-order line broadening, and high MAS frequencies to reduce the chemical shift anisotropy effects on the line widths and to avoid overlap between center bands and spinning sidebands.

In a recent publication by our group, investigations on H-(Ga)ZSM5 zeolites showed that water equilibration of the samples prior to the NMR measurements is indispensable for obtaining any ^{71}Ga NMR response of lattice gallium,¹⁹ comparable to earlier observations with ^{27}Al MAS NMR on H(Al)ZSM5 zeolites.²⁰ Moreover, after steaming of the gallosilicates for various times and equilibration of the steamed samples with acetylacetone (acac), the signal originating from tetrahedrally coordinated framework gallium was found to decrease with steaming time and simultaneously a signal appeared in the spectra, attributed to octahedrally coordinated gallium nuclei. The effect of the acac treatment on the visibility of the octahedrally coordinated species is similar to earlier observations with ^{27}Al MAS NMR investigations on dealuminated H(Al)ZSM5 zeolites.⁸ Later experiments on a series of gallosilicates with different gallium contents, however, have shown that the framework gallium can be measured relatively easily and reproducibly, but that detection of the octahedrally coordinated gallium is far more difficult and seems to depend very much on synthesis and/or treatment of the samples in a manner yet unknown. In a comparison of the hydrolyses of gallium(III) and aluminum(III) solutions, Bradley et al.²¹ found

that there must be a deviation in the hydrolytic behavior of these ions. It is thought that the higher polymers formed in the case of gallium are likely to differ in structure, as well as in the kinetics of their formation, from those occurring from aluminum. Apparently, the formation of different extralattice species also takes place in the pores of H(Ga)ZSM5. This extralattice material can in many cases no longer be detected even after equilibration of the samples with acac or water. The samples as published in ref 19, however, were found to be very stable, as subsequent drying and acac equilibration treatments resulted in the same ^{71}Ga MAS NMR spectra as published, even after a period of more than a year. Because of the difficulties with respect to the detection of the nonframework gallium, in the discussion of the results described in the present paper, only signals originating from tetrahedrally coordinated (framework) gallium have been considered.

To obtain more information about the properties of H(Ga)-ZSM5 gallosilicates, our ^{71}Ga MAS NMR investigations were continued. The thermal stability of the materials was measured by recording the ^{71}Ga MAS NMR spectra after calcination at various temperatures. In addition, the thermal stability in the presence of water vapor was investigated.

Moreover, special attention was paid to the quantification of the apparent ^{71}Ga MAS NMR line intensities of the gallosilicates containing various counterions, as until now no systematic investigation was carried out regarding this aspect.

Experimental Section

Catalyst Preparation. Preparation of the gallosilicates was carried out by a method based on the patent of Chen et al.,²² adding Ga_2O_3 instead of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ to the synthesis mixture, in the stage of gel formation. Crystallization was carried out during 6 days at 150 °C in a Teflon-lined autoclave. After crystallization, the zeolites were calcined (3 h, 550 °C), 3-fold ion-exchanged (1 h, 90 °C, 2 M NH_4NO_3) and finally calcined for a second time (3 h, 550 °C). The prepared gallosilicates will be referred to as Ga- x , where x represents the number of gallium atoms/unit cell, as determined by atomic absorption spectroscopy.

To see the influence of lattice defects on the gallium NMR response, one sample was treated for a further 68 h at 500 °C in a flow of water vapor saturated air (20 mL/min, vapor pressure of water about 2 kPa).

M^+ -exchanged zeolites ($\text{M}^+ = \text{Li}^+, \dots, \text{Cs}^+$) were obtained by 3-fold ion exchange of the zeolite with a 2 M solution of the alkali-metal chloride salts at 90 °C. Steaming of the zeolites was carried out with the NH_4^+ form of the zeolites in a flow of water saturated air (20 mL/min), containing about 28 kPa of water vapor. Thermogravimetric determinations of the water content of the water equilibrated samples were carried out in a Cahn electrobalance, heating about a 30-mg sample in a stream of helium. The effect of water removal on the detectability of the gallium was investigated by drying the samples for 16 h at 160 °C and transferring the zeolite powder to the spinner in a nitrogen-flushed glovebox.

Further details of the sample pretreatments such as temperature, etc., are mentioned in the Results.

^{71}Ga MAS NMR Measurements. NMR spectroscopic measurements were carried out on a Bruker AM 600 NMR spectrometer (^{71}Ga NMR frequency 183.0 MHz). Spectra were obtained using a home-built single-tuned probe, equipped with a Doty 5-mm double-bearing MAS assembly. Spinning speeds of approximately 8 kHz were employed, and chemical shifts were measured relative to the hexahydrated Ga^{3+} ion in a gallium nitrate solution.

To obtain quantitatively meaningful determinations of quadrupolar nuclei such as ^{71}Ga , important precautions have to be taken for the measurements, e.g., the use of short and powerful rf pulses.^{23,24} The pulse width used for the present measurements

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was 2 μ s with an rf field strength of 48 kHz. The pulse repetition time was 0.4 s, and the average T_1 values for ^{71}Ga NMR signals of the present materials are about 0.07 s, as determined by a progressive saturation experiment.

For the quantitative determination of gallium in the zeolites, the areas of the NMR lines obtained from the zeolite samples were compared with the lines measured from a known amount of hexahydrated Ga^{3+} ions in a $\text{Ga}(\text{NO}_3)_3$ solution. This reference solution was measured simultaneously with the solid material, while spinning at 8 kHz. This was done by placing a small Kel-F cup, containing the reference solution in the rotor. The remaining space was filled with zeolite powder. For comparison of the signal intensities obtained from the gallium in the solution and in the solid state, correction terms have to be applied, as in the former case all transitions of the gallium nuclei are excited and measured, while in the latter case only the central transition is measured. Further experimental precautions and theoretical backgrounds of this method for quantitative determinations have been described in the literature.²³⁻²⁶

An additional correction has to be carried out for the different effects of the spectrometer dead time (8.6 μ s) for the relatively sharp NMR line of the gallium in the reference solution (line width ca. 800 Hz) and the relatively broad ^{71}Ga NMR line originating from the gallium in the solid (line width ca. 3300 Hz). For the experimental conditions applied and assuming a single-exponential FID, a (relative) loss of gallium NMR signal intensity for the solid state as compared to the gallium in solution can be deduced of 14.6%, which means that the measured amounts of gallium in the appropriate samples have to be corrected with this percentage. Somewhat larger corrections have been applied for the significantly broader lines, e.g., for the uncalcined samples under the same conditions a correction percentage of 18.1% was applied, due to the larger line width.

The contributions of the spinning sidebands, visible in the spectra obtained with spinning at 8 kHz, have been determined in two ways. First, by integration of the peak areas in the spectra, and second, by carrying out a series of experiments with increased spinning frequencies (8, 10, 12, and 14 kHz), thus virtually eliminating the spinning sidebands.

^{29}Si MAS NMR Measurements. The ^{29}Si MAS NMR were carried out on a Bruker CXP-300 spectrometer (^{29}Si frequency 59.63 MHz), equipped with a standard 7-mm Bruker MAS assembly. Spinning frequencies of approximately 2.5 kHz were employed. For the CP MAS NMR measurements contact times of 10 ms were applied.

^1H NMR ("CRAMPS") Measurements. The ^1H NMR ("CRAMPS") measurements were also carried out on a Bruker CXP-300 spectrometer (^1H frequency 300.13 MHz), equipped with a standard 4-mm Bruker MAS assembly. A MREV-8 cycle was applied, the $\pi/2$ pulse time was 2.8 μ s. We realize that these conditions are not the most suitable for employing CRAMPS measurements. Spinning frequencies of 9 kHz were employed, and a pulse repetition time of 2 s. The samples were dried at 400 $^\circ\text{C}$ prior to the measurements and transferred to the spinner in a nitrogen-flushed glovebox. No further precautions were taken to prevent water adsorption on the zeolite during the NMR measurements. However, no changes were observed in the ^1H NMR spectra ("CRAMPS") over periods of ca. 15 h.

Results

General Features of the ^{71}Ga NMR Lines. For the uncalcined ZSM5 zeolite with 3.37 gallium atoms/unit cell ($\text{Si}/\text{Ga} = 28$) and containing the tetrapropylammonium ion (TPA^+), one ^{71}Ga NMR response was obtained at +155 ppm with a line width of about 4.8 kHz (Figure 1a, Table I). A peak in this region had earlier been observed in other gallosilicate structures and was

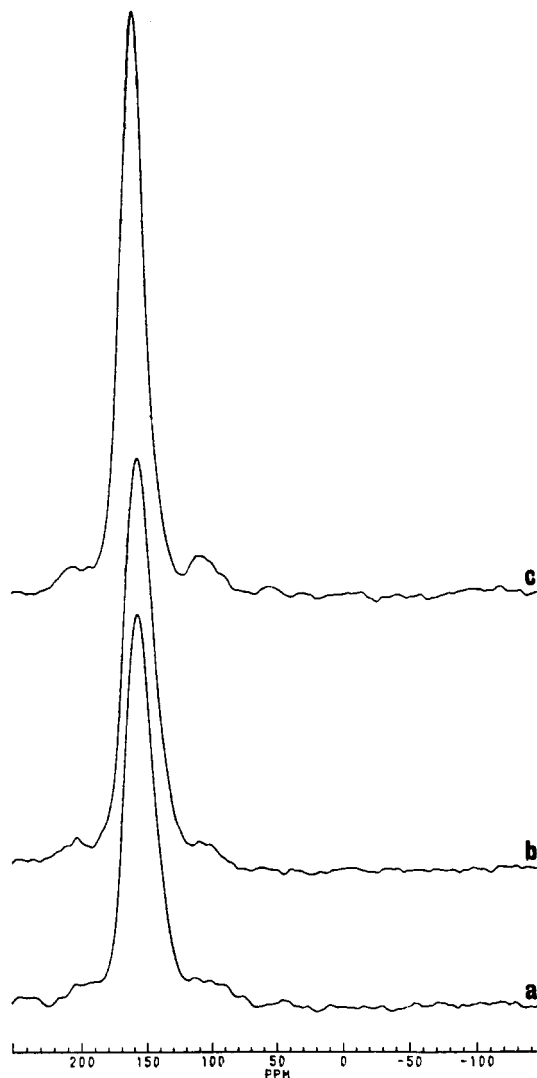


Figure 1. ^{71}Ga MAS NMR spectra of zeolite Ga-3.37: (a) uncalcined, dried; (b) uncalcined, H_2O equilibrated; (c) H^+ form, H_2O equilibrated.

TABLE I: Effect of Drying, Ion-Exchange, and Calcination Treatments on the ^{71}Ga MAS NMR Signal Intensity of Zeolite Ga-3.37

sample	H_2O , wt %	shift, ^a ppm	lw, ^b kHz	^{71}Ga MAS NMR	
				Ga/uc	% ^c
TPA^+ , dried		+154.6	4.8	1.92	59
TPA^+ , H_2O equil		+158.4	4.7	2.03	63
H^+ , H_2O equil	10.2	+161.1	3.3	2.42	71
H^+ , H_2O vapor, 68 h, 500 $^\circ\text{C}$	9.8	+161.1	3.0	2.35	69

^a Line position (top of peak). ^b Line width. ^c Percentage relative to AAS determination (values $\pm 2\%$).

identified as originating from tetrahedrally coordinated framework gallium.^{18,19} Quantitative determination of the peak area shows that this ^{71}Ga line represents about $59 \pm 2\%$ of the total gallium content (Table I), as measured by AAS. Figure 1b and Table I show that drying of the zeolite in this form has a negligible effect on the apparent NMR response, in contrast with earlier observations on the (Ga)ZSM5 zeolites in the H^+ form, where drying caused broadening of the lines beyond detection. After the pretreatments of the zeolites to make them suitable for catalytic uses (calcination, ion exchange with 2 M NH_4NO_3 and a second calcination), a shift in line position occurred (to about +161 ppm, Figure 1c) together with a decrease in line width to about 3.3 kHz. The percentage of gallium represented by this line after calcination and ion exchange is also higher (Table I), as compared to the uncalcined material.

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TABLE II: Quantitative Determination of Ga in H(Ga)ZSM5 Zeolites by Means of ^{71}Ga and ^{29}Si MAS NMR

sample	AAS, Ga/uc	^{29}Si MAS NMR, ^a Ga/uc	^{71}Ga MAS NMR, Ga/uc	% ^{a,b}
Ga-8.00	8.00	nd ^c	1.79	22
Ga-6.96	6.96	5.05	1.55	22
Ga-3.37	3.37	3.84	2.41	71
Ga-2.28	2.28	3.69	1.55	68
Ga-1.41	1.41	3.10	0.97	69

^a Calculated assuming a Gaussian line shape. ^b Percentages detected by ^{71}Ga MAS NMR relative to AAS determination (values $\pm 2\%$). ^c Not determined.

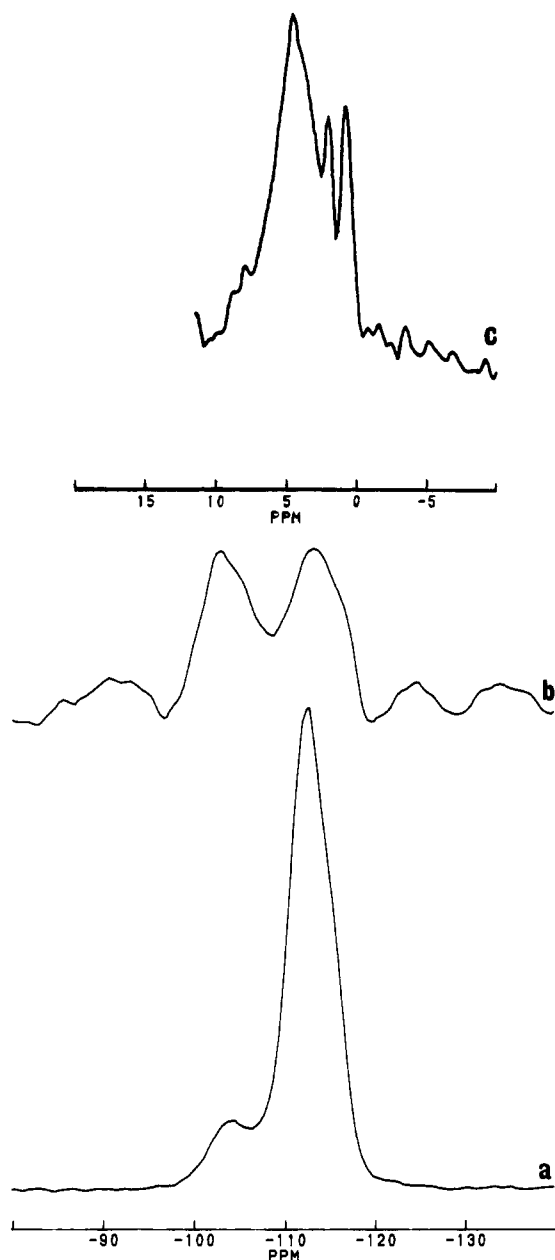


Figure 2. (a) ^{29}Si MAS NMR spectrum of zeolite Ga-3.37; (b) ^{29}Si CP MAS NMR spectrum of zeolite Ga-3.37; (c) ^1H (CRAMPS) NMR spectrum of zeolite Ga-3.37.

To see the influence of framework defects on the broadening of the line, the zeolite Ga-3.37 was heated at 500 °C in a stream of water-saturated air for another 68 h. For H(Al)ZSM5 zeolites, such treatment is known to induce migration of defects from inside the zeolite particles to the outer surface.^{28,29} The spectra of the

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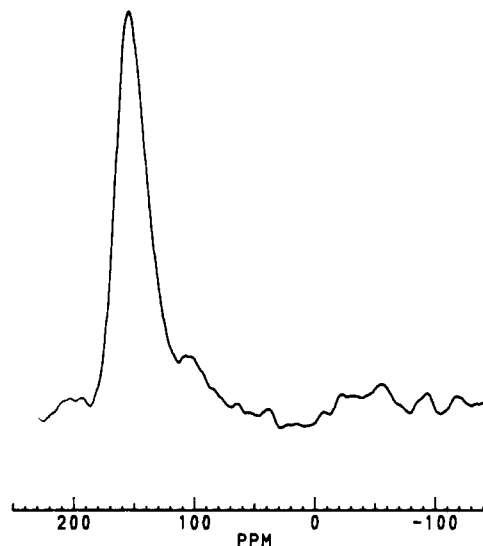


Figure 3. ^{71}Ga MAS NMR spectrum of zeolite Ga-8.00, indicating the existence of (tetrahedrally coordinated) extraframework Ga.

TABLE III: Alkali Metal and Water Contents of Ion-Exchanged Zeolite Ga-1.41

sample	a	b	c	d	e	f
Ga-1.41-H			10.6	0.97	69	
Ga-1.41-Li	0.19	0.23	8.6	1.34	91	69
Ga-1.41-Na	0.63	0.70	10.2	1.04	71	
Ga-1.41-K	1.06	1.52	10.2	1.32	95	
Ga-1.41-Rb	2.29	3.18	10.4	1.34	96	65
Ga-1.41-Cs	3.50	5.80	9.7	1.42	102	

^a Theoretical alkali-metal content (wt %), based on 1.41 Ga/uc and assuming exchange of 1 alkali-metal ion/Ga atom. ^b Actual alkali-metal content (wt %, AAS determination). ^c Weight percent of water adsorbed. ^d Ga/uc measured by ^{71}Ga MAS NMR. ^e Percentage of Ga measured by ^{71}Ga MAS NMR, relative to total Ga content (AAS determination, values $\pm 2\%$). ^f Percentage of Ga measured by ^{71}Ga MAS NMR after back-exchange of some samples to the Na^+ form, relative to AAS determination (values $\pm 2\%$).

gallosilicates after such treatment showed a reduction of the line width to about 3 kHz, but no significant change in the peak area.

Quantitative Determination of Gallium in Zeolites. The results of the quantitative determinations of gallium by ^{71}Ga MAS NMR in H(Ga)ZSM5 zeolites containing various amounts of gallium atoms/unit cell are summarized in Table II. The water contents of these samples were about 10–12 wt %, determined by thermogravimetric analysis. The table also presents the gallium contents as measured by AAS (bulk amount) and ^{29}Si MAS NMR (framework gallium). A typical ^{29}Si MAS NMR spectrum is shown in Figure 2a for a sample with a nominal Si/Ga ratio of 30. The corresponding ^{29}Si CP MAS spectrum is shown in Figure 2b. A ^1H NMR spectrum (“CRAMPS”)²⁷ of the same sample is shown in Figure 2c.

Table II shows that for zeolites with less than about 3 gallium atoms/unit cell, the apparent ^{71}Ga NMR signal areas are about $70 \pm 2\%$ of the theoretical values, based on the actual gallium content (AAS). The amounts of gallium that were found by ^{29}Si MAS NMR were significantly higher for all samples than measured by AAS. For zeolites with higher gallium contents, the percentages of gallium that are detectable for ^{71}Ga MAS NMR spectroscopy are much lower, e.g., in sample Ga-6.96 only about $22 \pm 2\%$ of the total ^{71}Ga NMR response is measured. In favorable cases, the presence of nonframework gallium in zeolites with high gallium contents shows up in the NMR spectrum, as shown for zeolite H(Ga)ZSM5-8.00 in Figure 3. As the lines in this spectrum, apart from the main peak, are measured in a broad range between 0 and +160 ppm, most of this response is

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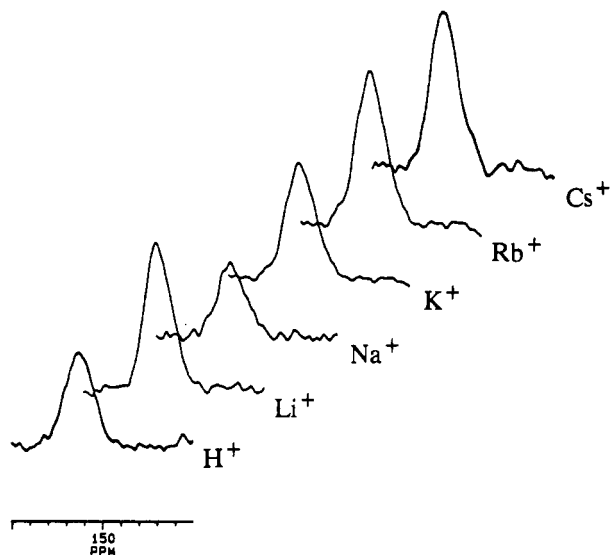


Figure 4. ^{71}Ga MAS NMR spectra of zeolite Ga-1.41, ion exchanged with different alkali-metal ions.

TABLE IV: Stability of Gallosilicate Ga-2.28 under Thermal and Hydrothermal Conditions (Steaming) at Various Temperatures during 3 h

treatment	Ga/uc ^a	treatment	Ga/uc ^a
calcination, 3 h at		no steaming	1.62
550 °C	1.62	steaming, 3 h at	
600 °C	1.59	500 °C	1.62
650 °C	0.72	550 °C	1.60
710 °C	0.36	600 °C	1.44

^a Detectability of framework gallium 71% in untreated samples; Ga detectability constant during gallium loss.

attributed to gallium nuclei in very distorted framework or non-framework positions.

The contents of the different alkali-metal ions in the ion-exchanged samples (AAS determination, column B), and the water contents of these samples (TGA determination, column C), are presented in Table III. This table also shows the theoretical alkali-metal contents, as calculated from the gallium content of the zeolite and assuming an exchange ratio of 1 alkali-metal ion/gallium site (column A). It is clear that in all cases an excess of alkali-metal ions is observed, increasing with the size of the cation. Thermogravimetric analysis on these samples shows no large variations in the water contents of the samples.

Table III and Figure 4 show further that varying gallium responses are measured in the samples containing different alkali-metal ions (columns D and E), although no variations in line widths are measured. Maximum ^{71}Ga signal intensities are obtained for the largest alkali-metal ions (Rb^+ , Cs^+), while for the H^+ and the Na^+ form of the zeolite relatively low signal intensities are measured. Generally, the ion effects are reversible, as upon back-exchange of the Li^+ and Rb^+ samples to the Na^+ form, a strongly reduced ^{71}Ga signal intensity is measured again (Table III, column F).

The effect of drying of the ion-exchanged zeolite on the ^{71}Ga NMR signal intensity is shown in Figure 5 for the Rb^+ form of the zeolite. Similar results have been measured for the Li^+ and the Cs^+ forms of the zeolite. It is clear that also for the alkali-metal exchanged zeolites, water equilibration is indispensable for making the framework gallium detectable, similar to earlier observations with the H^+ form.¹⁹ A noteworthy difference, however, is the fact that even in the dry state of the ion-exchanged samples still about 10% of the ^{71}Ga NMR response is left, while in the H^+ form the line completely diminishes.¹⁹

Thermal and Hydrothermal Stability of the Gallosilicates. The amounts of gallium atoms/unit cell of zeolite Ga-2.28, measured by ^{71}Ga MAS NMR, of the samples calcined at different temperatures in a helium/oxygen (80/20) atmosphere during 3 h,

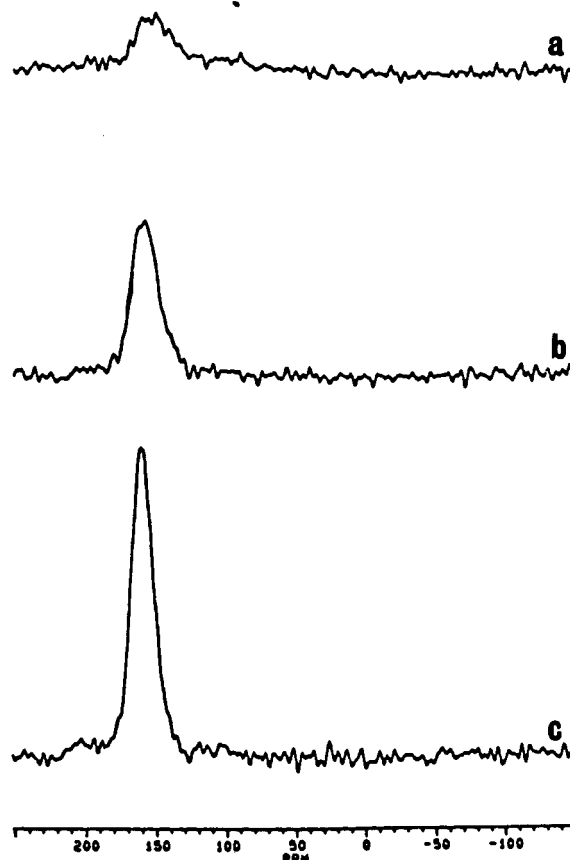


Figure 5. Effect of drying on the apparent Ga NMR signal lines for the Rb^+ exchanged Ga-1.41 zeolite; (a) dry; (b) after 2 h of laboratory air at room temperature; (c) after water equilibration.

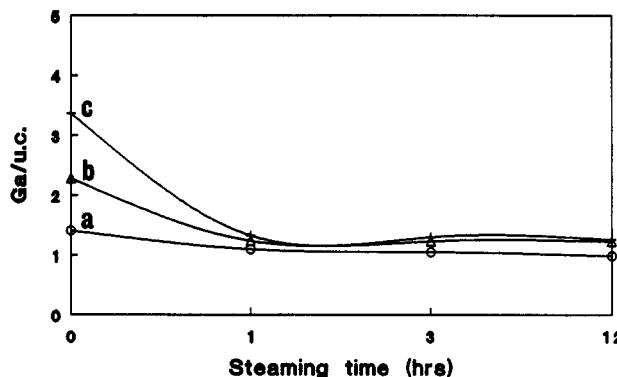


Figure 6. Loss of framework Ga during hydrothermal treatment of zeolites with varying Ga contents at 600 °C, as calculated from the ^{71}Ga MAS NMR spectra: (a) Ga-1.41; (b) Ga-2.28; (c) Ga-3.37.

are presented Table IV. Assuming that the NMR detectability of the gallium for these samples does not change during heat treatment, it is clear that up to temperatures of 600 °C, no loss of framework gallium is observed by the NMR technique. At higher temperatures, the ^{71}Ga NMR signal intensities decrease rapidly and the lines become broader, indicating a loss of framework gallium and probably a partial distortion of the zeolite framework as well.

The results of treatment under hydrothermal conditions are also included in Table IV. Under these circumstances, the loss of framework gallium and a possible destruction of the framework were found to start at a lower temperature: at 600 °C the loss of gallium NMR response is already substantial. The relative loss of framework gallium as a function of steaming time, observed for three gallium contents at 600 °C, is shown in Figure 6. This figure clearly shows that the removal of gallium from the framework increases with the gallium content of the material. The remaining content of framework gallium after 12 h of steaming,

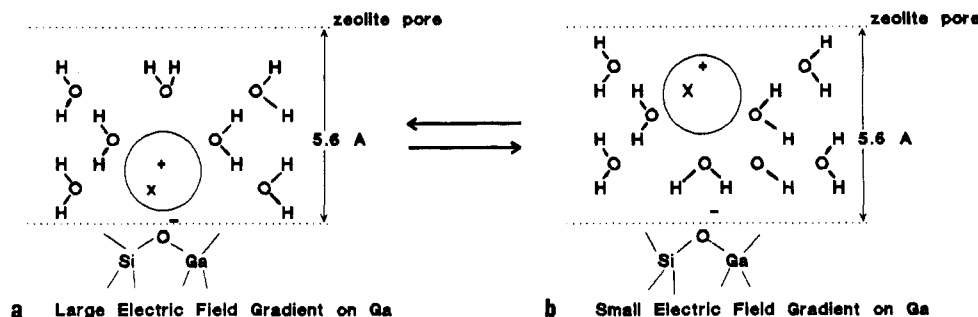


Figure 7. Model explaining the varying ^{71}Ga signal intensities obtained for different alkali-metal ions: (a) situation with large electric field gradient; (b) situation with low electric field gradient.

however, is largely independent of the initial gallium content. AAS determinations have shown that the total amount of gallium does not change during the steam treatment, indicating that the gallium removed from the framework does not sublime from the zeolite but is probably deposited in positions where it is not contributing to the measurable ^{71}Ga NMR signal.

Discussion

General Features of the ^{71}Ga NMR Responses. Application of ^{71}Ga MAS NMR measurements on uncalcined TPA(Ga)ZSM5 zeolites shows one relatively broad NMR response (4.8 kHz) at +154 ppm (Figure 1a, Table I). This line is assigned to tetrahedrally coordinated framework gallium.^{18,19} The amount of water adsorbed in the TPA⁺ form is very small (Table I), because the pores are inaccessible to water molecules, but this seems to be of little importance for the gallium detectability, as shown by the fact that even after extensive drying the same spectrum is obtained (Figure 1b). After calcination, ion exchanging with 2 M $\text{NH}_4\text{-NO}_3$, and a second calcination treatment of the raw material, a decrease in line width occurs to about 3.3 kHz (Figure 1c), and a higher percentage of gallium is measured (Table I). The line width for this sample is higher as compared to the line width published earlier,³⁰ which can be ascribed to a smaller amount of defects in the previous sample, as confirmed by the effect of an additional heat treatment, as described above. The (isotropic) chemical shift of this line after correction for the quadrupolar effects is 159.2 ppm.

The apparent changes in the spectrum observed after calcination are explained assuming that after this treatment, the electric field gradients, caused by the counterions (TPA⁺), on part of the gallium nuclei in the framework are replaced by those caused by (hydrated) protons. The latter effect is lower since a clear increase in the total gallium NMR signal intensity is observed. An explanation for this behavior might be a reduction of the (time averaged) electric field gradient on the gallium sites in the framework, caused by the spreading out of the positive charge over a larger complex, like the hydrated $\text{H}(\text{H}_2\text{O})_n^+$ ion (see discussion of mechanism proposed in Figure 7).

The changes in line widths during the calcination are ascribed to a reordering of the zeolite framework, due to the template removal during the first calcination, resulting in a more symmetrical coordination around most of the framework gallium nuclei, lowering the electric field gradients and the chemical shift dispersion. This effect is more pronounced after prolonged heat treatment in the presence of water vapor (Table I), as such treatment reduces the amount of lattice defects in the zeolite,^{28,29} thus decreasing the chemical shift dispersion and the distribution of quadrupolar interactions. In addition, calcination makes the pores accessible to water molecules.

Earlier experiments by our group³⁰ have revealed that the line width of the tetrahedrally coordinated gallium resonance at 14.1 T is dominated by a chemical shift distribution (approximately 2100 Hz). Measurements of both ^{69}Ga and ^{71}Ga isotopes, combined with field-dependent experiments, allowed the determination

of the approximate quadrupolar coupling constant, and its contribution to the line width (approximately 800 Hz). As the line does not show any characteristic quadrupolar features, it may well be that a distribution of field gradients exists. Remarkably, no significant variation of these parameters was found for samples with a gallium content varying from 1.4 to 3.3 gallium atoms/unit cell. The same holds true for a steam-treated sample. The result of these experiments is that the (average) chemical shift of the tetrahedrally coordinated gallium resonance in H(Ga)ZSM5 is 162 ppm. As no further line-shape analyses are performed in the present paper, the quoted shifts are simply those given by the spectrometers peak-pick routine.

A comparison of the above-mentioned gallium results to those obtained for Al in H(Al)ZSM5 structures shows that despite of the fact that the gallium line width is much larger than that for Al, this is due to the different NMR properties of the isotopes and does not point to a structural difference between H(Ga)- and H(Al)ZSM5.

Quantitative Determination of Gallium in Zeolites. The quantitative measurements on the H(Ga)ZSM5 zeolites, as presented in Table II, show that the ^{71}Ga MAS NMR lines, measured after water equilibration of the H⁺ form of gallosilicates with less than about 3 gallium atoms/unit cell correspond to about $70 \pm 2\%$ of the theoretical signal intensity to be expected from the total gallium content (AAS determination). In quantitative determinations such as these, important sources of errors can be the spinning sidebands,^{31,32} although spinning frequencies of 8 kHz were employed. This problem arises when the spinning frequency is less than the chemical shift anisotropy and the second-order quadrupolar interactions (in hertz) of the gallium in question. An additional difficulty in these spectra is that the main peak in the spectrum at +161 ppm is asymmetrical, making the spinning sidebands easier to distinguish from the main peak in the low-frequency range than in the high-frequency range. On the basis of variation of the integration boundaries, curve deconvolution, and a series of experiments in which the spinning rate was increased to 14 kHz, the contribution of the spinning sidebands has been determined to be 10–13% of the ^{71}Ga NMR signal intensities. Appropriate corrections were applied.

The gallium contents that were measured by ^{29}Si MAS NMR (Figure 2a) are for all samples higher than the contents determined by AAS (Table II). This can be explained by the fact that the signals of Q³(1Ga) and Q³(1OH) moieties coincide to a large extent. Similar interference may occur when residues of amorphous silica in the zeolites are present: the signals caused by such silica species appear in the ^{29}Si MAS NMR spectrum at the same position as the signals of the Q⁴ framework silica of the zeolite. The silanol nests can be made visible by ^{29}Si CP MAS NMR (Figure 2b) and by ^1H NMR (MAS or "CRAMPS", Figure 2c), but neither of these can be quantified easily.¹⁴ On the basis of the ^{29}Si CP MAS NMR spectra, we surmise that the surplus of gallium that is found by ^{29}Si MAS NMR is due to lattice defects; see above. Similar results were observed for the

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other starting materials. The presence of silanol groups is also confirmed by the ^1H NMR "CRAMPS" spectrum²⁷ of the same sample, as shown in Figure 2c. It is obvious that at least three types of protons are visible. We tentatively assign these signals to silanols (≈ 1.6 ppm), bridging silanols (≈ 3.2 ppm), and acid sites and/or water adsorbed on Lewis acid sites (≈ 5.2 ppm).

The problems inherent in quantitative determinations of lattice gallium by the above-mentioned methods grow substantially after steaming of the samples, as gallium is removed from the lattice with concomitant formation of silanols. The fact that lower gallium NMR signal intensities are measured than expected from the total gallium contents may very well originate from different effects which cannot always be distinguished. One explanation assumes that the detected ^{71}Ga NMR lines originate from gallium on different T sites, possessing electric field gradients of varying magnitudes, resulting in varying ^{71}Ga MAS NMR responses. The above-mentioned variations are also time dependent for each nucleus of this type. Eventually, all ^{71}Ga nuclei on T sites can be made to contribute to the ^{71}Ga NMR signal; see below.

For gallium amounts, exceeding about 3 gallium atoms/unit cell, the lines appearing at about +160 ppm correspond to about $22 \pm 2\%$ of the theoretical response, based on the total gallium content (Table II). Here an explanation different from that just presented might prevail. The lower percentages for these samples could well be due to the fact that an increasing part of the gallium is introduced in the zeolites as nonframework gallium. These gallium species possess large quadrupolar interactions, which make them undetectable by NMR. In some cases, the occurrence of nonframework gallium in zeolites with high gallium contents is visible in the spectra shown in Figure 3 (sample Ga-8.00), where a broad gallium NMR line appears in the spectrum, in addition to the line originating from the framework gallium.

From Table III it is clear that upon ion exchange of the zeolite with alkali-metal ions, an increasing excess is introduced in the zeolites with increasing ionic radius, as compared with calculations based on the gallium content and assuming an exchange stoichiometry of 1 alkali-metal ion/gallium ion. This can be explained as follows: in earlier ion-exchange studies on H(Al)ZSM5 zeolites, it was found that the largest alkali-metal ions (Rb^+ , Cs^+) exchange not only the Brønsted acid sites but also the SiOH groups of the framework.³³ Such silanol groups are present on the outer surface of the zeolite particles but also on lattice defects within the zeolite framework. Moreover, it is known that these larger ions have weaker interactions with the framework oxygen atoms next to the gallium atoms, so there may exist an excess of the hydrated alkali-metal ions, randomly dispersed in the zeolite pores. The influence of this excess of alkali-metal ions on the (framework) gallium NMR responses cannot be estimated, however.

Table III also shows that for zeolites exchanged with different alkali-metal ions but containing similar water contents, varying ^{71}Ga MAS NMR responses are measured (Figure 4). Higher signal intensities are obtained with the zeolite in the Li^+ , Rb^+ , or Cs^+ forms. In particular, after introduction of Cs^+ in the framework, nearly all gallium is detected with ^{71}Ga MAS NMR. Moreover, this behavior seems largely reversible: upon back-exchange of the Li^+ and Rb^+ forms to the Na^+ form, the apparent ^{71}Ga MAS NMR signals reduce to about 70% (Table III). Another remarkable observation in the ion-exchanged samples is the fact that some gallium signal remains even after drying of the samples (Figure 5).

From these observations we can conclude that there is gallium in at least two different locations in our samples:

(1) Extraframework gallium, which exists mostly in such a distorted environment that its resonance is too broad to be detected. The results described above indicate that this amount is negligible for the zeolites in the H^+ form, containing less than 3.37 gallium atoms/unit cell.

(2) Tetrahedrally surrounded framework gallium can be observed only if the countercharge in the zeolite pores is sufficiently

dislocated, i.e., in hydrated samples. This is the main signal observed in the spectra. In dried samples this signal is too broad to be detected. This is thought to be due to the large electric field gradient at the gallium site, due to the positive charge located in the vicinity of the GaO_4 tetrahedron. In fully hydrated samples, this signal is readily observable and shows no line width variation as a function of counter ion. This probably means that for this gallium the positive charge is dislocated sufficiently so that the electric field gradient at the gallium site is only due to distortions of the local tetrahedral surrounding.

The variations in ^{71}Ga responses observed for zeolites containing different counterions can be explained by assuming that the observed ^{71}Ga NMR signal is due not to gallium in one well-defined electric field gradient (efg) but rather due to an assembly of gallium nuclei experiencing different efg's as a function of time. This is depicted in Figure 7. The local charge distribution at the gallium site depends on the nature (radius, etc.) and solvation of the alkali-metal ions. When the counterion is located in the vicinity of the oxygen atom of the framework GaO_4 tetrahedron (Figure 7a), the gallium atom will experience a large electric field gradient, broadening the gallium resonance beyond detection. However, if the counterion is dislocated from the GaO_4 site (Figure 7b) gallium experiences a small efg and is readily observable. The detectability of the gallium is now thought to depend on the average time the counterion resides in both positions and the actual value of the field gradient in both situations. How the latter values precisely influence the response and line shape in this exchange process between visible and invisible gallium is not yet fully understood, but it is expected that the response decreases with an increasing field gradient in the situation with the charge located on the GaO_4 tetrahedron. From the fact that no line-width variation was observed as a function of the counterion in the fully hydrated state, we already concluded that in this case the efg is due only to distortions of the local tetrahedral surrounding. Thus the gallium response will depend most strongly on the efg the gallium experiences in the disturbed framework site. In accordance with our observations, we expect the field gradient in this state to be smaller for larger counterions, as the charge will be delocalized further from the gallium. Indeed, the gallium response increases with increasing ion radius. This is probably also the reason that a gallium signal remains in the dehydrated samples (i.e., low water loadings) for the samples with large counterions. Lithium forms an exception to the discussed behavior. In the Li^+ -exchanged zeolite, the alkali-metal ion has very strong interactions with the surrounding water molecules (structure-making properties of Li^+).³⁴ Moreover, there is sufficient space in the zeolite pore for the formation of a shell of water molecules around it. This implies that, in the case of a Li^+ counterion, the charge is more dislocated from the GaO_4 unit, as compared to the larger alkali-metal ions for which the formation of a complete shell of water molecules is not feasible for steric reasons. A model based on similar considerations was earlier proposed by Meinhold et al.,³⁵ who studied the aluminum visibility in H(Al)ZSM5 as a function of the water content of the zeolite.

Thermal and Hydrothermal Stability of the Gallosilicates. From Table IV, it can be concluded that the gallosilicates are thermally stable up to temperatures of about 600 °C. At higher temperatures the ^{71}Ga NMR response at +161 ppm decreases rapidly. For this observation, two explanations can be given. First, there might well be a loss of framework gallium and simultaneously a distortion of the zeolite framework. In these stages of gallium loss, however, the latter effect could not be followed by XRD spectroscopy. Also ^{29}Si MAS NMR is not suitable to investigate the structural changes in HZSM5 structures, for the reasons mentioned above. Due to the zeolite decomposition, also changes in detectability of the remaining framework gallium might occur, leading to a decrease of ^{71}Ga NMR response. The contribution

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of this latter effect to the apparent loss of total ^{71}Ga NMR response, however, cannot be distinguished from the actual loss of framework gallium, as no octahedrally coordinated gallium could be detected in the samples, even after extensive acac equilibration. After calcination at 710 °C, very small amounts of gallium remained in the framework.

Under steaming conditions the gallosilicates are less stable against heating than in dry atmosphere. Table IV shows that under steaming conditions the loss of framework gallium is initiated at temperatures of about 550 °C and that at 600 °C the loss is already substantial, especially during the first few hours of hydrothermal treatment. Simultaneously with an actual loss of framework gallium, also in this case changes in detectability of the framework gallium may occur. Moreover, the apparent loss of framework gallium depends on the gallium content of the material, as indicated in Figure 6. With increasing gallium content, the rate of gallium removal under hydrothermal conditions becomes relatively larger. Also for the determination of this gallium loss, the detectability of the gallium in the samples was assumed not to change during the steam treatment. It is quite remarkable that for zeolites with quite different initial gallium contents, the level reached after about 3-6 h of treatment is about 1.3 gallium atoms/unit cell. This value has been calculated taking into account that about 70% of the gallium is visible in the H^+ form of the zeolite (Table II), for both the parent and the steamed material. The loss of gallium to a well-defined framework gallium content indicates that varying stabilities of gallium on different T sites in the framework of H(Ga)ZSM5 exist. Theoretical calculations on this aspect can probably give more insight in this assumption, but that is beyond the scope of the present work.

Conclusions

The ^{71}Ga MAS NMR measurements described in this paper have provided new information about quantitative aspects of the determination of framework gallium in HZSM5 gallosilicates. No direct quantitative information is obtained for octahedrally coordinated gallium or for extraframework material.

Quantitative determination of framework gallium by ^{29}Si MAS NMR was unsuccessful, due to the presence of framework defects (silanol groups). These defects have been detected by ^{29}Si CP MAS NMR and ^1H NMR ("CRAMPS"). In the acid form of the zeolite, about 70% of the theoretical signal intensity is measured as a ^{71}Ga NMR line, assigned to tetrahedrally coordinated gallium. In the presence of Li^+ , Rb^+ , and Cs^+ ions, these NMR signals represent about 100% of the gallium.

We propose distributions of lattice gallium over different lattice positions (within a given sample), experiencing different, time-dependent electric field gradients, depending, e.g., on the nature of the counterions. Clearcut distinctions between the several contributing factors are not possible in all cases.

The H(Ga)ZSM5 zeolites were found to be thermally stable up to temperatures of 600 °C. In the presence of steam, the loss of framework gallium starts at 550 °C, and the rate of disappearance depends on the gallium content of the zeolite.

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Site-Specific Surface Interaction of Adsorbed H_2O and Halogens on CuInSe_2 Surfaces

M. Sander, W. Jaegermann,* and H. J. Lewerenz

Hahn-Meitner-Institut, Abteilung Solare Energetik, Glienicke Strasse 100, 1000 Berlin 39, Germany
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The interaction of adsorbed H_2O , I_2 , and Cl_2 on cleaved CuInSe_2 surfaces has been investigated in ultrahigh vacuum to model semiconductor/electrolyte interfaces. The semiconductor/adsorbate system has been characterized by UV and X-ray photoelectron spectroscopy (UPS, XPS), low-energy electron diffraction (LEED), low-energy ion scattering spectroscopy (LEISS), and surface photovoltage measurements (SPV). H_2O is physisorbed at 80 K and desorbs completely at 300 K. It preferentially interacts with Cu surface sites at low coverages. The H_2O dipole is oriented with the O pointing toward the surface which leads to a decrease of the work function by 0.9 eV. Semiconductor band bending or a surface photovoltage is not observed. At 80 K, I_2 is dissociatively adsorbed at low coverages and molecularly adsorbed at high coverages. At 300 K, only the iodine adatoms remain on the surface. They are preferentially bonded to Cu leading to a monolayer of CuI moieties. The adsorbed I_2 leads to a band bending of 0.5 eV, an increase of work function by 1.4 eV, and a surface photovoltage of 0.3 eV which corresponds to the theoretical expectation of ideal Schottky type behavior. At 80 K, Cl_2 is also dissociatively adsorbed at low coverages and molecularly adsorbed at high coverages. The chlorine adatoms preferentially interact with Cu sites, increasing their oxidation state. The work function is increased by 0.6-0.8 eV depending on the coverage regime. Semiconductor band bending or a surface photovoltage is not observed, indicating Fermi level pinning. Annealing at 300 K leads to the formation of Cu^+ , InCl_3 , and Se^0 . The observed differences in reactivity are explained on the basis of thermodynamic calculations of bulk reactions. The results of the model experiments are discussed in relation to photoelectrochemical solar cells and their performance.

1. Introduction

The solid/electrolyte interface is at present intensively investigated with a variety of spectroscopic techniques to elucidate the interrelation of its microscopic structure and electric potential distributions as well as charge-transfer processes across the interface. Various ultrahigh-vacuum (UHV) surface science techniques have been applied in addition to classical electrochemical measurements to improve the knowledge of metal/electrolyte interfaces.¹⁻⁴ A particular intriguing aspect is the

attempted simulation of electrochemical interfaces in UHV by adsorbing electrolyte components on well-defined single-crystalline metal surfaces.⁴⁻⁶

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