

Effect of hydrothermal dealumination of a synthetic faujasite by IR spectroscopy

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Abstract - Crystal structure of a faujasite dealuminated hydrothermally to different degrees has been studied by means of the FT-IR spectroscopy. It has been found that in early stages of dealumination, a partial hydrolysis of the framework aluminium occurs, which causes a Si-O symmetric stretch at 664 cm^{-1} to become active in the IR spectrum. In final stages of dealumination, expulsion of aluminium from the framework has been detected as revealed in the dramatic decrease in absorbance at $720\text{--}740\text{ cm}^{-1}$ characteristic of $\text{Al}^{\text{IV}}\text{-O}$ framework bonds, along with the appearance of the bands at 527, 612, 832, and 973 cm^{-1} , which were assigned to $\text{Al}^{\text{VI}}\text{-O}$ non-framework species. Expulsion of aluminium is accompanied by the local rearrangement of the crystal framework producing sp-hybridized siloxane bonds associated with the bands at 485, 1170 and 1200 cm^{-1} .

Modification of zeolites by hydrothermal dealumination is known to be basic to the production of a wide variety of ultrastable molecular sieves and catalysts, and is the subject of much research (ref. 1-3). At the same time, the mechanism of zeolites dealumination is under discussion till now (ref. 1-5).

To contribute to the clarification of this question, an attempt was made in the present work to refine the assignment of the bands in the IR lattice vibration spectra of faujasite samples dealuminated by McDaniel and Maher procedure (ref. 6 & 7) to different degrees, due to invoking the interpreted spectra of layered and skeleton aluminosilicates as closely related systems, as well as due to correlating the IR spectral behavior of the samples investigated to the corresponding ^{29}Si MAS NMR one. IR spectra were recorded using 0.5% KBr platelets on a Bruker IFS-115c Model FT-IR spectrometer over

the range of 400-1400 cm^{-1} under a resolution of 4 cm^{-1} . ^{29}Si MAS NMR spectra were measured and kindly put at our disposal by Dr. J. Klinowski. Characteristics of the samples investigated and specification of the modification conditions are given in Table.

TABLE . Characteristics of the samples investigated.

Sample	Produced by performing	Si/Al ^a total	Si/Al ^b framework
1	industrial synthesis (initial NaY sample)	2.37	2.4
2	primary NH_4^+ -exchange on 1, 873K steaming	2.37	3.1
3	secondary NH_4^+ -exchange on 2, 973K steaming	2.37	14.0
4	secondary NH_4^+ -exchange on 2, 1023K steaming	2.37	18.0
5	0.1 N HCl treatment of 4	-	-

^aanalyzed chemically, ^bassessed by ^{29}Si NMR due to (ref. 8).

IR transmittance spectra of the samples investigated are shown in Figure. Dealumination of the initial NaY sample at 873K is seen to cause a high-frequency (HF) shift of most structure-sensitive bands (ref. 7 & 9), resulting from the decreased average length and ionic character of T-O bonds, with T = Si, Al (ref. 10). Additionally, a slight band at 664 cm^{-1} appears in the spectrum 2 and exhibits a HF shift to 675-678 cm^{-1} at higher degrees of dealumination (spectra 3 and 4). Since this band attributed to the Si-O symmetric stretch is known to manifest a HF shift and increase in intensity on decreasing the content on tetrahedrally coordinated aluminium of layered and skeleton aluminosilicates framework (ref. 10 & 11), it is reasonable to associate the appearance of this band in spectra of dealuminated faujasite samples with arising "aluminium-deficiency" in their framework. The changes in the character of Al-O framework bonds may be directly detected by the changes in the spectral region of 720-780 cm^{-1} , whereby the higher the frequency of a band in this region and the greater the intensity of it, the stronger covalent character has the corresponding Al-O bond and the greater is the extent of those in the aluminosilicate framework, correspondingly (ref. 12). In this respect, the shift of the band from 718 to 741 cm^{-1} and a slight decrease in intensity indicates a lowering of the extent of covalent bonding of aluminium to the framework oxygen, simulating the so-called "aluminium-deficiency" effect; whereas no principal differences between the spectra 1 and 2 strongly suggest that aluminium remains a framework substituent in this stage of dealumination. Dealumination of the sample 2 at

higher temperatures causes drastic changes in the corresponding spectra 3 and 4. The dramatic decrease in intensity of the 741 cm^{-1} band directly indicates that "participation" of aluminium in building up the framework is extremely limited, i.e., aluminium is expelled from the framework. It produces the increase in the relative intensity of the TO_4 bending band at 465 cm^{-1} , accompanied by the development of the bands at 527 , 612 , and 832 cm^{-1} , on the one hand, and the appearance of the 482 cm^{-1} band accompanied by the HF shift and resolving of the highest frequency shoulder at 1155 cm^{-1} into 1168 and 1198 cm^{-1} , on the other hand.

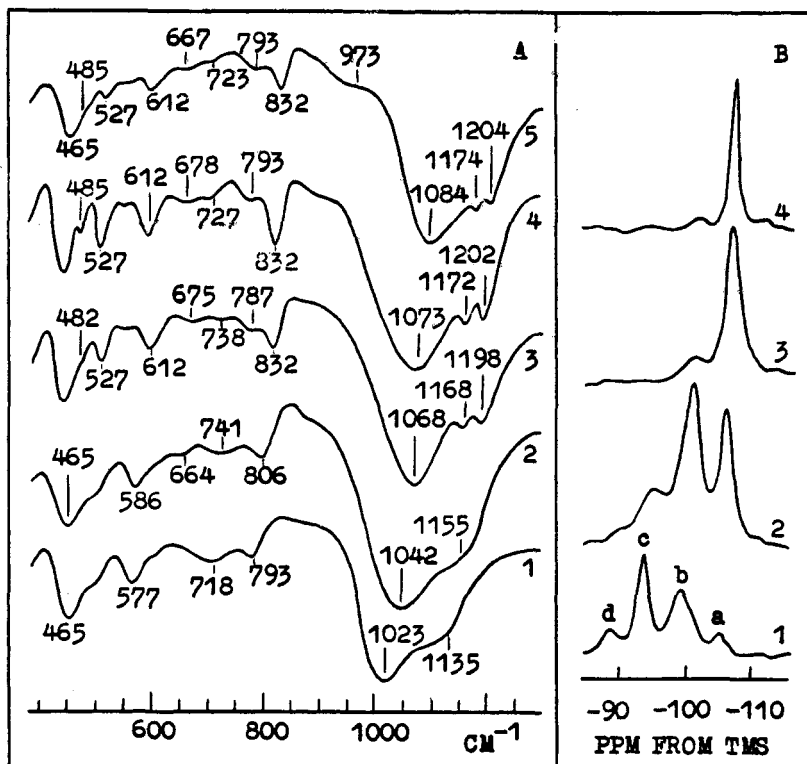


Figure 1. IR lattice vibration (A) and ^{29}Si MAS NMR (B) spectra of the samples investigated (the numbers of spectra refer to the listing of the samples in Table).

The first group of spectral changes is analogous to that observed in spectra of layered and skeleton aluminosilicates (ref. 10 & 11) on $\text{Al}^{\text{IV}}_2\text{O}_3$ - $\text{Al}^{\text{VI}}_2\text{O}_3$ transitions, whereby the absorbance at 524 cm^{-1} has been considered characteristic of $\text{Al}^{\text{VI}}\text{-O}$ species. It is thus reasonable to assume that the analogous bands in spectra of dealuminated faujasites represent vibrations of non-framework $\text{Al}^{\text{VI}}\text{-O}$ species as well. Insensitivity or positions of the bands at 527 , 612 and 832 cm^{-1} to the degree of the framework oxygen charge disbalance occurring on dealumination, as well as the increase in intensity of those with the degree of dealumination (compare spectra 3 and 4), and the detectable decrease in the same after the acid treatment (spectrum 5) argue no doubt in favor of such interpretation. Hereby, the removal of

most non-framework aluminium by acid treatment enables one to observe the band at 973 cm^{-1} assigned to the $\text{Al}^{\text{VI}}\text{-O}$ asymmetric stretch (ref. 10). The second group of spectral changes is to be considered indicative of a rearrangement of the crystal framework at high degrees of dealumination, whereby centering of new bands at 485 and 1200 cm^{-1} , with the latter being characteristic of the asymmetric stretch of close to linear siloxane bonds (ref. 10), indicates of the formation of normal sp^3 -hybridized siloxane bonds at sites of aluminium expulsion. So, the IR lattice vibration spectra of highly dealuminated faujasites represent a superposition of spectra of highly siliceous rearranged framework and that of non-framework $\text{Al}^{\text{VI}}\text{-O}$ species.

To ascertain the above conclusions, the ^{29}Si MAS NMR spectra of the same samples were analyzed. In the corresponding spectra of Figure, the $\text{Si}(n\text{Al})$ signals with $n = 0, 1, 2, 3$ denoting the number of framework aluminium atoms linked to a given silicon (ref. 8) are designated a, b, c, d, respectively. Redistribution of intensities of $\text{Si}(n\text{Al})$ signals in the spectrum 2 as compared to the initial spectrum 1 indicates of the change in the state of aluminium after the 873K treatment, while remaining of the $\text{Si}(n\text{Al})$ signals in this spectrum reveals that aluminium remains a framework substituent, for extra-framework aluminium would not be detected by this method (ref. 8). In this respect, the decrease in intensity of the $\text{Si}(n\text{Al})$ signals to negligible values and the contrasting increase in that of the $\text{Si}(o\text{Al})$ signal after the 973 and 1023K treatments (spectra 3 and 4) indicate the expulsion of aluminium from the framework, and strongly support the above interpretation of the IR spectra of highly dealuminated faujasite samples.

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