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INVESTIGATION OF THE STRUCTURE OF A FEW NATURAL ZEOLITES FROM MARATHWADA BY SOLID-STATE HIGH RESOLUTION ^{29}Si NMR SPECTROSCOPY

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ABSTRACT

The high resolution magic angle spinning ^{29}Si and ^{27}Al spectra of a number of natural zeolites have been studied. Using the spectra information about Si/Al ratio of these natural zeolites is obtained.

Key words: Zeolite, NMR and Crystal structure.

INTRODUCTION

It is well-known, that Nuclear Magnetic Resonance (NMR) method allows obtaining direct information about the crystal structures of zeolites. In NMR when a certain spinning nuclei in a strong magnetic field when irradiated by second weaker field perpendicular to it, gives rise to characteristic absorption of energy. Crystal structures and related adsorption, ion-exchange, catalytic and other properties of zeolites have been extensively investigated during recent years. The ordering of Si and Al atoms in zeolite framework is also very important for the spatial distributioin of non framework cation and the chemical property of zeolites, has also been studied. It has been shown that solid state high resolution ^{29}Si NMR spectroscopy of the framework silicon atoms is a very useful tool for structural studies of solid silicates and aluminosilicates[1-3]. In solid insoluble aluminosilicates with tectosilicate framework the ^{29}Si chemical shifts depend primarily on the degree of silicon substitution by aluminium in the lattice. Five distinct ^{29}Si chemical shift ranges are thus created, depending on the number of AlO_4 tetrahedra connected to the SiO_4 tetrahedron under consieration[2]. Information obtained from the ^{29}Si NMR spectra is related primarily to the type and regularity of Si/Al distribution in the lattice and describes the aluminosilicate provides a very accurate, reliable methdo to obtain direct information about the crystal structure and various physical and chemical properties of zeolite crystals. Several investigators studied NMR spectra of natural zeolites[4-6].

It was of interest to study ^{29}Si NAS and ^{27}Al MAS spectra of natural zeolites like heulandite, stilbite, natrolite, scolecite. With the help of NMR spectra, it was aimed to calculate Si/Al ratio.

EXPERIMENTAL

Samples

In the present study, samples of natural zeolites such as heulandite, stilbite, natrolite and scolecite were collected from different parts of Marathwada, Maharashtra State, India. Two varieties of heulandite were collected for its NMR study and designated as A and B. The crystals of natrolite were separated from geods. The trasnparent and translucent parts of the crystals were cleaned, crushed and sieved to get 106 µm sized crystals.

The samples of heulandite, stilbite, scolecite were also sieved to get 106 µm size crystals. The powdered samples were washed repeatedly and dried.

NMR measurements

All ^{29}Si MAS NMR spectra were recorded in a 47 Kg field at 59.627 MHz with pulse width 2µs and repitition time 3s. Reference for ^{29}Si is taken to be TEOS (Tetraethylorthosilicate).

For ^{27}Al MAS NMR spectra reference is Aluminium nitrate. The spectra recorded at 78.205 MHz. The pulse length is 1 µs with repetition time 200ms.

RESULTS AND DISCUSSION

Assignment of the NMR spectra

We have assigned NMR spectra to show degree of silicon substitution by aluminium in the second coordination sphere of Si atoms. The correct designation for a fully aluminium substituted framework silicon atom would be Q^4 (Al) in present case of investigation. We indicate in brackets the number of aluminium tetrahedra sharing oxygen with SiO_4 tetrahedron under consideration. The ^{29}Si MAS NMR spectrum of heulandite is as shown in Fig. 1.

Natural Zeolites

i) Platy variety

As it is already stated that natural zeolites of group VII, heulandite and stilbite belong to platy variety, were selected. We have different samples of heulandite designated as A and B and another sample of stilbite. The crystal structure of heulandite and silbite is based on T_{10} O_{20} units, which consist of four and five rings[7]. In case of sample A the signal of greatest intensity corresponds to the Si (0 Al) unit. Value assigned for this is - 104 ppm. The other strong line at -98 ppm and -92 ppm corresponds to Si (1 Al) and Si (2 Al) units respectively. In another sample of heulandite (sample B) signal of greatest intensity at -105.8 ppm is assigned to Si (0 Al) unit. Another strong line at -99.5 ppm, 94.3 ppm, corresponds to Si (1 Al) unit and Si (2 Al) unit.

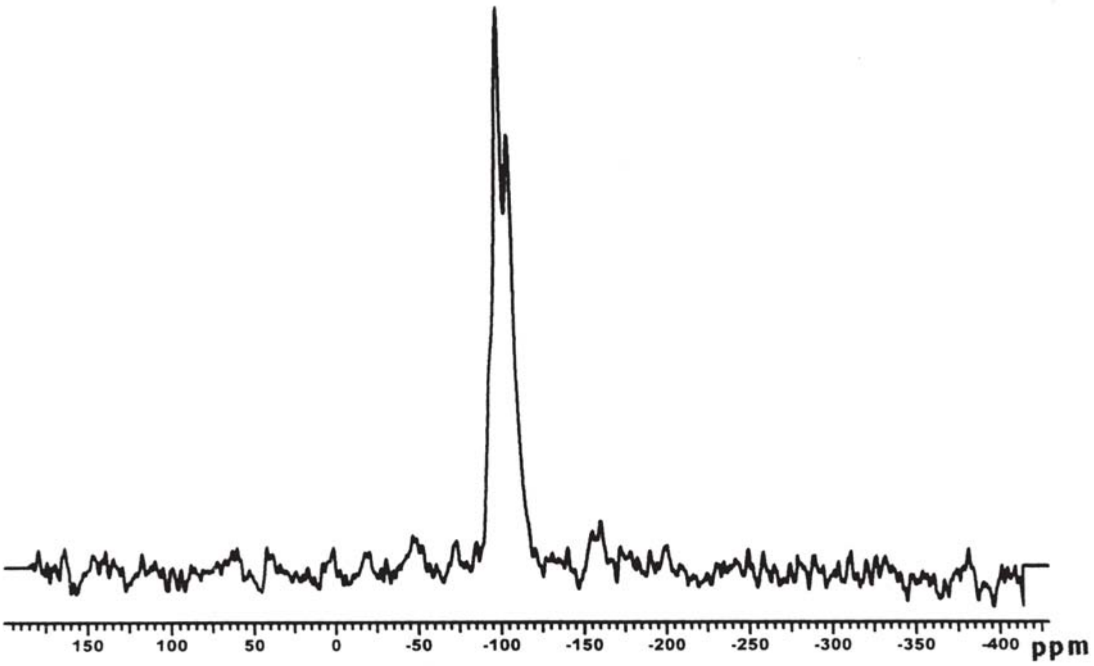

Fig. - 1: ^{29}Si MAS NMR spectra of Sample A

In case of stilbite the value - 100 ppm is assigned to Si (0 Al). The values - 101.8 ppm and - 100.7 corresponds to Si (1 Al) unit and Si (2 Al) unit respectively.

^{27}Al resonance is located at 55.61 ppm in case of sample A, at 55.60 ppm in case of sample B and 56.58 ppm in case of stilbite is observed.

Taking the help of NMR spectra, Si/Al ratios for all samples have been calculated. Si/Al ratio in case of sample A is 3.1, in case of sample B is 3 and in case of stilbite is found to be 3.5.

ii) Fibrous variety

The ^{29}Si spectrum of natrolite (transparent) consist of two lines at - 97 ppm and - 92.5 ppm can be assigned to Si (2 Al) and Si (3 Al) units respectively. In case of natrolite (translucent), two lines are observed. The values - 95.8 ppm and - 83.8 ppm can also be assigned to Si (2 Al) and Si (3 Al) units respectively. In case of scolecite peaks at - 94.8 ppm and - 83 ppm can correlated to Si (2 Al) and Si (3 Al) units respectively. Si/Al ratio for natrolite (transparent) is 1.7, for natrolite (translucent) is 1.8 and in case of scolecite it is found to be 1.5.

^{27}Al spectra shows resonance at 58.53 ppm in case of natrolite (transparent) and natrolite (translucent) samples. Resonance is observed at 47.80 ppm in case of scolecite.

Intensity distribution at ^{29}Si NMR lines changes in accordance with Si/Al ratio. Increasing Si/Al ratio leads to increasing intensities of ^{29}Si lines. This corresponds to lower degree of substitution of silicon by aluminium. For Si/Al =1, only the single Si (4 Al) line is present in several zeolites. For Si/Al = 1.5 - 2, the Si (3 Al) and Si (2 Al) lines have the highest intensities and for Si/Al = 3 - 5, the Si (1 Al) and Si (0 Al) lines are predominant.

In summary, ^{29}Si chemical shift for natural zeolites are investigated and presented in Table - 1.

Table - 1: ^{29}Si MAS NMR Isotropic chemical shifts of natural zeolites

Zeolite	Si/Al	Si (4 Al)	Si (3 Al)	Si (2 Al)	Si (1 Al)	Si (0 Al)
Heulandite (Sample A)	3.1	-	-	-92	-98	-104
Heulandite (Sample B)	3	-	-	-94.3	-99.5	-105.8
Stilbite	3.5	-	-	-100.7	-101.8	-110
Natrolite (Transparent)	1.7	-	-92.5	-97	-	-
Natrolite (Translucent)	1.8	-	-83.8	-95.8	-	-
Scolecite	1.5	-	-83	-94.8	-	-

Conclusion

The results obtained by ^{29}Si NMR spectra for various natural zeolites leads to following conclusions:

i) ^{29}Si spectra is sensitive to obtain direct information about crystal structure of natural zeolites

ii) ^{29}Si NMR spectra also provides qualitative information about zeolite structure and especially about Si/Al ordering in the aluminosilicate framework. The ^{29}Si chemical shifts display a regular dependence upon the number of AlO_4 tetrahedra connected to the SiO_4 tetrahedron.

iii) the ^{29}Si chemical shifts were used to establish presence of silicon tetrahedra on aluminium substitution, in case of zeolites.

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