

## Mössbauer Study of Hydrothermal Transformation of Natural Clinoptilolite into Y and P<sub>1</sub> Zeolites

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The hydrothermal transformation of Na-clinoptilolite to Na-Y and Na-P<sub>1</sub> zeolites has been studied by Mössbauer spectroscopy of well-characterized solid intermediate phases (XRD, IR, <sup>29</sup>Si MAS NMR, and thermodielectric analysis). The evolution of the quadrupole splitting of high spin Fe<sup>3+</sup> during the amorphization and crystallization processes which characterize the hydrothermal transformations indicates that octahedral sites are structure sensitive, while the tetrahedral ones fundamentally depend on the Si/Al ratio. Isomer shift values depend on Si/Al ratio in both cases. © 1991 Academic Press, Inc.

### Introduction

Natural raw materials used for the hydrothermal syntheses of molecular sieves include clays (1, 2), volcanic glass (3–5), and natural zeolites (6–8). These processes are really promising because of the availability and low cost of the used reagents. The control of the iron content in the raw materials as well as in the reaction products is of capital importance for the practical application of these materials, due to the fact that the presence of iron could be undesirable in the obtained product and the knowledge of its location makes it easier to manage the process. Iron can also be considered as a Mössbauer probe in zeolite reactions and it can be used as an analytical tool for several studies (9).

The information obtained about the state of iron in natural zeolites from Mössbauer

and related experiments (10) makes possible the use of Mössbauer spectroscopy to follow the kinetics of the hydrothermal syntheses when these minerals are used as raw materials.

A recent paper (11) reported the kinetics of recrystallization of Na-clinoptilolite to Na-Y and Na-P<sub>1</sub> zeolites by hydrothermal treatment with NaOH. In the present paper, using Fe<sup>3+</sup> as a useful Mössbauer probe in well-characterized samples, we show the applicability of Mössbauer spectrometry as a complementary method of study of zeolite synthesis in cases where iron is included in the synthesis gel.

### Experimental

Mössbauer spectra were obtained in a Wissell constant acceleration spectrometer in transmission geometry, with <sup>57</sup>Co in an Rh source. Iron surface density was less than 15 mg/cm<sup>2</sup>. REM computer program (12), based on Gauss-Newton methods,

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was used for spectra resolution and parameter determination. In the fitting procedure, all available a priori information concerning the spectral parameters was taken into account and a limitation of their ranges was imposed. At the beginning of the  $\chi^2$ -minimization process, fixing parameter value facility was also used.

The starting material for the hydrothermal transformation was zeolite rock from the Castillas deposit (Province of Havana, Cuba) with the following elemental composition (in weight%):  $\text{SiO}_2$ , 66.6;  $\text{Al}_2\text{O}_3$ , 13.0;  $\text{Fe}_2\text{O}_3$ , 1.3;  $\text{CaO}$ , 3.2;  $\text{MgO}$ , 1.2;  $\text{Na}_2\text{O}$ , 0.6;  $\text{K}_2\text{O}$ , 1.9; and loss by ignition, 11.7 and the following phase composition: clinoptilolite (85%), calcite, montmorillonite, quartz, and volcanic glass (15%). Before the hydrothermal transformation, it was totally cation exchanged into Na-clinoptilolite form and then treated with 7.5 M NaOH and 0.6 M NaCl solutions with a 1:1 liquid to solid ratio (in weight) at 373 K in polypropylene bottles where the hydrothermal transformation under autogenous conditions was carried out.

Samples after 1, 4, 8, 16, 24, 36, and 64 hr of treatment were taken for Mössbauer study. These samples were characterized by  $^{29}\text{Si}$  MAS NMR, XRD,  $\text{NH}_3$  adsorption, thermodielectrical analyses, IR spectroscopy, and scanning electron microscopy (11). The description of the characterization methods can be found elsewhere (13–19).

## Results and Discussion

Room temperature Mössbauer spectra of samples taken during the treatment are shown in Fig. 1. Two doublets provide the best fit in all cases. Isomer shifts  $\delta$  (relative to sodium nitroprusite), quadrupole splitting  $\Delta$ , and relative area of peaks  $A$  are reported in Table I.

The numerical resolution of natural clinoptilolite, mordenite, and erionite  $^{57}\text{Fe}$  Mössbauer spectra and related ion-ex-

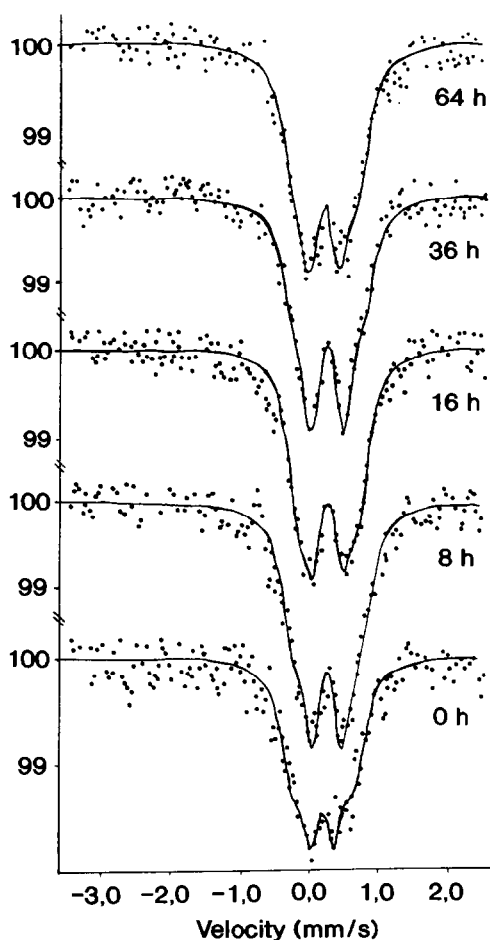


FIG. 1. Mössbauer spectra (transmission, % versus velocity, mm/s) of different steps of hydrothermal treatment samples.

change and dealumination experiments (10) indicated that  $\text{Fe}^{3+}$  in the form of high spin ion takes the place of aluminum in two locations of the aluminosilicate structure: extra-framework octahedral sites ( $\delta$ , 0.56–0.66 mm/sec;  $\Delta$ , 0.91–1.23 mm/sec) and framework tetrahedral sites ( $\delta$ , 0.52–0.72 mm/sec;  $\Delta$ , 0.35–0.46 mm/sec).

According to these results and the accumulated knowledge in aluminosilicate Mössbauer spectroscopy (20–22), the doublet 1 with higher  $\Delta$  value was assigned to

TABLE I

MÖSSBAUER PARAMETERS OBTAINED FROM THE NUMERICAL RESOLUTION OF THE SPECTRA OF SOLID SAMPLES TAKEN FROM THE HYDROTHERMAL TRANSFORMATION OF Na-CLINOPTILOLITE INTO Na-Y AND Na-P<sub>1</sub> ZEOLITES

Time	$\delta_1$	$\delta_2$	$\Delta_1$	$\Delta_2$	$A_1$	$A_2$
	(mm/sec)				(%)	
0	0.56	0.55	0.93	0.35	40	60
1	0.59	0.60	0.99	0.42	36	64
4	0.57	0.59	1.01	0.43	33	67
8	0.58	0.59	1.01	0.43	34	66
16	0.61	0.59	0.90	0.43	42	58
24	0.60	0.60	1.00	0.45	33	67
36	0.62	0.60	1.06	0.47	27	73
64	0.59	0.59	0.94	0.42	38	62

Note. Error for  $\delta_1$ ,  $\delta_2$ ,  $\Delta_1$ , and  $\Delta_2$  are (in mm/sec):  $\pm 0.02$ ,  $\pm 0.01$ ,  $\pm 0.04$  and  $\pm 0.02$ , respectively. Area errors are equal to  $\pm 2\%$ .

the octahedral sites and the doublet 2, to the tetrahedral ones. In Figs. 2-4, the spectral parameters versus treatment time are plotted.

From the characterization of the interme-

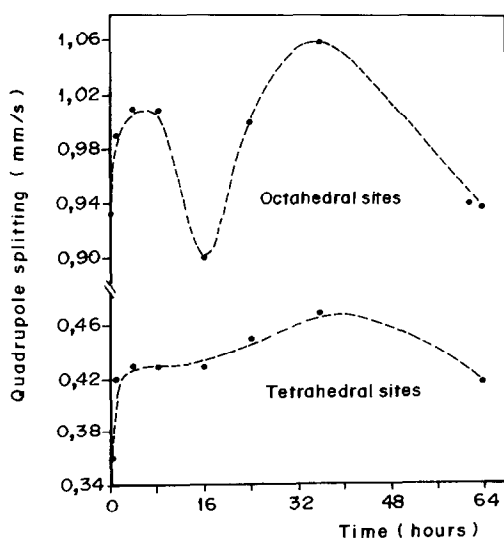


FIG. 2. Quadrupole splitting of hydrothermally transformed samples versus treatment times.

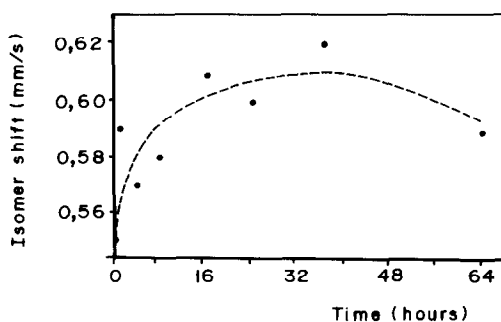


FIG. 3. Isomer shift (octahedral sites) of hydrothermally transformed samples versus treatment times.

diated phases, the mechanism of the hydrothermal transformation of Na-clinoptilolite to Na-Y and Na-P<sub>1</sub> was previously described (11) in the following way:

—From 0 to 8 hr, the crystallinity of the starting material (Na-clinoptilolite) decreases with a partial dissolution of the original clinoptilolite accompanied by a preferential incorporation of silicon into the liquid phase.

—After 8 hr, the formation of Na-Y occurs, and the crystallinity of Na-Y reaches a maximum at about 16 hr. (87% of Na-Y in the sample with a crystal size of about 1  $\mu\text{m}$  and a Si/Al ratio of 1.7).

—After 16 hr, a decrease of Na-Y crystallinity takes place and after 64 hr the formation of Na-P<sub>1</sub> is observed, indicating a progressive transformation of Na-Y into Na-P, where the Na-Y is directly the nutrient of the growing crystal of zeolite P<sub>1</sub>.

The evolution of crystallinity may be followed in Fig. 2 through the quadrupole splitting values of octahedral sites. The samples with higher crystallinity correspond to the minimum values of  $\Delta_1$ , while the more deformed octahedra of amorphous materials exhibit the maximum values. Therefore, it is possible to consider that octahedral sites are structure sensitive, a fact which has an analytical implication.

In Fig. 2 it is noted that there is an increase

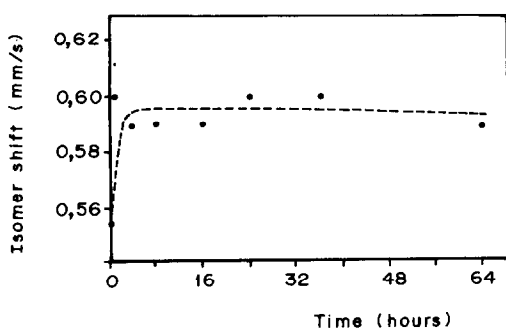


FIG. 4. Isomer shift (tetrahedral sites) of hydrothermally transformed samples versus treatment times.

in the quadrupole splitting values of the tetrahedral sites from the starting material Na-clinoptilolite to the solid intermediate Na-Y and to the final state Na-P<sub>1</sub>. The Si/Al ratio of Na-clinoptilolite, Na-Y, and Na-P<sub>1</sub>, determined from the relative intensities of the resonant lines (23) in the <sup>29</sup>Si MAS NMR spectra (11), were 4.4, 1.7, and 2.2, respectively. It is apparent that the quadrupole splitting of the tetrahedral sites fundamentally depends on the Si/Al ratio and are not structure sensitive, i.e., in the amorphous or less crystalline phases, (FeO<sub>4</sub>)<sup>-</sup> tetrahedra maintain their identity. The same effect should be found for octahedral sites, but this conclusion is difficult to be drawn because of the structural effect influence.

The dependence of isomer shift on the treatment time (Figs. 3 and 4) is fundamentally related with the Si/Al ratio in both cases, i.e., for tetrahedral and octahedral sites. This fact may be explained by taking into account that an increase in the Si/Al ratio decreases the negative charge in oxygen (24) and consequently the negative charge accessible to tetrahedral-coordinated Fe<sup>3+</sup>, which forces an expansion of their *d* orbitals (25), causing the increase of *s*-charge density at the iron nuclei, which in turn is observed as a decrease in the value of  $\delta$ .

In conclusion, it is possible to state that generally speaking the Mössbauer probe used in the present study is sensitive to change in the crystallinity of the sample and to the Si/Al ratio of the solid phase; these details are of analytical significance because they are some of the most representative parameters to be followed during a synthesis process of zeolite from aluminosilicate gels. The knowledge of the state of iron as is directly shown by Mössbauer spectrometry is of capital importance in the particular case where the raw material for zeolite synthesis is contaminated with iron or iron is included.

Finally, evidence was found of the direct relation between the aluminum content in the zeolite and the negative charge in the framework oxygen, a fact which is related with one of the most important zeolite properties, i.e., its acid-base character.

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