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Zeolites surface reactions pointed out by charge parameters

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Abstract

The diffusion potential technique was applied to determine the isoelectric point (IEP) of solid samples taken after different reaction times in two selected zeolite hydrothermal transformations (1) NaA to HS and (2) NaY to NaP. Both reactions were also followed by X-ray diffraction analysis of the solid phase.

Experiments included the study of solids consisting of different starting and final proportions of the phases. Differences were found between the IEP values obtained for these samples and those of corresponding mechanical mixtures of NaA/HS and NaY/NaP, prepared to the same composition. It was established that both transformations began onto the starting NaA and NaY zeolite surfaces, the final zeolite cover, and in some extent the surface of the former. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Zeolite transformation; Zeolite synthesis; Isoelectric point; Electric surface charges; Surface reactions

1. Introduction

The sensitivity of electrokinetic methods (osmotic pressure, electrophoretic mobility, microelectrophoresis, etc.) is enough to determine the isoelectric point (IEP) [1–3], from which it is possible to identify oxides and oxide surface coating. The microelectrophoresis method commonly used for IEP determinations is applicable only to one-component, micro-sized powder samples, composed of isolated particles, either coated or not. Mainly owing to its limitations, the method was not yet extended to IEP determination of samples of oxide mixtures.

The IEP of oxides or oxide mixtures can be obtained by measuring the diffusion potential through the suspension formed by these solids [4], with this value, the transport number of electrolyte ions modified by the charge suspension can be determined. The variation in the suspension pH allows the IEP to be determined. This value corresponds to the pH at which the suspension particles have zero total charge density, regardless of the spatial distribution of the components in the sample (as mixture or as support and coating phase).

Phase changes or crystal transformations processes usually begin in the crystal mother surface. Direct observation of these conversions is not always possible, so surface charge measure techniques can help to identify this surface process.

It is known that some molecular sieves, as type A and Y zeolites, are metastable in their hydrothermal synthesis environments, and that property allows the gradual zeolite transformation to a more stable crys-

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talline phase (from NaA to HS and from NaY to NaP, respectively). So, samples having two different phases are obtained during the course of the reaction.

Transformations of NaA to hidroxysodalite (HS) and of NaY to NaP zeolites occur slowly enough to allow samples with different proportions to be obtained and to evaluate the transformation degree. Comparison of IEP values measured for these samples with those of mechanical mixtures of pure zeolites, as was done elsewhere for simple oxides [4], will demonstrate the existence of surface reactions.

The aim of this work was to extend the use of the surface charge determination method (diffusion potential) from oxides to more complex crystalline phases, as was done for crystal transformations processes [5,6], for a better understanding of the metastable transformations occurring in a phase previously prepared by synthesis, and allowed to evolve at the same operating conditions.

2. Materials and methods

To study the hydrothermal transformation of NaA to HS and of NaY to NaP, two batch starting compositions were selected, which correspond to the standard molar ratios commonly used to prepare NaA and NaY. The raw materials used were commercial sodium aluminate, commercial water glass, NaOH (Carlo Erba, p.a.) and distilled water. The experiments were carried out in closed polypropylene containers, at $92 \pm 1^\circ\text{C}$, without stirring.

Table 1 indicates the components ratio used in the starting batch for the zeolite transformations indicated inside it.

The gels thus obtained crystallized well within a period of time, and produced either A or Y zeolite, after which HS and NaP, respectively, were observed to form rapidly.

The initial time was defined as that after which a total conversion towards NaA or NaY was reached,

while the final times were those required to obtain predetermined proportions of NaA/HS or NaY/NaP, respectively. Samples of the NaA/HS system were named: "A" while those of the NaY/NaP system as "B". The elapsed reaction times (in hours, for the NaA/HS and in days for the NaY/NaP systems) were indicated as a subscript: A₈, A₂₀, B₁, B₆, etc.

Solid samples were taken at different reaction times, centrifuged and washed until reaching pH = 10 in the washing water, and then dried at 110°C.

Mechanical mixtures of zeolites with different proportions were obtained by mixing predetermined amounts of the pure zeolites in aqueous media, under magnetic stirring. Solids were separated from the liquid by centrifugation, and then dried at 60°C.

A Philips 1732/10 equipment fitted with CuK_α radiation was used to obtain the diffractograms. The zeolite types obtained were identified by comparing the diffractograms with standards reported in the literature [7]. Zeolite contents were determined by XRD, according to the ASTM D-3906/80 method. For each zeolite type studied, the pure sample that reached the highest conversion was considered to be 100%.

Particle size and morphology were estimated by Scanning Electron Microscopy (SEM), using a Philips SEM 505 microscope.

IEP determinations of all samples were done by measuring the diffusion potential, in turn used to calculate the transport number (t^+) in KCl electrolyte, as described in previous work [4]. The diffusion potential was originated by the electrolyte ions moving within the charged sample between two zones having the same electrolyte (KCl) at different concentrations. Diffusion potential measurements were carried out with a Keithley 616 digital electrometer with Metrohm calomel electrodes. By plotting t^+ versus sample pH, the IEP is graphically evaluated as the pH for which $t^+ = 0.5$.

3. Results and discussion

The NaA-to-HS experiment was started with a batch composition that initially favored zeolite NaA crystallization, and then, as the reaction proceeded further, allowed the NaA to convert to HS zeolite.

Table 1
Molar relation (percentage) of components for the zeolite transformation indicated

Zeolite transformation	Na ₂ O	Al ₂ O ₃	SiO ₂	H ₂ O
NaA/HS	2.5	1.0	2.0	35.0
NaY/NaP	8.0	1.0	20.0	320.0

This is so because NaA zeolite is a metastable phase for the composition reached in the reacting mixture. In a first step, the sample obtained after 8 h of heating at 90°C showed the highest conversion into

NaA zeolite. Samples taken at shorter times allowed a gradual conversion of the amorphous starting gel into NaA zeolite. The second step, HS crystallization, to be observed began after, so from then on, the

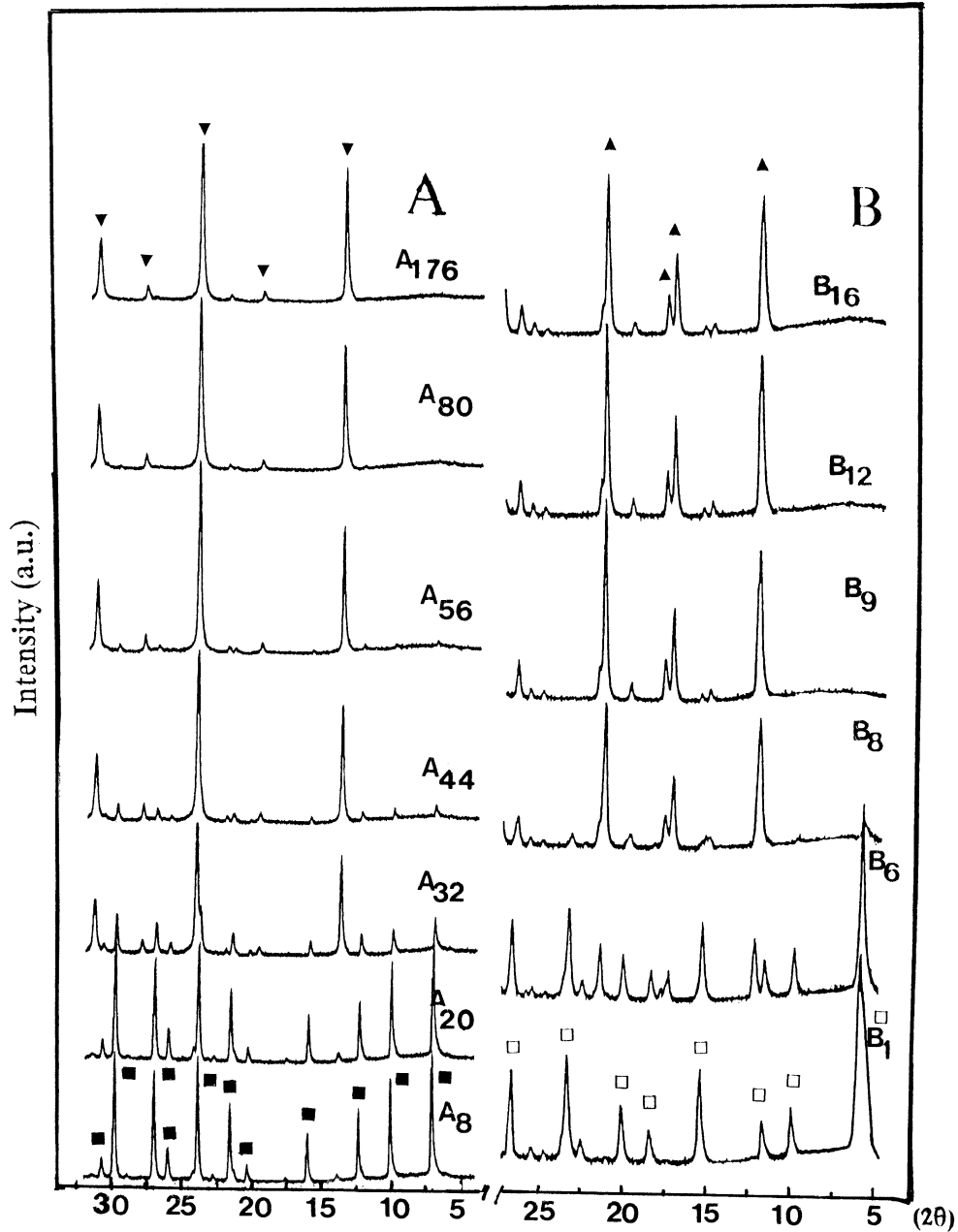


Fig. 1. X-ray diffractograms for samples obtained at different reaction times. Symbols indicated characteristics peaks for: (A) NaA (▼) and HS (◻), (B) NaY (◻), and NaP (▲).

Table 2

Semiquantitative values (XRD) for NaA, HS, NaY and NaP at the reaction times indicated

Sample (reaction time, h)	NaA (%)	HS (%)	Sample (reaction time, days)	NaY (%)	NaP (%)
A ₈	100	0	B ₁	100	0
A ₂₀	90	7	B ₆	67	33
A ₃₂	29	70	B ₈	10	90
A ₄₄	10	90	B ₉	0	100
A ₅₆	4	95	B ₁₂	0	100
A ₈₀	0	98	B ₁₆	0	100
A ₁₇₆	0	100			

samples possessed NaA and HS. The HS proportion increased with time.

In the NaY-to-NaP experiment, the product obtained by the complete gel crystallization was, after a

reaction time of 1 day, pure zeolite NaY. For longer reaction times, NaP crystals started to growth. As in the NaA zeolite experiment, crystallization was likely to proceed by replacing the first crystallizing zeolite phase by a more stable one.

X-ray diffractograms of samples taken at the indicated reaction times are shown in Fig. 1A (NaA-to-HS) and Fig. 1B (NaY-to-NaP).

In Fig. 1A, the peaks observed at 12.29, 8.71, 3.71, 3.29 and 2.9 Å indicate the presence of NaA, while those seen at 6.28, 3.63, 3.3 and 2.81 Å denote HS. Likewise, in Fig. 1B, NaY peaks appeared at 14.15, 13.73, 5.59, 4.32, 3.74, 3.28 and 2.83 Å, while those of NaP, at 7.14, 7.03, 5.05, 4.10, 3.19, 3.11 and 2.69 Å.

Fig. 1A, results for the samples taken at 20, 32 and 44 h, shows a rapid and definite NaA transformation into HS, as evidenced by the reducing inten-

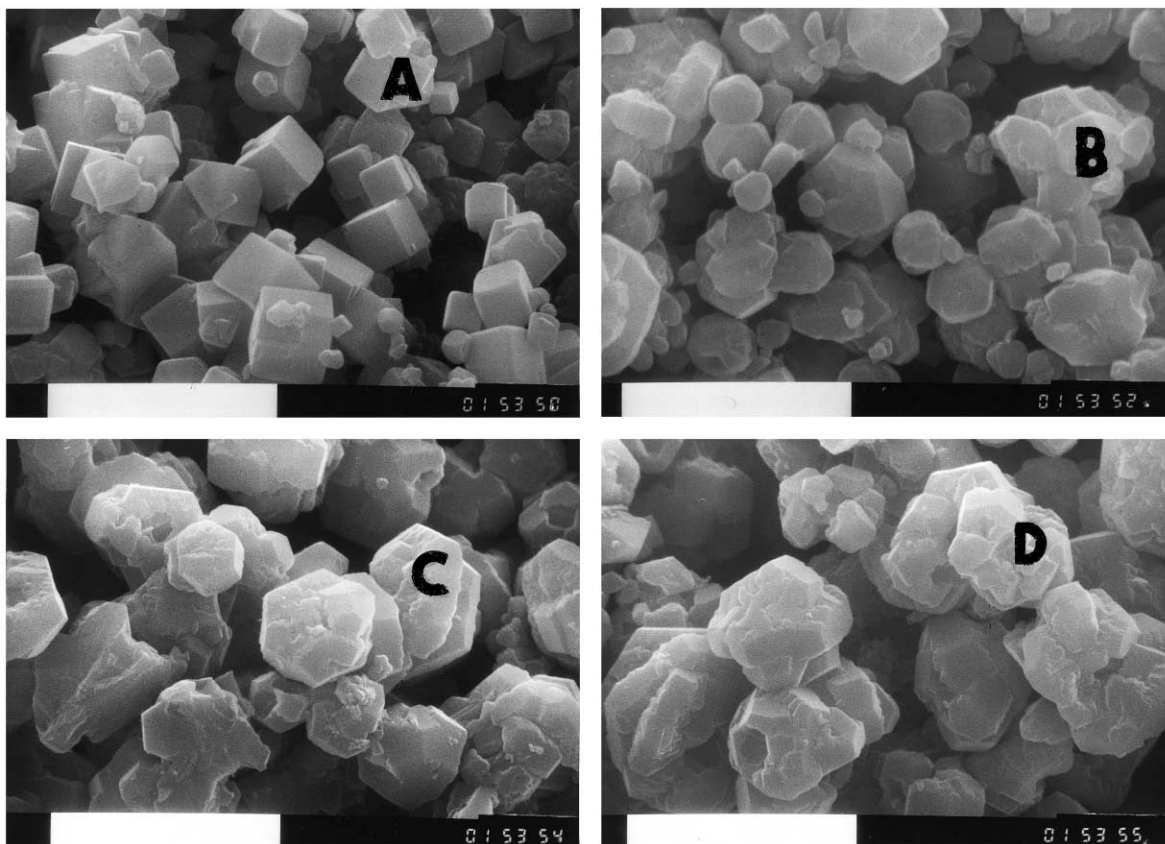


Fig. 2. Microphotographs obtained for NaA-to-HS transformation samples: (A) pure NaA, (B) A₃₂, (C) A₅₆, and (D) A₈₀.

sity of the peaks at 12.29 \AA (NaA) and the increasing size of that at 14 \AA (HS). For longer times, the transformation degree reached was such that the HS proportion was above 95%.

Fig. 1B shows that the transformation of NaY into NaP began after 6 days, as measured by the intensity peaks appearing at 4.10 and 3.19 \AA .

Table 2 indicates, for both transformations, the semiquantitative analysis obtained from intensity peaks corresponding to different reaction times.

Fig. 2 shows SEM microphotographs obtained for A_8 , A_{32} , A_{56} and A_{80} samples. The presence of NaA zeolite is shown by the $4\text{-}\mu\text{m}$ -sized cubic particles obtained after 8 h of crystallization (Fig. 2A). Fig. 2B depicts the micrograph of a sample having 70% NaA and 29% HS, where a morphology change from sharply edged cubes (NaA) to rounded shapes (HS) is evident. Fig. 2C (sample A_{56}) and Fig. 2D

(sample A_{80}) allows pure zeolite HS crystals to be observed.

Fig. 3 shows SEM micrographs obtained for B_1 , B_6 , B_8 , and B_{16} samples.

In the figure, it can be seen that the Y zeolite particles formed initially have a very small size, $< 1 \mu\text{m}$ (Fig. 3A). As the reaction proceeds, those small crystals turn into particle aggregates of NaP zeolite (Fig. 3B–D).

In Fig. 4, the transport number is plotted as a function of pH for pure samples.

The IEP values obtained for NaA and HS samples was pH 8.2 and 11.2, respectively, indicating a IEP_{pH} shift of 3.0 pH units, while, in the NaY-to-NaP conversion, it was 1.0. These differences allowed the evolution degree to be followed.

Fig. 5 shows the IEP_{pH} values obtained for different transformation times (indicated as semiquantita-

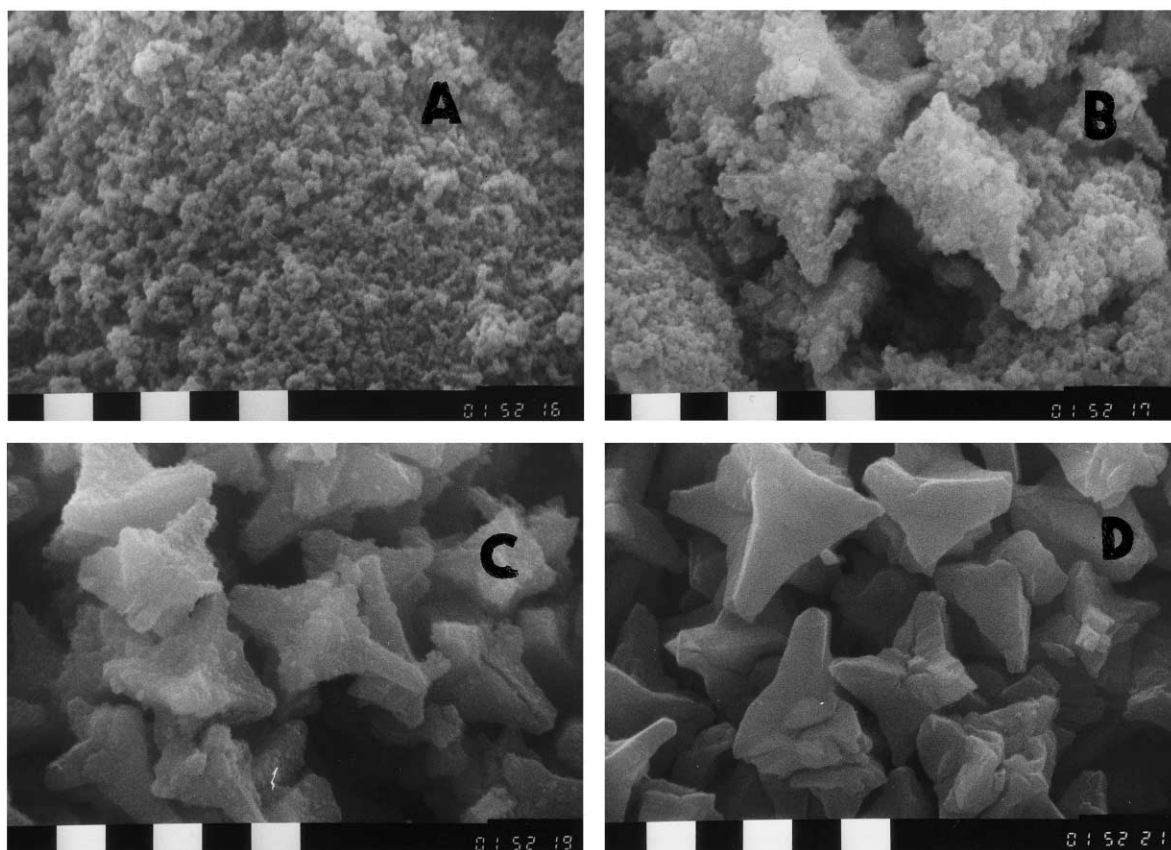


Fig. 3. Microphotographs obtained for NaY-to-NaP transformation samples: (A) pure NaY, (B) B_6 , (C) B_8 , and (D) B_{16} .

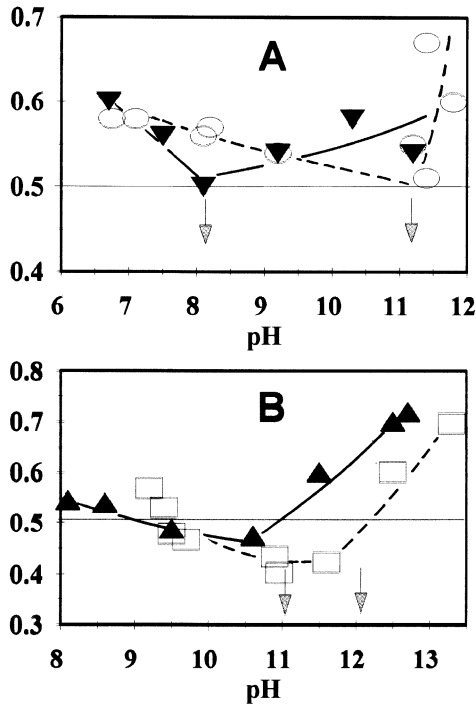


Fig. 4. Transport number against pH for pure samples: (A) NaA (\blacktriangledown) and HS (\circ), (B) NaY (\square) and NaP (\blacktriangle).

tive ratio in Table 2) as well as those of mechanical mixtures of NaA/HS and NaY/NaP.

In the NaA transformation, and in agreement to observations made in the XRD spectra, the IEP_{pH} of sample taken after the first reaction time (20 h) increases towards the IEP_{pH} of the HS pure sample. This would indicate that the NaA surface is being coated by the small initial particles of HS formed. This hypothesis will be analyzed latter.

In mechanically mixed samples, the IEP_{pH} values depended linearly on composition (NaA/HS), so indicating a similar exposed surface charge and lack of interaction between the two pure zeolites [8].

In contrast, the nonlinear line trend obtained of the IEP of samples having different transformation degrees would indicate that, as the reaction proceeds, the NaA surface was gradually coated, even at low HS content, so the IEP_{pH} value shifts toward the IEP_{pH} of pure HS.

Concerning the NaY-to-NaP transformation, the lower IEP_{pH} difference obtained in comparison with the NaA/HS samples caused less departure between

the curves (Fig. 5B). Even so, a IEP_{pH} difference can anyway be noted between mixture samples with 50% to 80% NaP and the corresponding reaction sample (NaP 33% and 90%). This indicates that this transformation was also different from a NaY/NaP mixture.

The nonlinear trend for IEP values obtained for NaY/NaP mixtures would be explained, as in $Al_2O_3-SiO_2$ oxide mixtures, by the different reactivity of the surfaces to OH groups [8,9], but further studies are required to understand the nonlinearity of the curve.

The hypothesis of a coating surface can be evaluated by utilizing the Knapps's equation [3], by which the surface coating percentage can be determined.

$$\%SC = \frac{MW_C(IEP_C - IEP_{S+C})}{MW_S(IEP_{S+C} - IEP_C) - MW_C(IEP_{S+C} - IEP_S)} \quad (1)$$

where subscript C and S indicate coating (HS or NaP) and support phase (NaA or NaY), respectively, whereas S + C indicates samples at different transformation time. The molecular weights of pure samples were: $MW_{NaA} = 365.0$, $MW_{HS} = 350.0$, $MW_{NaY} = 614.2$ and $MW_{NaP} = 523$.

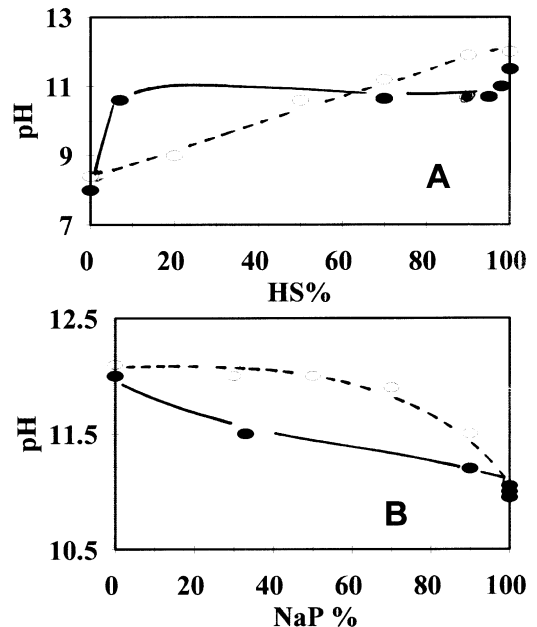


Fig. 5. IEP_{pH} values obtained for different transformation times (indicated as semiquantitative relation after Table 3) (\bullet) and mechanical mixtures of pure samples (\circ): (A) HS/NaA and (B) NaY/NaP.

Table 3
Surface coating (%) (as determined by Eq. (1)) of mother zeolites NaA and NaY, by HS and NaP, respectively

Sample (reaction time, h)	NaA coating (%)	Sample (reaction time, days)	NaY coating (%)
A ₈	0	B ₁	0
A ₂₀	40	B ₆	46
A ₃₂	49	B ₈	77
A ₅₆	70	B ₉	100
A ₈₀	79	B ₁₂	100
A ₁₇₆	100	B ₁₆	100

Data obtained after Eq. (1) were indicated in Table 3.

The percentage values obtained in the NaA-to-HS transformation indicates an important coverage of NaA by HS at low HS content, i.e., a 7% of HS (as determined by XRD) covered 40% of NaA surface. This also suggests the formation of very small particles of HS in the first 12 h of reaction.

In the NaY-to-NaP transformation, a proportion of NaP of 33% (as determined by XRD) coated 46% of NaY surface, so suggesting that the coverage occurs in a lower proportion.

4. Conclusions

IEP values measured in samples taken during the transformation of NaA to HS were different from those determined for mechanical mixtures of the same components at the same proportions. A similar

trend was found when comparing the NaY-to-NaP transformation with the mechanical mixtures. The conclusion drawn here is that the transformations proceed mainly at the surface of mother crystals.

Calculations of the proportion of coated surface indicate, for the NaA-to-HS transformation, an important formation of small HS particles in the first 12 h of reaction. In turn, for the NaY-to-NaP reaction, the newly formed NaP particles cover the mother crystals to a lower extent.

Acknowledgements

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