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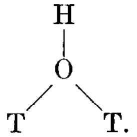
The Localization of Protons in Decationated Y Type Zeolites by Neutron Diffraction

Decationated zeolites of the Y type are intensively studied due to their interesting catalytic properties (*1*). Very important for the explanation of many sorption and catalytic phenomena is a knowledge of the structure, and X-ray diffraction methods are widely used for this purpose. However, for location of protons in decationated zeolites neutron diffraction is more suitable (*2*, *3*).

Using neutron diffraction we have studied microcrystalline zeolites NaY and $Na_{0.3}H_{0.7}$-Y (faujasite type) with chemical compositions $Na_{52.8}Ca(AlO_2)_{56}(SiO_2)_{137}$ and $Na_{13.4}CaH_{39.6}(AlO_2)_{56} \cdot (SiO_2)_{137}$, respectively. The samples were dehydrated at 350°C in a vacuum of 10^{-5} Torr (1 Torr = 133.3 N m^{-2}) and were then sealed in glass ampoules under vacuum. An OPUS powder diffractometer with high resolution ($\Delta d/d = 9.5 \times 10^{-3}$) (Institutt for Atomenergi, Kjeller, Norway) was used. Because the resolution was lower than with X-ray diffraction, we had to use a computer for the profile analysis of the Bragg lines (*4*). In this way we could distinguish 30 lines of observable intensities from 56 principally observable diffraction lines with $N = h^2 + k^2 + l^2 \leq 180$.

On the basis of previously published results (*5*, *6*) the space group *Fd3m* can be assumed for our zeolites. The location of the atoms, the multiplicity of the sites and the symbols in the Wyckoff notation are indicated in Table 1 in the first two columns (*7*). There is no direct information about the location of the hydrogen ions in decationated hydrogen faujasite. It is generally accepted that protons can form a bond with oxygen ions creating structural OH groups. Let us suppose that protons are located on the symmetry axis of a T–O–T complex at a distance about 1 Å (1 Å = 0.1 nm) from the oxygen ion as follows:



This means that they can be located at least in 4 positions H_i where they are connected to the positions of oxygen ions of the type O_i.

In order to test the diffraction method used we have calculated the parameters of the NaY zeolite structure. We started our structure refinement with the parameters given in the third column of the Table 1. For the NaY all 12 independent coordinates of T, O_i, S_I, $S_{I'}$, and S_{II} sites were refined together with 3 occupation factors of S_I, $S_{I'}$, and S_{II} and with 3 isotropic Debye–Waller temperature coefficients for cations, oxygen and T ions (see the fourth column of Table 1). To estimate the quality of the determination of the structure the reliability factor *R* was used, that is:

$$R^2 = \sum_i \left(\frac{{}_iI_{\mathrm{obs}} - {}_iI_{\mathrm{calc}}}{\delta_i I_{\mathrm{obs}}}\right)^2 \Big/ \sum_i \left(\frac{{}_iI_{\mathrm{obs}}}{\delta_i I_{\mathrm{obs}}}\right)^2,$$

where ${}_iI_{\mathrm{obs}}$ = observed intensity of the diffraction line, ${}_iI_{\mathrm{calc}}$ = calculated intensity, $\delta_i I_{\mathrm{obs}}$ = estimated standard deviation from the profile analysis. The reliability

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TABLE 1[a]

Ions	Site	Assumed starting parameters	Results	
			NaY	H, Na-Y
Na, Ca	16(c) S_I $x = y = z = 0.125$			
	occ. factor =	0.48[b]	0.25 (12)	0.55 (15)
	32(e) $S_{I'}$ $x = 0.25 - y = z = 0.125$	0.1859	0.1773 (43)	0.1859[c]
	occ. factor =	0.61	0.55 (13)	−0.11 (10)
	32(e) S_{II} $x = y = z =$	0.3485	0.3559 (28)	0.3469 (77)
	occ. factor =	0.95	1.00 (11)	0.29 (10)
H	96(h) H_1 $x = 0.25 - y = z = 0.125$	−0.0087[d]	—	−0.0171 (68)
	occ. factor =			0.179 (28)
	96(g) H_2 $x = y =$	0.1328	—	0.1328[c]
	$z =$	0.3031	—	0.3031[c]
	occ. factor =			0.015 (66)
	96(g) H_3 $x = y =$	0.3150	—	0.3128 (60)
	$z =$	0.1265	—	0.1244 (77)
	occ. factor =			0.168 (57)
	96(g) H_4 $x = y =$	0.3128	—	0.3128[c]
	$z =$	0.4811	—	0.4811[c]
	occ. factor =			0.051 (35)
O	96(h) O_1 $x = 0.25 - y = z = 0.125$	0.0189[e]	0.0211 (7)	0.0188 (10)
	96(g) O_2 $x = y =$	0.1218	0.1276 (13)	0.1199 (12)
	$z =$	0.2667	0.2687 (14)	0.2667 (15)
	96(g) O_3 $x = y =$	0.3021	0.3018 (9)	0.3045 (10)
	$z =$	0.0919	0.0834 (16)	0.0892 (16)
	96(g) O_4 $x = y =$	0.3005	0.3060 (10)	0.2991 (13)
	$z =$	0.4461	0.4443 (10)	0.4440 (23)
Si, Al	192(i) T $x =$	0.0716	0.0729 (13)	0.0756 (16)
	$y =$	0.1612	0.1571 (30)	0.1578 (36)
	$z =$	0.2504	0.2474 (16)	0.2480 (19)

[a] Origin at $\bar{4}3m$.

[b] Shoemaker's data published in (*5*).

[c] Parameters of the weakly occupied sites were not refined.

[d] Calculated values on the basis of the diagram in the text using Olson and Dempsey's parameters (*6*) and O–H distance $d = 0.967$ Å.

[e] Olson and Dempsey's parameters (*6*).

factor $R = 0.058$ in the case of NaY. The refined parameters for NaY are in reasonable agreement with previous results based on X-ray diffraction (*5*). The large estimated standard deviation of the estimated parameters (see Table 1, columns 4 and 5 in parentheses) reflects the small number of our diffraction data.

Encouraged with the above-mentioned results we have tried to test the distribution of protons within the following model. In the first step of the structure refinement it was supposed that the location of protons is possible not only at oxygen sites H_i, but also in the cationic sites S_I, $S_{I'}$, and S_{II}. Nevertheless, it was observed that within the limits of error nearly all cations are located at cationic sites S_I, $S_{I'}$, and S_{II} and all protons are present in positions H_i. Therefore in the final refinement only restricted distribution of protons was supposed, namely the cations located in S_I to S_{II} positions and protons located in H_i positions. The results are given in the fifth column of Table 1. The parameters of weakly occupied $S_{I'}$, H_2 and H_4 positions were not refined. The refined positions H_1 and H_3 lie near the initially calculated positions at a distance 1.26 ± 0.17 and 0.92 ± 0.20 Å from oxygens O_1 and O_3, respectively. The reliability factor $R = 0.048$.

For the H, Na-Y zeolite we can summarize that practically all the cations are located in S_I and S_{II} positions with 55 and 29% occupation, respectively. Nearly all the hydrogen ions are in H_1 and H_3 positions distributed with nearly the same occupation factor of 17.9 and 16.8%, respectively. This result is in good agreement with the conclusion of Olson and Dempsey (*6*) based on a comparison of the T–O_i distances from X-ray diffraction data. The ratio of the number of protons in H_1 and H_4 positions (that is in positions where the proton is oriented into the supercage) to the number of protons in H_2 and H_3 positions (where protons are directed inward to the sodalite units) is 56 ± 17 to 44 ± 17%. This result is also in agreement with the conclusions reached on the basis of infrared spectroscopic investigations of OH groups and of adsorption properties of the set of zeolites H_xNa_{1-x}-Y (*8–10*).

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