Concentration and Location of Hydroxylgroups in Hydrated Zeolite Linde 13 X, Hydrolysis by Washing, as Determined by Proton Magnetic Resonance at 90 K

W. D. Basler

Institute of Physical Chemistry of the University of Hamburg

Z. Naturforsch. **35 a**, 1417–1418 (1980);
received November 11, 1980

By H-NMR at 90 K, 0.3 OH-groups within one sodalite cage of zeolite Linde 13 X have been found. There are no ($\lesssim 0.1$) OH-groups in the supercages. The concentration of OH-groups is strongly increased after hydrolysis by washing.

Hydroxylgroups are importent for the catalytic activity of zeolites. Whereas IR-spectroscopy is very sensitive in detecting OH-groups, there is overlapping of the spectra of OH-groups and water molecules in hydrated samples. For a review of IR-studies of zeolites see e.g. Ward [1]. Therefore, proton nuclear magnetic resonance has been used to determine the number of OH-groups in these samples: Wide-line H-NMR spectra at lower temperatures ($T \lesssim 200$ K) show, besides a more or less broadened dublett of the immobile water molecules, an unstructured central line of about 0.2 mT linewidth, which has been attributed to OH-groups. By this method, about 1 OH-group per cavity of hydrated sodium faujasites Na-X and Na-Y has been found, see e.g. Oehme et al. [2] and other references cited there.

It is possible to prepare hydrated sodium faujasites which contain water exclusively in the supercages and not in the interior of the sodalite building units of the alumosilicate frame-work [3]. Comparing such samples with equilibrated samples it should be possible to determine separately the fraction of OH-groups within the supercages which is directly accessible and may therefore be important in catalytic reactions, and the fraction inside the sodalite units, only accessible for small molecules with diameter of less than about 0.25 nm.

To ensure the possibility of comparison we have studied the widely used sodium faujasite Linde 13 X of Union Carbide Corp., lot no. MI 320489, as supplied by the manufacturer.

The samples were dehydrated under shallow bed conditions (sample layer of about 1 mm). To avoid hydrothermal conditions, the temperature was raised to 670 K in steps of 50 K only when the pressure was less than 1 Pa. Finally the samples were held at 670 K, until the pressure was less than 1 mPa for 12 hours.

The wide-line H-NMR was done at 16 MHz with a Varian DP 60 spectrometer with V-4257 temperature control by N_2 gas. 75 scans of 8 min were accumulated and the signal of the probe without sample was subtracted by a Varian C-1024 CAT.

At the given S/N-ratio (see Fig. 1) the conditions of undistortedly recording both the dublett and the central line were found to be fulfilled by the following settings: Exciting field strength $B_1 = 0.3\ \mu$T, modulation field strength $B_M = 80\ \mu$T, sweep rate 0.5 mT/min and time constant 3 sec.

In agreement with [2], after dehydration no proton signal could be observed at an estimated limit of detection of 0.1 H per cage under the conditions of recording, i.e. with a longitudinal relaxation time T_1 less than about 10 s. By pulsed NMR at

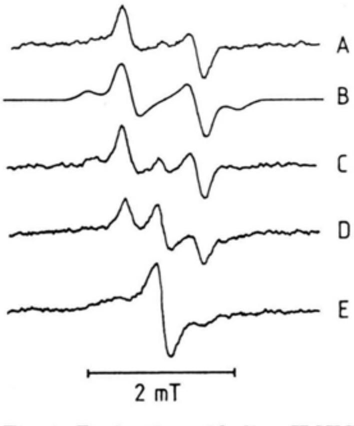

Fig. 1. Derivative wide-line H-NMR spectra of hydrated zeolites at 90 K. A: Linde 13 X (Na-X) with 3.5 H_2O/cage (37 mg H_2O/g), only in the supercages. B: Calculated derivative dublett powder spectrum with Gauß broadening. C: Linde 13 X with 3.5 H_2O/cage in sorption equilibrium. D: Linde 13 X with 5.4 H_2O/cage after washing with 2.5 L H_2O/g at 295 K in 3 days. E: (Na, H)-ZK-5 with 3.5 H_2O/cage.

Requests for reprints to Dr. Wolf D. Basler, Institute of Physical Chemistry of the University of Hamburg, Laufgraben 24, D-2000 Hamburg 13, West-Germany.

0340-4811 / 80 / 1200-1417 $ 01.00/0. — Please order a reprint rather than making your own copy.

60 MHz and improved conditions of sensitivity no proton signal with $T_1 \lesssim 10$ s could be found at the limit of 0.01 H per cage. It follows that essentially all water molecules and OH-groups have been removed by the dehydration at 670 K.

When loaded with 3.5 H_2O per cage, located only in the supercages, the derivative spectrum A of Fig. 1 has been observed. It agrees well with the derivative powder spectrum of a dublett. Fitting with an isotropic Gauß-broadening of the dublett, a dublett splitting of $2\alpha = 1.01 \pm 0.03$ mT and a second moment $M_{2G} = 1.5 \pm 0.5\ 10^{-8}\ T^2$ are obtained (derivative spectrum B of Figure 1).

No central line could be detected without ambiguity. Only a trace of a central line of estimated intensity of 0.1 protons per cage may be extracted from the difference between experimental and fitted derivative dublett powder spectrum, which is in the order of signal noise or may be caused by imperfect compensation of the signal of the probe.

Then sorption equilibrium of the water molecules between the supercages and the sodalite cages has been established by a mild heat treatment of 350 K for 3 days. Thereafter, derivative spectrum C of Fig. 1 has been observed, showing a central line of intensity of 0.3 ± 0.1 protons per cage. This central line cannot be caused by the heat-treatment as an identical spectrum was measured using samples which had been dehydrated to the same water content at 295 K, i.e. avoiding any heating during pumping.

The whole experiment has been repeated another two times with corresponding results. It may be concluded that the central line originates from protons in the sodalite cages.

If a line splitting has the angular dependence of $3\cos^2\theta - 1$, which is true of the intramolecular H-H-dipole interaction of the water molecule, a dublett with a central line may result from slow tetrahedral jumps [4]. The Na-ions in sites S1′ resp. S2′ have just this symmetry (for cation positions in zeolites see e.g. the review of Smith [5]). Therefore, we have studied the central line as a function of temperature. No significant change of its intensity has been found between 90 and 200 K (above 200 K there is the begin of motional narrowing of all water molecules), excluding thermally activated slow jumps of water molecules between the Na-ions inside the sodalite units as responsible for the central line.

Consequently it can be concluded that there are 0.3 OH-groups per cage in hydrated zeolite Linde 13X as supplied, nearly all of them within the sodalite units.

By washing zeolites can be hydrolysed [2]. We have washed zeolite Linde 13X by passing 2.5 L deionized (specific conductance 2 μS/cm) water per g zeolite at 295 K in 3 days through a sample layer of 5 mm height. The derivative spectrum D shows a clearly increased central line, giving about 1.5 OH-groups created by washing.

In [2], no increase of the OH-concentration by washing has been reported. This result may not be conclusive as fully hydrated samples have been examined. In such samples many kinds of OH-groups, i.e. created by water dissociation by means of multivalent cations, hydrolysis by washing, treatment with complexing agents or even structural OH-groups from synthesis, cannot be measured by low temperature wide-line NMR. Their line is broadened by the dipole interaction with the water protons to such an extent that it completely overlaps with the dublett of the water protons and no separated central line is observed at higher water coverages [6].

For comparison zeolite (Na, H)-ZK-5 which has 4 structural OH-groups per cage has been measured under the same conditions with 3.5 H_2O per cage. The result is shown as derivative spectrum E in Figure 1. Using its central line as a calibration, a concentration of 0.4 OH-groups per cage is calculated for Linde 13X as supplied.

Acknowledgement

The author is indebted Prof. Dr. H. Lechert for helpful discussions and the "Deutsche Forschungsgemeinschaft" for its support of this work.

[1] J. W. Ward in J. A. Rabo, Zeolite Chemistry and Catalysis, ACS Monograph 171, Washington D. C. 1976.
[2] W. Oehme, D. Freude, S. Klepel, H. Pfeifer, and H. Schmiedel, Z. phys. Chemie Leipzig **259**, 1137 (1978).
[3] W. D. Basler in J. R. Katzer, Molecular Sieves-II, ACS Symposium Series No. 40, Washington D. C. 1977.
[4] U. Pschorn and H. W. Spiess, J. Magn. Reson. **39**, 217 (1980).
[5] J. V. Smith in J. A. Rabo, Zeolite Chemistry and Catalysis, ACS Monograph 171, Washington D. C. 1976.
[6] W. D. Basler, in preparation.