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CATION DISTRIBUTIONS AND LOCATION OF CHEMISORBED GROUPS IN FAUJASITE ZEOLITES[1]

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The crystal structure of NaX, NaLSX and NaY zeolites (faujasites with various Si/Al) with chemisorbed methyl cations $(CH_3)^+$ or $(CD_3)^+$ have been investigated by powder neutron diffraction. The magic angle spinning (MAS) method was used for recording of ^{13}C MAS NMR spectra of adsorbed species. Powder neutron experiments were carried out at 7 K and 294 K. The complete structural parameters were determined by Rietveld analysis of powder neutron patterns. Difference Fourier maps were used to locate the Na^+ cations and the chemisorbed CD_3 or CH_3 groups. The significant effect of chemisorbed methyl cations on the distribution of sodium cations in the lattice of chemisorbed zeolites was detected.

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1 Introduction

Zeolites and related microporous materials have common and diverse applications in a wide variety of industrial processes that use catalysis or molecular separation. There is a continuous need to develop novel materials that would improve efficiency and economics of catalytic processes. There is a great deal of fundamental interest in understanding how zeolites function at the atomic or molecular level. This knowledge will provide the means to design novel catalyst materials.

Nature of acid or basic sites and the distribution of sodium cations and chemisorbed methyl groups in the zeolitic lattice belong to the most important problems of surface chemistry. Theoretical investigations [1, 2] demonstrated that chemical properties of protons are controlled by actual basicity of the lattice oxygen atoms and by the character of bonds where protons are attached. It is well known that chemisorbed carbenium ions on zeolites and other aluminosilicates are bonded to basic lattice oxygen atoms, forming thus surface alkoxy species [3]. Experimental support was obtained also from the results of diffraction methods, where neutron diffraction provided direct evidence on the location of protons in faujasites with various H^+/Na^+ ratios [2]. The

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preparation of the surface alkoxy species is usually based on the reaction of methyliodide with zeolitic cations or acid protons. Methyl ions, evolved in the reaction of adsorbed methyliodide with reactive free sodium cations (or acid protons), create the bridging form of surface methoxy compounds which are detectable by ^{13}C MAS NMR because of typical chemical shift of their signal [2, 3]. The chemical shift of bridging methoxy carbon is very sensitive to the electronegativity of the lattice oxygen atom. It is evident that chemisorbed methyl ions (cations) take part in the charge compensation of the skeleton negative charge and that they substitute the removed positive charges of zeolitic cations (or acid protons in OH) producing e.g. sodium iodide clusters in extra- lattice positions or water molecules as in the case of the reaction of methanol with OH groups.

The aim of our study was to estimate the regular distribution of cations and the location of chemisorbed species CH_3^+ in the lattice and to elucidate the role and participation of various lattice oxygen types in chemisorption of methyl cations. We have shown in the previous studies [4] that methyl groups are located on NaX at new positions associated with oxygen atoms O_1 or O_4.

2 Experimental

The preparation of samples for neutron diffraction and NMR experiments was carried out as follows: sample of zeolite was dehydrated under vacuum of 10^{-3} Pa in a glass vessel at 400 °C for 10 hours. Powdered zeolite was then transferred under vacuum into a thin-glass cylindric vessel (with diameter of 12 mm, and height of 35 mm) and sealed off for diffraction experiment. A portion of the same sample was sealed off under vacuum in a tube for MAS NMR measurement as described earlier [3]. The mentioned methyl iodide was enriched before ^{13}C NMR measurement with a small amount of $^{13}CH_3I$, in order to increase the ^{13}C content in adsorbate and to facilitate the detection of chemisorbed species. Chemisorption of methyl iodide was carried out in a special all glass-device.

The high resolution ^{13}C MAS NMR spectra were measured on a BRUKER DSX200 spectrometer equipped with a magic angle spinning probehead at 50.32 MHz with proton decoupling using pulse programs for Hahn echo and for cross polarisation (details see in [3]).

For diffraction experiments the samples were loaded either with CH_3I or with CD_3I. Neutron powder diffraction patterns were collected at temperatures of 298 K and 7 K on the KSN-2 diffractometer at the LVR-15 research reactor in Řež near Prague [4]. This apparatus was equipped with a close circuit liquid helium cryostat - type CP-62-ST/5 (Cryophysics SA). The wavelength of 0.1362 nm was used and the resolution $\delta d/d = 0.00075$ was achieved. The complete structural parameters were determined by the Rietveld analysis of powder neutron diffraction data using the GSAS software package [5] including the difference Fourier maps.

3 Results

Our experimental data allow to compare the changes in the occupation of positions of the lattice atoms in original evacuated NaX [6] or NaLSX [7] and in the same sample after chemisorption of methyl iodide. We observed significant changes in the distribution of the lattice elements after chemisorption of methylium ions. These changes were detected not only in the occupation

Tab. 1. Occupation numbers of cationic sites in dehydrated faujasites NaX and NaLSX.

Sample	Cation site	Type	Occupation
NaX	SI	16c	3
	SI'	32e	29
	SII	32e	31
	SIII'(1,2)	96g	21
	SIII'(3)	96g	9
NaLSX	SI	16c	0
	SI'	32e	25
	SII	32e	32
	SIII'(1,2)	96g	34
	SIII'(3)	96g	8

numbers of cationic sites but sometimes also in coordinates of Na^+ cations where a splitting (at 7 K) is demonstrated of the position SI into two sites Na2 and Na3, which are separated at helium temperature but merged at room temperature. Cations are distributed over six possible sites as proposed by Olson [8] in the frame of the Fd3 space group. In recent publications [8, 9] the distribution of Na cations in faujasites was also tested by high resolution ^{23}Na MAS NMR. The NMR results altogether confirm the results obtained by diffraction methods. It is clear that also our neutron diffraction results, presented in the Tab. 1, are well in line (considering various composition of materials and experimental deviations) with the observed cation distribution in all NaX and NaLSX samples published in literature.

Structural parameters of methyl groups were determined by means of the difference Fourier maps. Nuclear density contours at the O_1 and the O_4 oxygen denoted by M_1 and M_2 are remarkable. Estimated their distances from the oxygen atoms are given in Tab. 2. Let us try to turn attention to the observed fact that the distances M_1–O_1 (or M_1–O_4) and M_2–O_1 (or M_2–O_4) given in Tab. 2 are spread in the interval from 0.15 to 0.17 nm. It has been shown that in NaLSX the position M_1 as well as M_2 assigned to CH_3 group (or CD_3 group) exhibits a shorter distance to O_4 than to O_1, although in NaX structure the situation is inverse. It is assumed that this effect is associated with the amount of particles in supercages. Also an experiment with argon, which was adsorbed after the preparation of surface methyl groups and which filled the supercages and restricted the movement of CH_3, has shown a weak decrease in M_i–O_j ($i = 1, 2$; $j = 1, 4$) distances. Comparing this distance with the published C–O bond length for bridging methoxy group [10] in compact nonporous crystals, it is clear that the distances we observed in microporous crystals are longer. This can be explained by taking into consideration at least two factors: firstly, rotation and precession mobility of the C–O bond of anchored methyl group, and secondly, the interactions of the considered chemisorbed CH_3 (or CD_3) group with other species, e.g. with other lattice oxygen atoms [10]. Further lengthening of the bonds may be possible only through strong intermolecular interactions or under the influence of force field gradients in the zeolitic supercavities.

Tab. 2. Selected distances of chemisorbed methyl groups from lattice oxygen O_1 and O_4. (*Adsorbed molecules per unit cell, M_1, M_2– chemisorbed methyl groups.)

Sample	NaX	NaX(+Ar)	NaLSX	NaLSX
T [K]	7	7	7	298
CH_3 * [mol/u.c.]	15.3	14.6	26.4	24.8
M_1–O_1 [nm]	0.1653(5)	0.1663(4)	0.1573(6)	0.1627(6)
M_1–O_4 [nm]	0.1764(4)	0.1670(4)	0.1535(5)	0.1530(5)
M_2–O_1 [nm]	0.1661(5)	0.1556(5)	0.1712(6)	0.1656(6)
M_2–O_4 [nm]	0.1789(4)	0.1572(5)	0.1572(5)	0.1548(5)

4 Conclusions

Chemisorption of methylium ions at nucleophilic lattice oxygen sites has a remarkable effect on the distribution of cations in the lattice. It demonstrates that long-range forces and variations of electrostatic field gradients significantly change the cations distribution.

In X faujasite methyl ions are located at O_4 and O_1 lattice oxygen atoms.

The complete structural parameters of NaX and NaLSX type of zeolitic catalysts were determined.

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References

[1] W. J. Mortier, J. Sauer, A. Lechler: *J. Phys. Chem.* **88** (1984) 905
[2] Z. Jirák, S. Vratislav, V. Bosáček: *J. Phys. Chem. Solids* **41** (1980) 1098
[3] V. Bosáček: *J. Phys. Chem.* **97** (1993) 10732
[4] S. Vratislav, M. Dlouhá, V. Bosáček: *Physica B* **276-278** (2000) 29
[5] R. B. Von Dreele: *J. Appl. Cryst.* **30** (1997) 517
[6] S. Vratislav, M. Dlouhá, V. Bosáček: *Applied Physics A* **74** (2002) 1320
[7] S. Vratislav, M. Dlouhá, V. Bosáček: *Physica B* **350** (2004) 407
[8] D. H. Olson: *Zeolites* **15** (1995) 439
[9] S. Caldarelli, A. Buchholz, M. Hunger: *J. Am. Chem. Soc.* **123** (2001) 7118
[10] V. Bosáček, S. Vratislav, M. Dlouhá: *Collect. Czech. Chem. Commun.* **69** (2004) 1537