

s5.m19.p4 **Structure of zeolite MFI with tetrabutylammoniumfluorid as template.** O. Kovalev<sup>a</sup>, H.Gies<sup>a</sup>, <sup>a</sup>Institut of Geology, Mineralogy and Geophysics, Ruhr-University-Bochum, D-44780, Bochum, Germany. E-mail: oleg@kovalev.de

**Keywords:** Rietveld method; Zeolite MFI; Tetrabutylammonium

Organic molecules plays a structure-controlling role by the hydrothermal synthesis of porous materials. [ 1 ]

Importance of tetraalkylammonium cations as structure-directing templating molecules by the synthesis of zeolite MFI were reported several times [ 2, 3 ].

MFI (ZSM-5) with tetrabutylammonium cation as template has been crystallized in SiO<sub>2</sub>/TBA<sup>+</sup>Br<sup>-</sup>/NaF/H<sub>2</sub>O system under hydrothermal conditions. Control of products of synthesis was organized by measurement on Philips powder diffractometer modified at home.

X-Ray powder patterns for the structure solution were obtained on a Siemens D-5000 automatic powder diffractometer with monochromated CuKα<sub>1</sub> radiation (λ=1.54059 Å) and 6<sup>0</sup> position sensitive detector. The data were collected from 5-85 ° 2θ with a step width of 0.007758° 2θ. Number of data points was 10147.

For the Rietveld analysis the program FULLPROF [ 4 ] was used which operates with least square routine based on the original Rietveld-Hewat program. Because of relative stable silica framework 299 geometry restraints were introduced in the refinement

Symmetry of zeolite MFI structure (as synth.) with tetrabutylammonium cations as non-framework species was defined as orthorhombic ( S.G. - P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> ), because of appearance on X-ray diffractogram of additional reflexes, forbidden for symmetry Pnma, typical for calcinated MFI or contained templates with shorter alkyl chains [ 3 ]

Unit cell parameters were a=19.5590(3) Å, b=19.3690(3) Å, c= 13.068329(2), α=90.00°, β=90.00°, γ=90.00°.

Agreement factors: Rp: 2.01%, Rwp: 3.27%, Rexp: 1.39%, Chi2: 5.53

Localisation of guest molecules was carried out via analysis of Fourier synthesis maps (observed and differential) with program GFOUR 04.00.[4] Differential Fourier synthesis maps shows some peaks, they are occurred on positions assigned to channels of structure. The sorbed tetrabutylammonium cations prefer the position at the intersection of channels. The localisation and rotational orientation of the sorbates can be as following described. Guest molecules lies at the intersection of straight and sinusoidal channels with orientation of butylchain along of channel.

Decrease of symmetry of zeolite MFI with tetrabutylammonium as sorbate molecule compared to calcinated phase of MFI is in consequence of distribution of fluor at the positions of structure.

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[2] H. van Koningsveld, *Acta cryst. B*, **39**, 1983

[3] H. van Koningsveld. *J. of Molec. Catal.* **134**, 1998

[4] FULLPROF Suite, 2004

s5.m19.p5 **Investigations of Structure Parameters of Chemisorbed Zeolitic Catalysts (faujasite type).** Stanislav Vratislav, Maja Dlouha, Vladimir Bosacek, *Czech Technical University in Prague, Faculty of Nuclear Sciences and Physical Engineering, Solid State Engineering, Brehova 7, Prague, Czech Republic. E-mail: vratislav@troja.jffl.cvut.cz*

**Keywords:** Neutron diffraction; Structure analysis; Zeolites

Chemisorbed methyl groups in the zeolitic lattice belong to the most important problems of surface chemistry. Theoretical investigations as well as experimental results 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. Experimental support was obtained also from the results of diffraction methods, where namely neutron diffraction provided direct evidence on the location of protons in faujasites with various H<sup>+</sup>/Na<sup>+</sup> ratio. The aim of our study was to estimate the location of chemisorbed species in the lattice and to elucidate the role and participation of various lattice oxygen types in chemisorption of methyl cations. We have made an attempt to estimate regular distribution of cations and chemisorbed species over the lattice and to locate chemisorbed CH<sub>3</sub><sup>+</sup> ions at different oxygen atoms. Well-developed crystals of NaY, NaX and NaLSX with high content of sodium cations and with low content of defects and decationation were used in this study. The reaction of methyl iodide with sodium cations was used for the preparation of anchored methyl groups in the structure of zeolites. <sup>13</sup>C MAS NMR spectra were measured on a BRUKER DSX200 spectrometer. Neutron powder diffraction patterns were collected at temperature of 298 and 7 K on the KSN-2 diffractometer, which is placed at the LVR-15 research reactor in Rez near Prague. The complete structural parameters were determined by Rietveld analysis of powder neutron diffraction data using the GSAS software package. Our structural parameters for the initial dehydrated bare samples and parameters for characteristic chemisorbed NaX and NaLSX samples are given in [1]. The occupation numbers of cations and the location of CD<sub>3</sub> groups were determined. Zeolite LSX (low silica X) has a Si/Al ratio of 1 and represents the highest number of charge-compensating cations among all faujasites. Parameters of NaLSX given in [2] were refined in both recently discussed space groups, as in Fd3 space group as in Fddd (orthorhombic) group but without any significant difference. Cations are distributed over six possible sites in the frame of Fd3 space group. The occupation numbers of Na cations in chemisorbed NaX has been decreased for SI' and SI'' in contrary to the increase for SIII in comparison with the initial NaX. S<sub>II</sub> is practically fully occupied in both of the lattice atoms in original evacuated NaX and in the same sample after chemisorption of methyl iodide. We observed serious changes in the distribution of the lattice elements after chemisorption of methyl ions. These changes were detected not only in occupation factors but sometimes also in coordinates of Na<sup>+</sup> cations. Our results are well in line with these findings of the other authors [2].

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[2] S. Vratislav, M. Dlouha, V. Bosacek, *Applied Physics A* **74** (2002) 1320-1323.