Zeolitic catalysts with chemisorbed methyl groups. S. Vratislav$^1$, M. Dlouhá$^1$, V. Bosácek$^2$, $^1$Faculty of Nuclear Physics and Physical Engineering, 115 19 Prague 1, Czech Republic, $^2$Heyrovský Institute of Physical Chemistry, 182 23 Prague 8, Czech Republic

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NaX and NaY zeolites, as well defined crystalline solids, are objects of special interest in chemistry, because they represent not only a very important group of catalysts applied in chemical industry, but also a very promising material for basic research in catalysis. Problems concerning the nature of acid or basic sites, their amount and distribution of their strength in the zeolitic lattice, belong to the most important tasks of physical chemistry.

The aim of our study was to estimate the location of chemisorbed species in the lattice and to elucidate the role and participation of lattice oxygen types in chemisorption of methyl groups. We have decided to carry out our experimental study on well developed crystals of NaX and NaY with high content of sodium cations and with low content of defects and decactionation. The reaction of methyl iodide with sodium cations present in the lattice, controlled by $^{13}$C MAS NMR, was used for preparation of anchored methyl groups in the structure of zeolites. Distribution of chemisorbed methyl groups and sodium cations in the structure of NaX and NaY zeolites was studied by neutron diffraction and NMR technique. Chemisorbed methyl groups were prepared in the structure by chemical reaction of methyl iodide with reactive sodium cations available in SII and SIII positions of sodium cations in NaX and NaY zeolites. Distribution of chemisorbed methyl groups and sodium cations in the structure of NaX and NaY zeolites was studied by neutron diffraction and NMR technique. Chemisorbed methyl groups were prepared in the structure by chemical reaction of methyl iodide with reactive sodium cations available in SII and SIII positions of sodium cations in NaX and NaY zeolites. Distribution of chemisorbed methyl groups and sodium cations in the structure of NaX and NaY zeolites was studied by neutron diffraction

Two ammonium zinc gallophosphates were hydrothermally synthesised and characterised using single crystal X-ray diffraction. The first compound (NH$_4$)$_4$[Zn$_4$Ga$_4$P$_8$O$_{32}$] crystallises in a cubic I2 3d space group, with a = 13.456(1) Å and was refined to R (on F) = 2.47 %. It is a zeolite analcime (Na$_{13}$Al$_{24}$Si$_{13}$P$_{11}$O$_{96}$.16H$_2$O) analogue and has an open-framework structure with a distorted 8-member ring channels. Zn and Ga atoms share the same crystallographic site in the framework with the partial occupancy of Zn/Ga = 0.67/0.33. Ammonium cations, which lie on the 3-fold axes in the channels, compensate for a negatively charged framework. The interesting feature is low structure symmetry compared to most of the analcime-like structures, which crystallise in a cubic I4 3a space group. This is not only due to the (1) ordering of Ga and P in the framework, which is usually not present in the rest of the structures, but also to the (2) concentration and location of extra-framework NH$_4$ cations. Namely, in synthetic phosphorus-substituted analcime structure Na$_{13}$Al$_{24}$Si$_{13}$P$_{11}$O$_{96}$.16H$_2$O, Al and P/Si sites are ordered, but the structure symmetry is still higher (I4 3d) than in our structure. In natural analcimes Al is randomly distributed over Si framework sites up to the ratio Al/Si = 1:1.

The second compound (NH$_4$)$_4$[Zn$_4$Ga$_4$P$_8$O$_{32}$] is an accompanying phase that appears in the synthesis. It has a monoclinic symmetry, space group P21/a, a = 9.406(1) Å, b = 9.881(1) Å, c = 8.612(1) Å, $\beta$ = 90.58(1) °, and was refined to R (on F) = 2.7 %. The structure is isostructural with a feldspar paracelsian (BaAl$_2$Si$_2$O$_8$) analogue and has an open-framework structure with a distorted 8-member ring channels. Zn and Ga occupy two crystallographic sites with partial occupancy Zn1/Ga1 = 0.53(6)/0.47(6) and Zn2/Ga2 = 0.47(6)/0.53(6). NH$_4$ cations in the pore openings are bonded to the framework oxygens with seven different hydrogen bonds.

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