

**[o.m3.p5] Zeolitic catalysts with chemisorbed methyl groups.** S. Vratislav<sup>(1)</sup>, M. Dlouhá<sup>(1)</sup>, V. Bosáček<sup>(2)</sup>,  
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 Keywords: zeolites, neutron diffraction, structure analysis

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 ions. 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 decationation. The reaction of methyl iodide with sodium cations present in the lattice, controlled by <sup>13</sup>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 faujasites. Methyl cations CH<sub>3</sub><sup>+</sup> (methyl ions), evolved during reaction, react immediately with the lattice oxygen forming surface bonded methyl groups. The polarized covalent bond of methyl carbon to lattice oxygen resembles that of many methoxy compounds as demonstrated by <sup>13</sup>C NMR signals of chemisorbed surface species at 54 and 56 ppm TMS for NaX and NaY, respectively. Changes in the distribution of structural sodium cations in the lattice after chemisorption of methyl cations has been detected. The location of methyl groups was also estimated. The location at O1 lattice oxygen type was found to be most probable for NaY<sup>1</sup>. In NaX<sup>2</sup> were nuclear densities of chemisorbed methyl detected at O1 and at O4 lattice oxygen.

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[2] S. Vratislav, M. Dlouhá, V. Bosáček, *Physica B* 276-278 (2000) 929-931.

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**[o.m3.p6] Zinc-Gallophosphate Analogues of Analcime and Paracelsian.** N. Zabukovec Logar<sup>1</sup>, A. Golobic<sup>2</sup>, M. Mrak<sup>1</sup> and V. Kaucic<sup>1</sup>, <sup>1</sup>*National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia,* and <sup>2</sup>*Faculty for Chemistry and Chemical Technology, University of Ljubljana, Aškerceva 5, 1000 Ljubljana, Slovenia.*  
 Keywords: gallophosphates, analcime, paracelsian.

Two ammonium zinc gallophosphates were hydrothermally synthesised and characterised using single crystal X-ray diffraction. The first compound (NH<sub>4</sub>)<sub>16</sub>[Zn<sub>16</sub>Ga<sub>8</sub>P<sub>24</sub>O<sub>96</sub>] crystallises in a cubic I213 space group, with a = 13.456(1) Å and was refined to R (on F) = 2.47 %. It is a zeolite analcime (Na<sub>16</sub>[Al<sub>16</sub>Si<sub>32</sub>O<sub>96</sub>].16H<sub>2</sub>O)<sup>1</sup> 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 Id-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<sub>4</sub><sup>+</sup> cations. Namely, in synthetic phosphorus-substituted analcime structure Na<sub>13</sub>Al<sub>24</sub>Si<sub>13</sub>P<sub>11</sub>O<sub>96</sub>.16H<sub>2</sub>O, Al and P/Si sites are ordered, but the structure symmetry is still higher (I4132) 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<sub>4</sub>)<sub>4</sub>[Zn<sub>4</sub>Ga<sub>4</sub>P<sub>8</sub>O<sub>32</sub>] 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, β = 90.58(1) °, and was refined to R (on F) = 2.7 %. The structure is isostructural with a feldspar paracelsian (BaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>)<sup>2</sup>, which has a 3D framework and very elliptical 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<sub>4</sub><sup>+</sup> cations in the pore openings are bonded to the framework oxygens with seven different hydrogen bonds.

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[2] J.V. Smith, "The crystal structure of paracelsian, BaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>", *Acta Cryst.* (1953), 6:613-620.