

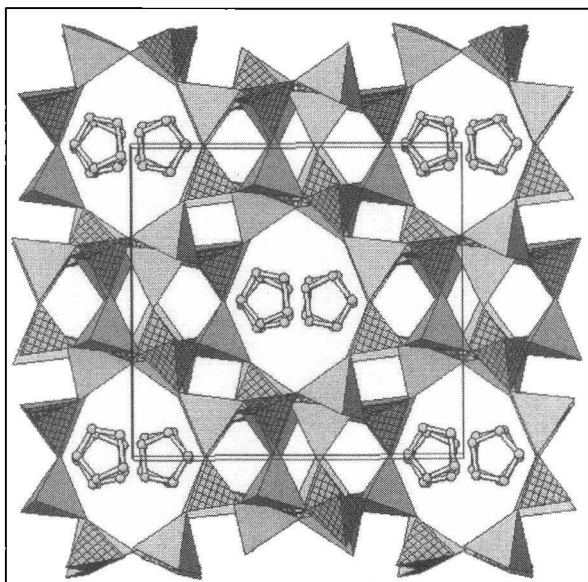
MICROPOROUS SYNTHETIC METALLOPHOSPHATES: ZEOLITE-ANALOGUE STRUCTURES AND NOVEL OCTAHEDRAL-TETRAHEDRAL FRAMEWORKS

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Zeolite minerals and their synthetic analogues are useful in many industrial applications because of their great variety of interesting properties. Beside ion exchange capacity for water softening or humidity adsorption for drying processes, the catalytic activity of slightly modified zeolites combined with their shape selectivity is very important for further utilizations. Therefore not only chemical modification of known zeolites is a worthwhile research area but also the intensive search for new microporous materials with enhanced catalytic activity and novel framework structures. Microporous metallophosphates are a promising class of materials which show similar properties like zeolites together with high catalytic activity of the incorporated transition elements.

Hydrothermal and solvothermal synthesis procedures in teflon-lined steel-autoclaves under autogenous pressure and temperatures ranging from 160°C to 200°C are appropriate for the crystallization of microporous metallophosphates. We have prepared iron-aluminophosphate laumontite (FAPO-LAU) and iron-aluminophosphate sodalite (FAPO-SOD), two zeolite analogues with tetrahedral framework structures of alternating $[\text{PO}_4]^{+}$ - and $[\text{MeO}_4]^{-/2-}$ -tetrahedra. Microprobe analyses and crystal structure analyses (MoK α , CCD detector) showed that



in the case of FAPO-LAU 32.4 % of the tetrahedral metal sites are occupied by Fe^{2+} -ions, in the case of FAPO-SOD the Fe^{2+} -substitution is 34.1 %.

Fig. 1
Polyhedral representation of the crystal structure of FeAPO-LAU (view along cell axis c). $[\text{PO}_4]$ and $[\text{MeO}_4]$ are the dark and light shaded tetrahedra. Inside the channels reside $\text{C}_3\text{H}_3\text{N}_2^{-}$ molecules.

At higher temperatures a second type of micro-porous metallophosphate crystallizes from our synthesis experiments - octahedral-tetrahedral frame-work structures consisting of an assembly of different shaped polyhedra, which have been firstly described in 1994 by MEYER & HAUSHALTER [1]. We have synthesized and characterized an ironaluminonitrate $\text{NH}_4[\text{FeAl}_2\text{P}_3\text{O}_{12}(\text{H}_2\text{O})_2]$ and an iron gallio phosphate $\text{NH}_4[\text{FeGa}_2\text{P}_3\text{O}_{12}(\text{H}_2\text{O})_2]$ with microporous frame-works of 8-ring channels along [1 0 -1] and strongly elongated channels along [0 0 1]. Confirmed by Mössbauer spectroscopy and structural investigations we find Fe^{2+} in distorted octahedral coordination, Al^{3+} or Ga^{3+} in distorted trigonal bipyramids and P^{5+} in tetrahedral environment.

We have described here different microporous phosphate structures with iron incorporated into the framework either in tetrahedral or in octahedral coordination. The results demonstrate very well the remarkably structural variety of microporous metallophosphates compared to aluminosilicate zeolite structures.

Acknowledgement

The project is supported by the austrian Fonds zur Förderung der wissenschaftlichen Forschung (FWF) under P13663-GEO. We thank U. Brendel for performing the synthesis experiments.

References

- [1] MEYER, L. M. & HAUSHALTER, R. (1994): The first octahedral-trigonal bipyramidal-tetrahedral framework oxide: hydrothermal synthesis and structure of $\text{K}[\text{Ni}(\text{H}_2\text{O})_2\text{Al}_2(\text{PO}_4)_3]$. - Chemistry of Materials 6(4), 349-350.