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Referee's report on the PhD thesis of Mgr. Valeryia I. Kasneryk

“Design of zeolite materials with tailored interlayer structure
and tunable textural properties”.

The PhD thesis presented by Valeryia I. Kasneryk is devoted to control the structure and textural properties of zeolites using different ways of post-synthesis treatment: the ADOR (Assembly – Disassembly – Organization – Reassembly) transformation and post-synthesis modification resulted in degermanation and alumination.

The main goals of this work were:

- to investigate general applicability of the ADOR (Assembly – Disassembly – Organization – Reassembly) approach through its expansion on UOV, CIT-13, IWW, and IWR germanosilicates;

- to synthesize new zeolite materials based on transformation of mentioned zeolites;

- to elaborate the ADOR approach applying chemical vapor treatment;

- to develop methods of modification of prepared zeolite materials by post-synthesis degermanation and alumination, design of hierarchical zeolite materials and to perform detail characterization of obtained novel zeolite materials by different methods.

Even from the introduction chapter, one can see that V.I. Kasneryk is very familiar with the state of the art representing the synthesis of germanosilicate zeolite materials and the ADOR strategy for new zeolite synthesis, developed for zeolites with UTL topology. Dissertation contains a large number of important and valuable experimental results. Importance and scientific relevance of the results is demonstrated by the fact that they were published in five publications in renowned scientific journals co-authored by Mgr. V.I. Kasneryk. Published results were subjected to thorough review process and therefore their relevance cannot be doubted.

In my opinion, the most important achievements of this work are:

- successful demonstration of the possibility of applying the ADOR approach (initially developed for UTL zeolites) for germanium-rich zeolites with UOV, IWW, IWR and CIT-13 topology, in the structure of which are present the D4 rings;

- preparation of novel IPC-12, -13, 17 and -18 zeolites, which to date have not been obtained by other (direct) methods;

- realization of the ADOR strategy by the treatment of zeolite with H_2O/HCl vapors, i.e. without direct contact of material with the respective solution;

- the development of approaches to increase the stability of the "silica" layers in some B-containing zeolites (IWR) including decreasing of the boron amount, variation of Si/Ge ratio, adding source of fluorine or using seeding approach.

I would like to make some remarks, comments and questions:

1. In the title of subparagraph 3.2.3 there is an error in the SDAs name used for synthesis of zeolite with UTL topology.
2. The isosteric heats of Ar adsorption data for IPC series not discussed in the PhD thesis, but only in the published article. However, the method of isosteric heats calculation is described in subparagraph 3.5.
3. The mechanism of incorporation of aluminium atoms in UOV zeolite framework proposed in the work, which includes an intermediate stage of lamellar material formation, seems to me insufficiently justified. My main doubts concern the possibility of re-designing of D4 rings from already hydrolyzed (and removed from the interlayer space?) germanate species and aluminum cations.
4. Is it possible to applicate the ADOR approach for preparation of new high-silica isostructural analogues of germanosilicates? May be with using of additional SDAs and/or silica sources. And what about possibility of pore size increasing after ADOR transformation?

Notwithstanding the above-mentioned questions and comments I consider submitted dissertation valuable and relevant. In view of the amount of experimental work, the quality of the work and the excellent way of summarizing the results, I do not hesitate to strongly recommend the acceptance of this thesis for public defense and to give the highest mark for the entire work.

Dr. Oleksiy Shvets