Review of the dissertation thesis

Charles University, Prague, Faculty of Science, Study program: Physical Chemistry

Student: **Quidi Yue**

Thesis title: **Labile elementosilicates as intermediates for design of novel materials**

The presented dissertation work of the student is based on two papers in renowned scientific journals, one of them in very prestigious Nature Communications. The student participated especially in a large part of the first publication, where he synthesized CHA zeolites and performed their characterization. Another three publications forming the part of the dissertation work have been submitted recently.

Overall, the student is author and co-author of 12 publications in impacted journals plus those three submitted publications. It proves the student's ability to carry out scientific work and to actively participate in writing papers.

The work of the student focused on the design of a series of elementosilicate zeolites with tunable properties (in particular morphology, porosity, or acidity) either through controlling the crystallization mechanism or by manipulation with the zeolite structure and chemical composition.

The goals of the dissertation work are clearly defined, with preamble explaining the importance of the issues/problems which are solved.

In the Introduction the author shortly overviews the basics of the zeolite chemistry. The following more detailed text is devoted to the zeolite crystallization and especially to the reversed crystal growth, which is one of the topics of the presented work. This mechanism has not been described before in zeolite synthesis systems. He also determined, what conditions are needed for this mechanism to occur. The Introduction part is well-written with a lot of references, which testifies good knowledge on the topic of zeolites.

Experimental part starts with the list of reagents, which is a little bit unnecessary here, but perhaps might be useful for younger students when these experiments are to be repeated. Quite large set of zeolites was prepared. The following part of the Experimental chapter is devoted to the description of post-treatment of germanosilicate zeolites.

Very interesting is the method of Nano X-ray tomography used for the characterization of AST zeolite, which helped to answer questions connected with the crystal growth of the studied zeolite.

Very useful for the understanding of the Results and discussion text is the scheme on page 43. Very nice, almost educational, is picture (Figure 4.2) overviewing both discussed crystallization mechanisms.

The work is exceptional in its very careful and thorough experimental work leading to very interesting results.

A controllable crystallization mechanism between the classical and reversed crystal growth in AST zeolite was established based on fine tuning of the interplay among inorganic and organic components under synthesis conditions. A truly reversed crystal growth, in which crystallization starts at the surface of amorphous aggregates and then proceeds towards their centers, was demonstrated for the first time. Both kinds of crystallization mechanisms and details of inner structure of intermediate particles were confirmed by electron microscopy studies, while the internal development of crystallinity and voids within the large aggregates upon the reversed crystal growth was visualized by ex-situ X-ray tomography for the first time.

The fundamental functions of SDA and F^- ions, that control the crystallization route and crystal growth rate, were determined for the first time.

Understanding the details of growth mechanisms and pathway-determination factors provides a better insight for control of crystal growth, which is important for the improvement of synthesis approaches and design of various forms of crystalline materials.

In the next part of his work the author optimized the ADOR process, which gave him an opportunity to prepare new types of zeolites, which cannot be prepared both by classical way and by traditional ADOR method.

By a newly developed vapor-phase-transport (VPT) rearrangement technique, which controls the mass transport within the interlayer of zeolite IWW the author managed to transform it to IPC-18 zeolite. Furthermore, this newly developed VPT rearrangement approach was successfully applied for the ADOR transformation of a series of germanosilicate zeolites.

The mechanisms of transformation of starting zeolites and formation of new structures was elucidated with the help of combination of several advanced techniques, like TEM and synchrotron XRD.

The text contains several examples of schemes clearly and comprehensively overviewing either the experimental works or principles governing various aspects of formation of zeolites under study. This proves the author's ability to orient himself in the issues of zeolite preparations and transformations.

The work also contains aspect of more application focus, that is M-CHA (M = Si, B, Al, Ga, and Ti) materials with different framework compositions prepared through an isomorphous substitution. The obtained materials showed distinct separation ability when applied for CO2/CH4 gas mixture.

Regarding the presented thesis dissertation, I have the following questions:

– A part of the Experimental chapter is devoted to the description of post-treatment of germanosilicate zeolites (p. 38). What about post-treatment of other elementosilicate zeolites? Does the author tried to do some experiments in this way?

- In Chapter 4.1.3, the ratio of the used starting components was changed, due to increased relative amount of DEDMAOH, HBr was added. Why HBr was used, and not another acid? Why a mixture of DEDMAOH and some other DEDMA salt (e.g., chloride) was not used?

My impression from the presented dissertation is that it further shifted the knowledge about the chemistry of zeolites and the work is an indispensable source of information, both from experimental and fundamental points of view, for the future studies in this field.

The thesis is well written, the text is clear and confirms the authors ability not only for scientific work but also to explain it very clearly. The scope of work performed by the author within his PhD study, as presented in the submitted dissertation and attached publications, is considerable and appropriate.

For these reasons, I can state that the work of Mr. **Qiudi Yue, MSc.** meets all the conditions set for dissertations in the study program.

I therefore **recommend** the thesis for defense.

Pardubice, 28th August 2021

Doc. Ing. Vítězslav Zima, CSc., DSc.