

August 17<sup>th</sup>, 2016 in Pardubice

**Referee's report on the PhD thesis of Ing. Jan Přečh**  
**“Synthesis and post-synthesis modification of novel 2-dimensional zeolites”**

Submitted dissertation deals with results of synthesis, characterization and catalytic testing of novel porous titanosilicate materials. Study focuses on preparation and characterization of large and extra-large pore zeolitic titanosilicates, as well as hierarchical and layered titanosilicates derived from zeolitic precursors. In addition, ADOR transformations of Ti-UTL into Ti-IPC-2 and Ti-IPC-4 zeolites are reported. Material synthesis and characterization part is accompanied by application part, where results of catalytic testing of the materials in the epoxidation of bulky olefins and selective oxidation of bulky organic thioethers are reported. Large set of bulky reactant consisting of six olefins and three sulphur containing compounds was tested.

Introductory section reports on previous studies in the topic and refers to more than 150 references, which document student's overview and orientation in the problematics. 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 authored and co-authored by Mr. Přečh. Published results were subjected to thorough review process and therefore their relevance can not be doubted. However, I have some questions and comments listed below that do not dispute the results obtained in this thesis. They can serve as topics for discussion:

- TON (turn-over-number) value is used in this thesis as a measure of activity of titania species in the catalysts. However, TON is a function of time (or lifetime of the catalyst based on definition) and therefore catalyst comparison by this quantity (especially if reaction time is not the same or it is not mentioned as often happens when the results are compared with data published by other groups) can be misleading. Why do you use TON and not TOF value?

- Author states on page 76 that the differences between conversion of cyclooctene on Ti-CON(TBOTi) with Si/Ti=450 (conversion 37% after 4 h) and Ti-CON(TiCl<sub>4</sub> sol) with Si/Ti=81 (conversion 26% after 4 h) indicate that epoxidation does not occur in the whole volume of the zeolite crystal but mainly close to the external surface. I think that simple comparison of conversion level is not sufficient. The level of conversion can be controlled also by lack of oxidant, so conversion of hydrogen peroxide should be mentioned as well. The difference in the conversion should be given of fast decomposition of peroxide over catalyst prepared from TiCl<sub>4</sub>. Please, discuss this during defense of your thesis.
- Ti-containing zeolites prepared by ADOR transformation from Ti-UTL are not tested in the reactions (except Ti-IPC-2 in oxidation of diphenylsulphide and dibenzothiophene). The reason is obvious – too small pore diameter and diffusional hindering. I would like to ask student whether he has an idea about the reactions in which these materials could exhibit good catalytic activity and profit from their pore structure.
- Experimental data obtained over titania-silica pillared materials evidence that not only isolated framework tetrahedrally coordinated titania species are the active sites. Does student have some idea about structure and concentration of other species contributing to the catalytic activity of such catalysts? Are they located exclusively on the surface of pillars?
- Reactions investigated in this thesis are rather slow. The conversions higher than 10% are reached after few hours of reaction in some cases. Is there some limit catalyst productivity in these reactions in which a catalytic system starts to be interesting for industrial application?

Notwithstanding the above-mentioned questions and comments I consider submitted dissertation valuable and relevant. Thesis meets the criteria for this type of work and it's my pleasure to recommend it for defense.

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