



Review report of a doctoral thesis

The doctoral dissertation of Jin Zhang entitled "Design of sustainable catalysts by post-synthesis modification of germanosilicate zeolites" deals with post-synthesis modification of germanosilicates, including germanium recovery and recycling, as well as with detailed characterization and application of the new materials as catalysts. The experimental work was performed at the J. Heyrovský Institute of Physical Chemistry of the Academy of Science of the Czech Republic and at the Department of Physical and Macromolecular Chemistry of the Faculty of Science at the Charles University under the supervision of Dr. Mariya Shamzhy.

The thesis deals with the design, preparation and testing of solid Lewis acid catalysts that have a potential application particularly in the area of fine chemicals synthesis. The research results were published in 6 scientific articles in top journals in the field of catalysis and material science (all with an $IF > 4.0$). In three of these articles, Jin Zhang is the first author.

The thesis is very well written and has a logical structure providing enough experimental details and demonstrating the scientific capabilities of the student. The literature part gives a good overview about zeolites, but I am missing a more detailed discussion on the current use of zeolites in transalkylation and isomerization of zeolites. Moreover, the example of FCC catalyst is not precise as lanthanum exchanged dealuminated (ultra-stabilized) Y zeolite is used rather than La-Y. More importantly, the literature part does not provide information on the studied model reactions and the state-of-the-art of the use of zeolites in these applications, e.g. ketalization of glycerol.

In the experimental part, the yield or selectivity are related to a single product (or a group of products). This needs to be reflected in the formula. Moreover, specific details of the GC analysis, such as temperature profile, split ratio, etc. should be given.

Furthermore, I have several questions:

1. Regarding the title of the thesis, what is the definition of sustainable catalysts? In which aspects are the catalysts presented here sustainable and what is their advantage as compared to other catalysts?
2. Why was ketalization of polyols selected as a model reaction?
3. From the sustainability point of view, direct synthesis rather than a synthesis route involving the germanosilicate intermediate would be desirable. What are the limiting factors preventing the direct synthesis routes?
4. In the TOF calculations, the number of acid sites determined from pyridine adsorption is used. Is this the total number of Lewis acid sites? If so, is there any effect of the acid sites strength on the reaction rate and/or selectivity?



5. According to Table 4-8, the concentration of Brønsted acid sites was $0 \mu\text{mol/g}$, however, the spectra in 4-23 indicate presence (although a minor one) of Brønsted acid sites (a small peak at around 1545 cm^{-1}) not only in the BEA-derived samples, but also in the other samples. Could these be quantified?
6. In Table 4-10, TOF is reported also for the BEA catalyst. How was the contribution of Brønsted acid sites to the reactant conversion taken into account?
7. What was the carbon balance in the experiments with furfural?
8. What were the other products of furfural conversion that are not reported in Table 4-10? Their overall yield (over UTL and BEA) was $>5\%$, in one case even $>20\%$.

In summary, the reviewed thesis is a high-quality scientific work that fulfills, in my opinion, all requirements needed for obtaining a PhD degree. Therefore, I fully recommend the thesis of Jin Zhang to be defended orally and awarded by the PhD degree.

In Prague, 27.8.2021



doc. Ing. David Kubička, Ph.D. MBA