

Review of the Doctoral Thesis of Mgr. Jin Zhang

The title of the Ph.D dissertation: Design of sustainable catalysts by post-synthesis modification of germanosilicate zeolites

Supervisor: Dr. Mariya Shamzhy

Advisor: Dr. Jan Přech

The post-synthesis modifications of the structure and chemical composition of germanosilicate zeolites coupled with Ge recycling and with tailored acidic characteristics is the main topic of dissertation. Subsequently using different types of Lewis-acid catalyzed reactions the structure-acidity-activity relationship over prepared zeolites was evaluated. This goal of the thesis has been fully achieved.

Importance of the thesis and results:

The comprehensive bibliography consisting of 212 references is well written and provides a very good background for the following research. This thesis was focused on the design of large pore and extra-large pore germanosilicate zeolites as potential catalysts for Lewis-acid catalyzed processes. Such type of catalysts is especially suitable for conversion of bulky molecules, usually formed during biomass valorisation. This is a very interesting area of catalytic research, therefore, the choice of catalytic performance of the studied zeolites was focused on such type of processes. The thesis contains plenty of experimental results on preparation of materials and their evaluation in various acid catalyzed reactions. All results are clearly interpreted, what is typical also for presented scientific papers. For characterization of prepared materials and analysis and identification of reaction products many techniques have

been used. In all the investigated systems the correlations between properties of catalytic materials and their activity, selectivity or recycling properties are provided.

Practical application of results

The described method for post-synthesis modifications of germanosilicate zeolite catalysts, especially coupled with Ge recycling, provides a more economic way for their further utilization. Presented preliminary catalytic results indicate that these large pore and extra-large pore zeolites could be potentially suitable candidates for selective conversion of bulky molecules, typically obtained from biosources.

Questions and comments:

1. As is mentioned in the Table 4-10 and in the text, in the MPV reduction of furfural the primary product of furfural reaction is furfuryl alcohol. However, it is well known, that in the presence of acid catalysts furfural dissolved in alcohols is easily converted to the corresponding acetals. The formation of furfuryl isopropylacetal was not identified in the reaction mixture?
2. In the ketalization of glycerol with acetone and 2-butanone strong differences in glycerol conversion over germanosilicate zeolites were observed (Table 4-3, Runs 3 and 6). In the dissertation is mentioned that this may indicate diffusion-controlled regime of the reaction for bulky reagents. In both experiments bulky is glycerol and moreover, reaction time in batch system is very long, 3h, to control the diffusion.

Final evaluation

The area of the research is modern and interesting for material science and potentially also for practical application. As is demonstrated in the experimental part the author presented high expertise in the field of materials preparation, characterization and the catalysts testing. It clearly shows that the PhD student can solve independently complicated scientific problems. Very positive is, that in the conclusion of the thesis the candidate outlines the areas for continuation of the research in this field.

On the bases of these facts my opinion is that the reviewed thesis fulfills all requirements needed for obtaining PhD degree. I fully recommend the thesis of **Mgr. Jin Zhang** to be defended orally and awarded by the PhD degree.

Bratislava, 22.8.2021

Prof. Ing.Milan Hronec,DrSc

Slovak University of Technology,

Bratislava

.