Oponent review of the dissertation thesis

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

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Title of the thesis: **Design and catalytic application of novel nanostructured materials**

The author focused on the preparation of a series of specific zeolitic catalysts in order to gain insight into the relationships between key properties of zeolites (such as their structure, morphology, chemical composition, availability of acid sites and other functional groups and layer arrangement) and their effectiveness as catalysts, supports for other active phase or nanostructured components of colloidal systems. For this purpose, the author used a number of characterization techniques.

The result of this work is a design of a group of isoreticular zeolites of the Al-IPC type with gradually changing micropore size, but with preserved morphology, aluminum content and concentration of acid sites. Research on these reticular Al-IPC zeolites has revealed a clear relationship between the size of the pores present in the catalyst and their catalytic activity.

The author also compared the texture and catalytic properties of zeolites with one-dimensional pores prepared by various techniques, which allowed him to improve the method of incorporation of aluminum into the structure of zeolites. Surface modification of zeolitic nanocrystals has improved the resistance of these nanomaterials to aggregation, both in suspension and under catalysis conditions. Part of the author's work consisted in the preparation of MWW type zeolites with different layer arrangements and chemical composition as carriers of active substances (cobalt oxide) for removal / disposal of volatile organic compounds, where it was found that the aluminum content of the carrier has a positive effect on the catalytic activity of the active substance.

From the application point of view, the study of the catalytic activity of the studied substances for the dehydration of ethanol and tetrahydropyranylation of alcohols is interesting.

The aim of the study is clearly described and summarized in six points at the beginning of the dissertation text.

The introductory part briefly presents an overview of zeolitic structures and their applications in catalysis. A more detailed description is given of layered zeolites, their synthesis and the use of the ADOR strategy for the preparation of new types of zeolites and the use of these zeolites as catalysts. Another type of materials described are nanostructured zeolites, having a larger surface area compared to micron particles, which can be advantageously used in catalytic reactions. The author further describes the preparation of zeolitic nanocrystals and their use in catalysis. In the last part of the introduction, the author describes postsynthetic isomorphic substitutions in the zeolitic lattice.

In the experimental part, the author describes the preparation of individual zeolitic materials. More attention should be paid to this description, as some wordings in the text do not make sense and require more effort from the reader to understand it (for instance, „donated as“ should read „denoted as“).

The most comprehensive part of the thesis is devoted to the results. A number of chapters begin with a brief overview of state-of-the-art, which is not common in theses, but here allows the reader to gain a basic insight into the issues studied. The result part is divided into four main parts. The first part is devoted to isoreticular zeolites. In chap. 4.1.2 the author describes in detail the method of incorporating aluminum into the lattice of isoreticular zeolites. In this context, a two-step adsorption of quinoline and acetonitrile on the studied materials was developed to distinguish the location of acidic sites by FTIR.

Furthermore, the catalytic efficiency of isoreticular zeolites prepared by a combination of the ADOR method and isomorphic substitution of aluminum was studied. The first example is the

dehydration of ethanol, where the author analyzes in detail the data obtained with respect to the pore size in the zeolites used. In the study of tetrahydropyranylation of alcohols, a decrease in the extent of conversion with increasing length of alcohols was observed, as expected. An interesting experiment (Chapter 4.1.3.2) is to compare the efficiency of IPC-6 zeolite, which can be considered as a structural combination of IPC-2 and IPC-4 zeolites, with the efficiency of a physical mixture of these two zeolites, i,e, IPC-2 and IPC-4. The higher catalytic activity of the IPC-2/IPC-4 mixture is explained by the difference in the location of active acid sites, where the IPC-2/IPC-4 mixture shows a higher proportion of "external" acid sites. This is consistent with the highest catalytic efficiency of IPC-7 zeolite.
Further part of the author's work (Chapter 4.2) was devoted to the preparation of aluminum enriched zeolites from germanosilicates. The results and conclusions presented by the author in this chapter are solidly supported by experimental data, especially NMR spectroscopy and FTIR. Even in this case, the author applied the prepared materials as catalysts, this time in the alkylation of aromatics.
In the section devoted to zeolitic nanoparticles, the author describes their preparation and modification by surface silylation and verification of the size of the prepared particles by TEM (the size of the scale given in Fig. 4-19 is too small and practically illegible). In addition, the aggregation properties of the prepared silylated zeolites depending on the type of the silylating agent and the catalytic efficiency of the thus prepared zeolite nanoparticles were studied. Here I lack an explanation for the fact that zeolite in the form of nanoparticles (albeit aggregated) shows a lower conversion than in the form of microparticles.
The last main chapter of the Results is devoted to a somewhat different topic, namely the use of zeolites as a support for the cobalt-based catalyst used for VOC oxidation. The prepared materials were characterized in detail using XRD, BET, FTIR, chemical analysis, XPS, TEM and SEM. The catalytic efficiency of the prepared materials was studied for the oxidation of toluene and propane as examples.

Conclusion
Despite some flaws in English the theses are well written from the scientific point of view. All conclusions made are based on sound data. The author is well oriented in problematics of zeolite chemistry and chemical catalysis. The research in these fields includes a broad range chemical and physical methods, which the author was able to manage. The thesis confirms that the author is very well oriented in this problematics and is capable of independent scientific work. This is proved also by the high-quality papers the author published on this topic.
The thesis of Mr. Yong Zhou, MSc. meets all the conditions set for the dissertations in the study program.
I therefore **recommend** the thesis for the defense.

In the frame of the defense I would like to ask the following questions:

1) What is the application of tetrahydropyranylated alcohols?
2) In the preparation of Al-enriched **AFI** zeolites, you used 7,11-dimethyl-6-azoniaspiro [5.6]undecane as a structure directing agent. Why did you use this rather unusual and exotic compound? Is not it possible to use a structurally simpler compound?
3) How the silylation of the nanoparticles influences the catalytic properties of the prepared materials?

Pardubice 28th August 2020 Doc. Ing. Vítězslav Zima, CSc., DSc.