Review of the dissertation thesis

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Title of the thesis: **Rational synthesis of zeolitic materials and their characterization by advanced electron microscopy methods**

In the Introduction part, the author describes current state-of-the-art in the field of zeolites, defines what metal@zeolites are and states synthesis strategies to encapsulate metal nanoparticles into zeolites, including post-synthetic methods, co-crystallization strategy, and a 2D to 3D zeolites transformation approach. The ADOR (Assembly (A), Disassembly (D), Organization (O), and Reassembly (R)) synthetic method is described more in detail, which can be used not only for the synthesis of new zeolite materials, but also for incorporation of different metal atoms into the zeolite framework. Last part of the Introduction section is devoted to the application of metal@zeolites, namely in metal-nanoparticles catalyzed reactions. Issues connected with the catalysis using metal@zeolite materials are described. One important issue is an interaction between metal particles and the zeolite support, which as the author writes, "is still challenging, due to the very limited number of suitable systems allowing precise experimental and theoretical investigation". The way, in which this part of the thesis is written, confirms thorough knowledge of the studied topic.

The Synthesis part is written in a logical manner starting from the synthesis of structure directing agent (SDA) and then going to the synthesis of zeolites. Preparation of metal@zeolites is then described. Here, in my opinion the term "swelling mixture" is not an appropriate one and should be more specific. In the synthesis of Pd@zeolite, dealumination of the zeolite was carried out first, and the treated zeolite was then impregnated using a Pd salt solution. Impregnation method was also used for the synthesis of Pd-Ce catalyst, using MFI gallosilicate as a starting zeolite material from which gallium was removed (how much Ga was removed?). Impregnation method was used also for the preparation of Rh@X-BEA (X = H, Na), starting from preactivated H-BEA or Na-BEA.

Characterization techniques are described in a clear manner. For the catalytic studies, the following model reactions were used: hydrogenation of nitriles, dry reforming of methane, oxidative dehydrogenation of ethane – here I appreciate an international cooperation with other groups dealing with the same topic (Inha Univ.). The work was complemented by DFT calculations, which were done by a cooperating team at CU.

In the Results and discussion text, the author switches between first person singular ("I compared") and passive voice ("was done") which sis rather unusual approach to writing the thesis, but it makes the text quite vivid and readable.

In the first part of the Results and discussion, the author presents the strategy for confinement and stabilization of metal nanoparticles into layered zeolite supports. The author investigated metal-silanol interactions in zeolite precursors.

In Results and discussion, the author presents strategy for stabilization of sintering-resistant metal subnanometric nanoparticles in zeolites (Chapter 4.1), based on the work published in Angew. Chem. Int. Ed., 2023, 62, e202213361. The strategy is nicely and clearly depicted in Figure 4.1.1.

The author claims that Rh@IPC-C22 has a novel architecture. To investigate the influence of C22 surfactant on the structure of Rh@IPC-C22, the author prepared IPC-C22 using C22 but without a Rh source and presented their pXRD patterns and textural data. In my opinion, statement that both materials have similar pXRD pattern is a little bit daring, as both materials show pXRD more typical for rather amorphous material (Ch. 4.1.1, Fig. 4.1.4).

The prepared Rh catalyst was then tested on hydrogenation reaction (p. 71, Ch. 4.1.3).

The author presented the pathways to improve the metal stability in the metal@zeolite materials by creation of silanols in the zeolite supports.

In my opinion the core of the dissertation is based on the work published in Angew Chem. Int. Ed (on Rh@IPC). This part was done very meticulously and I appreciate how the author considered various aspects which could influence the character of the resulting materials. This part is complemented with a study on characterization and application of metal@zeolite catalysts prepared from commercial zeolites, USY and BEA, which was published in other two papers.

Regarding the work I have the following questions to the author:

1) As follows from Figure 4.1.2, there is almost linear dependence of the interlayer distance of the swollen material (IPC-1P) on the number of carbon atoms in the surfactants, which indicates similar arrangement of the molecules of all three surfactants in the interlayer space. Does the author have any idea, how these surfactant molecules are arranged in the interlayer space of the zeolite precursor?
2) As follows from Table 4.1, the highest loading of Rh was observed for the surfactant with the shortest chain (C12). What do you expect could happen if you use a surfactant with even shorter carbon chain?
3) Why is Rh@IPC prepared with the C12 surfactant denoted as Rh@IPC-4_C12, while other Rh@IPCs are denoted without that "-4" (i.e., Rh@IPC_C16, and Rh@IPC_C22)?
4) Why is Rh@IPC-4_C12 missing in the pXRD pattern in Figure 4.1.3 (a)?
5) In the case of Pd loaded on commercially available zeolite (USY) and on dealuminated USY, the loading of Pd was 2.05 wt% for Pd@USY and 1.96 wt% for Pd@deAl-USY. Why the amount of loaded Pd is lower in dealuminated USY?
6) As regards the work of Pd@deAl-USY and Pd@USY, I have not found any reference to a published paper. Does it mean that this work has not been published yet?

The dissertation thesis is written in a clear, logical and readable way. I appreciate the almost flawless language in which the dissertation is written. The style of the thesis is professionally cultivated, relevant and formally correct. The main objectives of the work have been fulfilled. The used strategy is well described in the thesis and corresponds to the tasks defined in the Aims of the study. The text of the presented dissertation confirms that the author is very well oriented in the field of interest and is able to do independent scientific work. During the doctoral study, the author published three papers in renowned scientific journals devoted directly to the topic of the presented thesis and is also a co-author of other seven scientific papers.

I therefore **recommend** the thesis of MSc. Ang Li for the defense.

Pardubice 10.5.2024

Doc. Ing. Vítězslav Zima, CSc., DSc.