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UNIVERSITY
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Opponent's opinion

Doctoral dissertation

M.Sc. Ang Li

**Rational synthesis of zeolitic materials and their characterization by
advanced electron microscopy methods**

Supervisor: Mgr. Michal Mazur, Ph. D.

Advisor: Prof. Ing. Jiří Čejka, DrSc.

The topic of the doctoral thesis is related to the rational design and synthesis of effective catalysts based on metal@zeolite systems for selected catalytic reactions. The following issues were included in the doctoral thesis: (1) Incorporation of Rh nanoparticles into hierarchical zeolitic materials by swelling of the layered zeolite precursor IPC-1P; (2) Deposition of Pd nanoparticles into commercially available USY zeolites and their dealuminated forms; (3) Preparation of MFI nanosponge zeolites modified with bimetallic platinum-cerium alloy particles. The studies are focused on the determination of the metal-zeolite interaction, which, in consequence, may affect the size and morphology of metal particles as well as their thermal stability and, above all, their catalytic properties. The studies consist of the synthesis of the zeolite-based catalytic materials; detailed physicochemical characterisation of the catalysts by using various experimental methods including: TEM, XPS, NMR, FTIR, and many others; DFT calculations as well as verification of the catalytic properties of zeolites modified with metals in (1) hydrogenation of nitriles; (2) dry reforming of methane; and (3) oxidative dehydrogenation of ethane.

The concept of a doctoral thesis is very interesting and refers to an in-depth analysis of various methods of metal deposition into zeolites, resulting in catalytic systems with appropriate catalytic properties in selected chemical reactions. The goals of the doctoral thesis were clearly and precisely formulated. The introductory part of the doctoral thesis presents issues related to the structure, properties, and methods used for zeolite synthesis, as well as various strategies for the introduction of metal species into zeolites. Moreover, examples of the use of such metal@zeolite systems in catalytic applications were presented and discussed. This part of doctoral thesis is very well prepared in terms of selected content as well as the form of its presentation. In the experimental section, a detailed description of experimental procedures, including the synthesis and modification of zeolites as well as methods used for catalyst characterization and catalytic tests, are presented. The description of the methods used, in particular, the synthesis of catalytic materials, is detailed enough to verify them in other laboratories. The results of the doctoral project are presented, analysed, and discussed in relation to the most recent literature reports. The conclusions proposed by the author are based on the results of scientific research and demonstrate his very solid knowledge in the field of research. The presented studies are largely innovative and have a significant contribution to the development of

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knowledge in the field of metal@zeolite systems in catalysis. The studies of MSc. Ang Li, done in the frame of a doctoral thesis, resulted in three scientific papers published in top-ranked journals (Angew. Chem. Int. Ed., ACS Catal., Catal. Today).

In my opinion, the doctoral thesis was prepared correctly, it meets the standards of very good doctoral theses, and the results presented are valuable contribution to the development of knowledge in the field of designing zeolite-based catalysts. However, I would like to address some questions and suggest some problems for discussion during the defence of doctoral thesis:

- 1) Has the author observed changes of the chemical composition of delaminated forms of ICP zeolite in comparison to the parent zeolite?
- 2) Was the leaching of rhodium species from Rh@IPCs observed under the conditions of catalytic hydrogenation of benzonitrile? Was the rhodium content in the catalyst analysed before and after the catalytic test?
- 3) Has the author observed the sublimation of noble metals under conditions of thermal treatment or catalytic tests of dry methane reforming?
- 4) What is the author's opinion regarding the optimal method for the synthesis of metal@zeolite systems, considering their catalytic performance as well as the simplicity, reproducibility, and cost of their preparation?

Final conclusion:

The doctoral dissertation is a valuable contribution to the field of metal@zeolite synthesis with the controlled size and morphology of deposited metal particles as well as verification of their catalytic performance in the selected catalytic processes. The results of these studies were published in leading international journals. M.Sc. Ang Li demonstrated the ability of independent and creative scientific work. The dissertation prepared by M.Sc. Ang Li meets all the requirements and standards of a very good doctoral dissertations, and I definitely recommend it for defence.

Kraków, 25th April 2024

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