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Oponentský posudek disertační práce

Theoretical Investigation of Mechanisms of Chemical Reactions Taking Place in Microporous Materials, submitted by Miroslav Položij.

Miroslav Položij, in his Master thesis, by means of computational chemistry try to get a better understanding of three chemical reactions, with industrial relevance, that takes place over two microporous materials. In particular, the candidates work is focused in providing an atomistic view of the reaction mechanism of Friedländer and Knoevenagel reactions over CuBTC metal organic framework and intramolecular cyclization of unsaturated alcohols catalyzed by acid zeolite, H-MFI. The thesis itself it is very well written and structured and it starts with a nice and detailed introduction about the microporous materials used as catalysts, as well as the problematic of accurate computational modeling of gas/phase reactions. Clear and accurate description of the models and methods used during the work it is provided ensuring understanding and work reproducibility. Before presenting the results, the relevance and problematic of each reaction is also given. After that, a section presenting results obtained for each chemical reaction investigated are presented and mechanistic insights provided through discussion.

The introduction points out the relevance of porous materials in industry and a very comprehensive view about the structure, physico-chemical properties and applications of metal-organic frameworks (MOFs) and zeolites is given. At this point, some hints about computational modeling of MOFs and zeolites is provided as well as the problematic of performing a realistic and accurate investigation of processes involving solid materials. In the methodology description it is clearly stated that models and methods selection is an important issue in reaction mechanism investigation over microporous materials. A careful and illustrative explanation of the possible models (periodic or cluster) and methods (DFT and post-HF methodologies) used in this thesis is given, as well as the pros and cons of each selection. Even more, it is pointed out a working strategy to achieve a systematic and reliable study of the reaction mechanisms over microporous materials with a compromise between accuracy of the model/method selection and computational cost. I would like to emphasize here the extensive and systematic investigation presented by the candidate, not only regarding methodology test for each investigated reaction but also about the possible active sites, molecules adsorption complexes and reaction pathways. Regarding the complexity of the work presented by the candidate, it is quite easy to follow and understand due to the nicely and elegant structured presentation of the data. For the three chemical reaction investigated, the same strategy is used to present the work: (i) brief but concise description of the reaction investigated, (ii) detailed information about the methodology used, (iii) results obtained during the investigation and (iv) discussion of the results. But perhaps the most remarkable aspect of this work is the further understanding of the chemical reaction investigated thanks to the atomistic view provided about the catalytic active sites and the reaction mechanism itself. In particular, the introduction of multi-center active sites in microporous catalyzed reaction and the point this effect can promote or limit catalytic activity of the primary active site. I would pick up the study of the condensation

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of malonitrile and benzaldehyde (via Knoevenagel reaction) over CuBTC as example of the consistency of the work presented by the candidate. The participation of the oxygen atoms of the carboxylate group as cooperative sites is proposed based on a cluster model calculations. This would be already in agreement and supported by the experimental data, but this hypothesis is further investigated using a more realistic periodic model to ensure catalyst description.

Regarding the extraordinary quality of the Master thesis presented by Miroslav Položij his theoretical investigations have been combined with experimental studies in four publications in international peer journals that, in my opinion, back up candidate's research work. I considered this research track above average the early carrier stage of the candidate. I believe that a nice and thorough work is presented by Miroslav Položij and I strongly recommend Miroslav Položij Master thesis to be awarded with the maximum qualification.

Questions to be answered by the candidate:

1. In the case of H-MFI, the selection of T12 as Si by Al substitution position it has been made based on topological or energetic criteria?
2. Regarding Knoevenagel reaction in CuBTC, do you think it would be possible to use any spectroscopic technique such as IR to characterize the intermediate structure confirming the formation of the carboxylate defect?
3. About the simultaneous interaction of pent-4-en-1-ol with a pair of acid sites in H-MFI, the intermediate species investigated is stabilized by 14 kJ mol–1 with respect with the single-cation site and looking to the equilibrium geometry it seems clear that no further stabilization would be achieved for TS-O1 like structures. Also in agreement with the experimental data, increasing H population does limit zeolite activity. Thus, it seems no H arrangement would favor this reaction. Why do you think this happens? Which are the structural or chemical limitations that avoids molecule cyclization and TS structure stabilization?

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