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Reviewer's Report on the Habilitation Thesis of Lukáš Grajciar
"Towards reliable simulations of nanoporous materials under operando conditions"

The work of Dr. Grajciar, summarized in his habilitation thesis, is focused on computational investigation of nanoporous materials for the purpose of understanding their physicochemical properties, adsorption processes and reactivity. The results elevate this understanding to a higher level, enabling predictions under operando conditions understood as involving the presence of a solvent and reactive species under not-ambient conditions. This is as much of a challenge for experimental science as it is for theoretical approach. The author applied several algorithms, including machine learning potentials suited for big data and large experimental systems.

The thesis is based on a collection of 14 scientific articles, all published in highly impacted international journals, important not only to theoretical and computational chemists but also to those doing experimental studies in laboratories. The [apers were published between 2015 and 2023. According to the Web of Science Core Collection, Dr. Grajciar co-authored a total of 32 papers which were cited over 1500 times. The H-index of 18 is higher than average at this stage in the scientific career (scientometrics obtained at 18.04.2023).

The thesis is surprisingly heterogeneous and diverse, because the term "nanoporous" covers acidic and cationic forms of zeolites, as well as MOFs with and without open metallic centres. Operando has also a capacious meaning – concerns physisorption at low temperatures, interaction of small molecules at different conditions or even hydrolysis at ambient conditions.

The introductory part is concise but comprehensive and allows a non-specialist to gain basic knowledge, required to understand the scientific background and explains the problems that needed to be resolved and, at least partially, were resolved as results of Dr. Grajciar's work. I especially appreciated the efforts towards making the computational results experimentally verifiable.

The author divided the thesis into two parts, the first devoted to methodological advances and the second – to specific applications. I understand the motivation for this division, but as an experimentalist I prefer the second approach – directly explaining how the methodology had to be developed (or changed) to solve a specific scientific problem.

The motto used by dr Grajciar was taken from the song but resembles (recently changed) motto of Olympic games, which now reads *"Citius, altius, fortius – communiter"* and fits to Dr. Grajciar's

work, because it is closely intertwined with the experimental work done by excellent collaborators from around the world: Germany, England, Scotland, China, and even using samples of American origin.

The thesis puts into perspective the achievements of Dr. Grajciar and for organize the results published in a series of publications that were previously known to me, but until now I focused rather on the experimental side, and sometimes surprising conclusions – the striking example being the lability of zeolitic oxygens.

At this point I like to cite one of Dr. Grajciar statements: "Using these MLPs, we were, e.g., able to reveal more than twenty thousand additional zeolite framework candidates within the synthetic feasibility range". This is a very encouraging conclusion, allowing to expect that for a long time we will not run out of problems needed to be solved.

The usual point of all reviews is indication of linguistic errors and typos, serving as a proof that the reviewer read the work carefully, but I decided to skip this point, with one exception. The way Dr. Grajciar cited publications was very confusing, I was often not sure whether the author was referring to his own work or citing someone else's, which had to be checked by going back to the list of references.

My questions for the habilitation thesis defence comes from the perspective of the experimentalist who wants to take advantage of the modelling, and development of the calculation methods:

1. In your thesis I know your opinion on the perspective of the rational design of novel materials, but my question is related to the rational design of 2D zeolites – we still do not know the basic principles which are governing their formation (as opposed to growing as 3D frameworks) and there is still a matter of accident to obtain new layered zeolites or at best making "educated guesses". I would like to know your opinion on the perspective of this specific branch of zeolite science. In other words, how can you (theoretical chemist) help us (experimentalist).

2. I am also interested in the time scale for the calculations in the "operando mode". You can observe formation of defects and bond breaking and formation – how quick are these processes, can you transfer the time scale from the calculation to the real-life or rather real-chemistry? And how does it change with temperature?

I know that these are very general questions, and it is much easier to ask them than to answer, but your comments and possible insight should be very valuable and useful to me.

Conclusion

In my opinion in his thesis Dr. Grajciar justified his scientific independence, maturity, and significance of his work. The habilitation thesis entitled "Towards reliable simulations of nanoporous materials under operando conditions" by Lukáš Grajciar **fulfils** requirements expected of a habilitation thesis in field of chemical sciences.