Review report on PhD thesis of MSc. Ho Viet Thang


The PhD dissertation of MSc. Ho Viet Thang deals with theoretical description of active sites present in several three- and two-dimensional zeolite materials. This work was motivated by recent advances in zeolite synthesis related to introduction of two-dimensional analogues of traditional zeolites with potentially better practical properties. The improvement is achieved mainly by reducing diffusion limits via introduction of supplementary larger channels. Importantly, it is desired to preserve the properties of active sites known from the traditional materials.

MSc. Ho Viet Thang analyzed properties of the most practically important Brønsted and Lewis acid sites. He applied a smart strategy in which he examined in parallel 3D and 2D analogues of several zeolite topologies employing identical computational methodology. By doing this, he captured the most important differences between the nature of acid sites while going from 3D to 2D materials. The density functional theory with corrections for dealing with dispersion interactions is used, both in periodic and non-periodic schemes. Geometric features of the acidic sites are analyzed. Simulations of vibrational spectra of CO probe molecule and the stretching of O-H groups are performed. The chemical shifts of NMR trimethylphosphine oxide probe are also calculated. Adsorption energies of the probes are used as another feature to characterize active sites. Eventually, a catalytic reaction mechanism occurring in one of hierarchical zeolite structures is investigated.

The thesis opens (Chapters 1 & 2) with a general introduction including presentation of the zeolitic structures, and continues (Chapter 3) with a detailed description of the considered 3D and 2D zeolite frameworks. I must stress that the hard task of presenting the zeolite structures was completed very well; even a non-specialist should have no difficulty with understanding the structural information included therein. Computational methods are discussed in the following chapter (Chapter 4). It consists of a brief description of the density functional theory, introduces more advanced methods for dealing with dispersion interactions and spectra modelling, and includes computational details employed by the student in his work. As a theoretician, I particularly appreciate the brief but informative content of this chapter; without going into well-known fundamentals of quantum chemistry.

Original results are presented and discussed in the final chapter (Chapter 5). The calculated properties of both Brønsted and Lewis acid sites are presented for all considered
structures. A detailed discussion of the spectra of CO and O-H is provided, and the mechanism of the aldol condensation reaction is investigated at the very end. These results are based on five papers published in high impacted journals (attached the thesis). Overall, Mr. Ho Viet Thang demonstrated that active centers in 2D zeolites preserve most of their features known from corresponding 3D structures with only a small decrease of acidity. This conclusion is of vast practical importance as it shows that improved catalytic activity of 2D materials can be achieved by lifting diffusion limits while preserving the chemical character of active sites. It should be stressed that a careful comparison of the calculated properties with available experimental data was made and an excellent agreement was obtained in all cases.

The dissertation of MSc. Ho Viet Thang is well structured and presented, with a good balance between the introductory, theoretical, and applications-related chapters. The language is very clear and the graphical presentation of the structural data is exceptionally good. There are very few typos and errors in grammar. I would like to stress that the results (Chapter 5) are presented and discussed in a very rigorous and clean way which is not a trivial task while presenting such a volume of research. I found some minor issues. For instance, the classical harmonic oscillator is discussed in details in Chapter 2.4, which is a little surprising, while there is no mention about the quantum nature of molecular oscillations. In Figs. 20 and 27, there is no explanation of the presented sets of curves. Also, I would welcome some general introduction of practically important issues, for instance, more examples of reactions occurring at the considered acid sites, some discussion of the diffusion limits in the microchannels, or information about practically important loadings of the channel networks.

Despite the above minor deficiencies, my overall opinion about the presented dissertation is very positive. In particular, the scientific level of the presented work is very high, as evident from the attached papers. MSc. Ho Viet Thang obtained original and significant results. Their importance is not limited to the field of theoretical or physical chemistry, they seem important also for practical uses of zeolites.

I suggest the following points to be discussed during the defense:

1. The adsorption energy calculated for TMPO probe in 3D MFI structure using PBE and PBE-D3 methods shows that the dispersion correction is very substantial, often more than doubling the non-corrected value (Table 11). What is the reason for such high dispersion? Also, are there any caveats related to the applicability of the dispersion correction in such cases?

2. In most cases, only C-down adsorption complexes are discussed for the CO probe. Are O-down complexes obtained and stable at the same binding sites?

3. More general, what are advantages and disadvantages of periodic and cluster models of zeolitic materials?
Conclusion

This is a solid and interesting PhD dissertation covering large body of work on advanced and important topics. The scientific level of the presented results is very high. The author demonstrated ability for an independent and creative work in the field of theoretical physical chemistry. Therefore, in my opinion, MSc. Ho Viet Thang fulfills the conditions for obtaining a PhD degree. Based on my evaluation of the presented dissertation, I recommend this thesis for a public defense.

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