



Opponent's Review of the Dissertation Thesis

Author: Ing. Jakub Halánek

Title: Adsorptive Separation of Small Molecules on Zeolitic Materials

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Study program: Physical Chemistry

Brief Characterization of the Thesis

The presented thesis describes adsorption properties of small pore zeolites with CHA, LTA, UTL-derived and UOV-derived structures. The thesis focuses particularly on CO₂/CH₄ separation and alkanes/alkenes separation. Within this scope, the thesis investigates effects of variables such as type of framework heteroelement, type and concentration of present EF alkali cations and zeolite structure on these separations. The thesis is a combination of 5 scientific articles out of which 3 has been already published in high quality scientific journals. The other 2 are under review. Ing. Halánek is the first author of 3 of them (1 published).

Evaluation of the Thesis

Citing David S. Sholl and Ryan P. Lively paper from Nature 2016 "Seven chemical separations to change the world", purifying mixtures without using heat would lower global energy use, emissions and pollution — and open up new routes to resources. The present thesis addresses two of those 7 costly separations (CO₂ purification and alkane/alkene separation), which I find very important and timely. The thesis discloses several very promising materials, which may advance developing of novel separation processes which would be less energy intensive than the state-of-the-art ones. Methodology of the thesis seems to me well-chosen and the datasets seem complete and convincing. The thesis has number of strong points: I appreciate a clear introduction and the brief but well written theoretical overview of adsorption. Also, I appreciate the thesis seems to me complete and well presented. Finally, I think that the PCR based separation of propane and propene, although not fully reproducible and showing to be dependent on not very specific silica debris partially blocking the pores, is an important contribution, which shows a novel possible direction to decrease energy costs of this separation.

Weak points of the thesis are minor. It is a pity that an example of the IAST selectivity calculation is not provided. I think this would be very useful particularly for less experience followers. Also, it would be good to deeper review existing data for materials exhibiting so-called trap-door effect (e.g. Cs⁺ exchanged CHA) in the CO₂/CH₄ separation in the text of the thesis (there just mentioning its existence seem to me too brief). The distinction is explained in introduction to paper III. FT-IR spectra discussion on pages 50 and 51 is difficult to follow since band positions for particular species are not given in the text.

Formal Errors and Typos

The thesis is written in English and its formal quality is high. One can only spot czechisms in some places (e.g. page 26 "finer applications", "...both with respect to the framework and the EF-cations...") or the sentence constructions are redundantly complex (e.g. page 48 "Interestingly, however, whereas in the case...") but I don't consider this an important problem. Number of typo and formal errors is very low.

On page 12, eqn. (3) and (4), q_m is not defined (I guess it is a monolayer uptake).

Also, on page 31, Table 1, T_B , T_c and d are not defined (I guess these are boiling and critical temperature and a kinetic diameter).

A list of abbreviations and equations notation would be helpful for easier reading.



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Questions and Comments for Defence

- 1) I would like to ask the student to provide an example of the separation IAST selectivity calculation.
- 2) It is a bit surprising for me that the highest predicted separation selectivity for the CO₂/CH₄ separation is predicted for Li⁺ exchanged CHA (the smallest cation) although recent works describe advantages of Rb⁺ and Cs⁺ cations (large), which exhibit so-called trap door effect. Could the student comment on differences in separation mechanisms through whole Li-CHA to Cs-CHA set (through whole I.A group of the periodic table)?
- 3) I don't understand why a CHA exchanged with larger cation (Na⁺) should exhibit a better accessibility of channels but the one with smaller cation (Li⁺, page 49). Could the student comment on this?
- 4) Paper I contains also data on Ti-CHA. What is the reason for not mentioning them in the thesis at all?
- 5) Page 60, Fig. 24 - Is there any explanation why UTL exhibits quite different propane and propene uptakes while the isotherms for the OKO are practically identical?
- 6) May the Ge present in UTL and UOV zeolites somehow influenced the adsorption behaviour in the hydrocarbon separations?

Conclusion

In conclusion, the dissertation by Ing. Jakub Halánek meets all the requirements for a doctoral thesis. The candidate has clearly demonstrated his ability to conduct an independent scientific work as well as to collaborate with colleagues. **I thus recommend his dissertation for defence.**

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