



## Review report on a doctoral thesis

**Author of the thesis:** M.Sc. Mehran Sajad

**Title of the thesis:** Production of light olefins via (oxidative) dehydrogenation of light alkanes over nontraditional heterogeneous catalysts

**Academic supervisor:** prof. Ing. Roman Bulánek, Ph.D.

### Thesis summary

The doctoral thesis deals with dehydrogenation and oxidative dehydrogenation of ethane and propane to produce light olefins, such as ethylene and propylene. The thesis is focused on developing novel catalysts, describing their active centers and understanding the role of these centers with respect to the catalyst activity, selectivity and their stability. The thesis is based on five research articles; four of them were published in journals with an impact factor. M.Sc. Mehran Sajad is the first author in four of five presented articles. The thesis summarizes the published findings and provides a good overview of the research performed and results obtained.

### Thesis evaluation

From the formal point of view, the thesis is well structured, written in good English with only a minimum of typos. The thesis provides also an overview of abbreviations used that is, however, incomplete (e.g. ODH or ODHP are not explained here) and lists also chemical formulas, which cannot be considered as abbreviations (e.g. KCl, LiCl, etc.). The orientation in the thesis would be easier if page numbers and also the headings of the articles in between the articles in the appendix were provided. Finally, the quality of some figures is rather poor (e.g. Fig. 11 and 12) and, in some cases, the descriptions of the results are unclear – e.g. in part 6.2 it is not clear what is meant by “spent catalyst”, i.e. if regeneration was or was not part of the history of a sample that is characterized”.

From the scientific point of view, the thesis addresses all salient points of the work very well. Despite the work is scientific in its nature, I would welcome a better setting of the topic in the industrial perspective to demonstrate the huge practical potential of the work. The experimental part is concise, providing enough information to follow the presentation and discussion of results although some details are missing, such as description of most of the characterization methods.

The reading of the thesis has inspired me to several questions that could be discussed during its public defense:

1. Please specify your contribution to each of the articles.

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2. In the introduction, it is stated that acetone is synthesized from light olefins. Please elaborate how.
3. What are non-traditional heterogeneous catalysts? How are they defined?
4. Steam cracking is claimed to be a low selective process – what is the ethylene selectivities in ethane steam cracking and how does it compare to ethane ODH?
5. What are the environmental and engineering concerns related to the use of chlorides from the future industrial application point of view?
6. What was the mass balance in the experiments?
7. How precise is the mapping of composition by EDS? How many samples were measured and spots in the sample averaged? Was the distribution throughout the sample homogeneous?
8. Was the structure of FAU preserved? The signal of FAU in XRD is drastically reduced when looking at the fresh catalyst and gone in the spent samples.
9. Regarding the work objective, what was the rate of deactivation and did it (if so, how) correlate with the loss of chlorine?
10. Pd NPs: In Figure 6, values in the range 2-8 Å are shown, while Figs 7 and 8 demonstrate the mean Pd size to be 2 and 8 nm. Which is correct?
11. Considering that the Pd NPs are in the nm range, are they really located in the pores? If so, how do they fit in and what is their shape? What is the accessibility of the Pd surface to the reactants in catalysts prepared by encapsulation of Pd?
12. What was the crystal size of the studied zeolites?
13. Is cracking actually an important side-reaction in propane dehydrogenation? Methane was observed as a side-product. What was the selectivity to ethane and ethylene?
14. What was the amount and nature of C deposits?
15. In case of the impregnated catalyst (Fig. 11) the rate increased 5-times (1<sup>st</sup> cycle vs. 4<sup>th</sup> cycle). Why?
16. What is the reason for significantly lower TOF over Pd/MFI in comparison with the rest of the studied catalysts?
17. It is suggested that “the productivity and stability of the encapsulated samples are higher than those of the impregnated counterpart”. What is the evidence of the better stability of the encapsulated catalysts?
18. Why was selected impregnation rather than ion-exchange that would allow obtaining smaller and more uniform Pd NPs?
19. Why was not used siliceous MFI when comparison is made with siliceous IPC materials?
20. What is the error of TOF determination? What is the error of Pd specific surface area determination?
21. The Pd surface area for the TOF calculation was determined based on the TEM measurements of Pd NPs. Is this method suitable? What is the potential weakness?
22. Please provide an explanation of the data reported in Fig. 21 with a focus on the difference between the left and right chart.
23. Coupling of C1 species is mentioned on page 58. Is there a direct experimental evidence of this reaction? What is the extent of the coupling reaction in comparison with the C-C cleavage reaction? Does it depend on the propane conversion (and how)?





In summary, the reviewed thesis is a high-quality scientific work that fulfills, in my opinion, all requirements needed for obtaining a PhD degree. Therefore, I fully recommend the thesis of Mehran Sajad to be defended orally and awarded by the PhD degree.

In Prague, 27.11.2023

doc. Ing. David Kubička, Ph.D. MBA

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