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Review Report on Dissertation Thesis

M.Sc. Mehran Sajad:
"Production of light olefins via (oxidative) dehydrogenation of light alkanes over nontraditional heterogeneous catalysts"

The presented dissertation thesis is designed as an annotation of papers published in a total of four peer-reviewed journals, with one additional manuscript prepared to submit. With the exception of "Publication I", these are well-established journals publishing significant research works in the field of heterogeneous catalysis (three Q1 papers and one Q2 paper). The PhD candidate listed as first and/or corresponding author on three of these contributions. The submitted dissertation is clearly structured with references to published papers included at the end of the dissertation. A discussion of the most important findings obtained and corresponding conclusions are therefore the key parts of dissertation.

Undoubtedly, the dissertation is dedicated to the quite current problem of obtaining light olefins representing fundamental feedstock for a number of technologies of highly valuable products. In particular, both ethylene and propylene have been representing the cornerstones of organic technology for decades. However, the existing technologies based on fluid catalytic cracking or steam cracking are costly and particularly problematic in terms of the currently highlighted problem of sustainable economy (high energy costs and CO_2 emissions). An alternative promising catalytic pathway such as oxidative dehydrogenation of light alkanes has been therefore studied.

This dissertation preferentially addresses this challenging issue of selecting suitable catalysts revealing high catalytic performance, and is therefore highly current on a global scale. The selection of three catalytic alternatives and their validation does not lack originality (supported alkali chlorides, supported noble-metal nanoparticles and hexagonal boron nitride) and their challenging experimental validation is documented in the present dissertation. I consider the choice of catalysts to be very reasonable, in line with current trends (e.g., see *Liu et al: J. Phys. Chem. Lett. 2021, 12, 36, 8770–76*), and probably very rational in terms of the expected industrial-scale realizations. In particular, I appreciate the dissertation's assessment of the influence of critical parameters of catalysts such as chemical composition, crystallinity, textural properties, reaction conditions, pretreatment/regeneration effect, stability, catalytic activity, and selectivity of the catalysts and also that parent and spent catalysts were considered to explore the physicochemical changes that occurred during the reaction. The PhD candidate within the thesis experimentally evaluated a number of phenomena, problem of catalyst deactivation (e.g., alkali chloride), discussed suitable methods of anchoring the catalyst to the support (metal nanoparticles), newly addressed the problem of time dependence of the boron-based catalyst efficiency, and put forward a new hypothesis on the mechanism of catalysis of this, perhaps the most promising catalyst, for the real applications.

The thesis reveals a standard structure. An Introduction part involves a brief state-of-the-art concerning both of direct dehydrogenation and oxidative dehydrogenation. The experimental part is quite sufficient in the chosen approach of the dissertation, which is based essentially on the comments on the attached publications in which the PhD candidate has participated, since details are available in the parent publications. However, the core part of the dissertation is Chapter 6, which summarizes the results of the catalytic performance of the studied reactions for the formation of light olefins, particularly both ethene and propene. The final evaluation of the results obtained is clearly given and in particular the boron nitride-based catalyst seems to be favored by the author.

There are only a few typographical errors and formal mistakes found in the thesis. However, these shortcomings do not diminish the undeniable professional value of the work for the development of the field of heterogeneous catalysis.

Finally, I would appreciate answers to the following rather general questions in the framework of the dissertation defense discussion:

1. The published papers formed the basis of the dissertation show a relatively broad team of authors from various institutions participating in the research activities described above. Could the PhD candidate therefore specify his personal contribution to the submitted thesis explicitly?

2. Currently, ethene is mainly produced in a highly energy-intensive steam-cracking or fluid catalytic process. However, already in 2006, the U.S. Dept. of Energy (see *https://www1.eere.energy.gov/manufacturing/resources/chemicals/pdfs/ng_ethylene.pdf*) tried to develop a new efficient alternative to this method in catalytic oxidative dehydrogenation, which directly produces ethene from crude ethane found in natural gas in a single step. However, it was absolutely necessary to develop a new catalyst. Do you have any information on whether such a catalyst has already been developed in the USA, or how it differs from your catalysts, and whether real technology based on oxidative dehydrogenation on this principle is already in operation anywhere in the world?

3. Recently, there have been studies of oxidative dehydrogenation using CO_2, e.g., see *Li et al: Oxidative dehydrogenation of light alkanes with carbon dioxide, Green Chemistry 2, 2021*, and many others. What is your opinion on this possibility?

4. What prospects for the real industrial utilization do you expect in the technological application of complex nanocomposite catalysts also utilizing for this reaction based on $MoVNbTeO_x/TiO_2$ catalyst?

In conclusion, the submitted dissertation fully meets the conditions required for the submission and defense of a dissertation, it brings new scientific knowledge for different types of selected catalysts. Last but not least, the results are, in my opinion, also practically applicable.

I fully recommend the submitted dissertation of Mehran Sajad for defense.

In Prague, on 22nd November 2023

Ing. Karel Soukup, Ph.D.

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