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Kraków 30.03.2019

Review Report on the PhD Thesis
Submitted to Institute of Physical Chemistry
Polish Academy of Sciences

Author: Damian Giziński, MSc
Title: "Liquid-phase chemoselective flow hydrogenation over resin supported catalysts for synthesis of industrially relevant chemicals"
Scientific Supervisors: Jacinto Sá PhD, DSc, Prof. IPCPAS

The presented review report is organized in the following sections: project background and aims, general description of the thesis, specific comments followed by final evaluation statement.

Project background and aims

With population growth the demand for chemicals continues to grow dynamically. Heterogeneous catalysis is at the center of the chemical industry, thus new catalytic materials and processes are of crucial importance for a sustainable future of our society. The design, development and implementation of efficient heterogeneous catalytic processes, based on both fundamental and applied research, will have a great impact on our lives.

A large part of industrial chemical processes are carried out over heterogeneous catalysts, with the ultimate goal of obtaining high

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performance of the catalytic systems (high activity, selectivity, stability, cost-effectiveness, etc.). Nowadays selectivity for the desired product in a multi-pathway reaction, and thus eliminating unwanted byproducts, is one of the key factors to be controlled by researchers.

Damian Gizinski's thesis concentrates on the elaboration of active and selective supported catalysts (based on low-cost metals and resin) for production of practically relevant intermediate products and the evaluation of several factors affecting the catalyst performance. Thus, this thesis addresses the highly relevant and vital area of research in heterogeneous catalysis.

General description of the thesis

The submitted thesis presents a comprehensive research including synthesis, characterization and catalytic performance evaluation of the synthesized catalytic materials in the chemoselective hydrogenation of unsaturated aldehydes in liquid phase. For a PhD thesis, quite a few problems are addressed, which can be classified into general categories: design of the catalyst, development of its synthesis protocol (preparation of metal nanoparticles and grafting them on resign), catalyst testing in various conditions (T, P), process optimization including catalyst morphology modulation studies, and, as a final point, the elaboration (based on the research results) of the complete catalytic flow system.

The thesis comprises 120 pages and follows the classic structure of PhD thesis in science. It begins with introduction and literature background (chapters 1 and 2), which directly lead to the aim of the studies (chapter 3). The experimental section (chapter 4) is followed by sections describing the experimental results, discussion and general conclusions of the work (chapter 5). The final sections include a list of the Author's publications and presentations followed by the bibliography with almost 200 references.

Chapter 1 and 2 provide a thorough overview of the relevant fields, progressing from the basics (Introduction) to more specific information concerning the objectives of the thesis (literature background). The literature for this part is carefully referenced (156 references) and a comprehensive bibliography contains all the key papers representative for the discussed fields. It is worth mentioning here, that most of the references are from the last decade, showing the current interest in the subject. The

literature survey directly leads to the main goals of the thesis, which are presented in chapter 3.

The Experimental (chapter 4) and Results and discussion (chapter 5) sections include a thorough investigation with the use of a broad gamut of classic and advanced characterization methods, including: XRD, XPS, XAS, SEM, HR-TEM, FTIR, TGA and the catalytic tests, together with "academic" long term stability. In general, the results represent accurate studies. The accomplished research lead to internally consistent conclusions about chemical composition, structure, morphology, catalytic performance with the emphasis on controlled selectivity as well as micro-reactor technology. I would like to emphasize that the studies concern quite broad, as for PhD thesis, area of research. In the final section (chapter 5.5) the general conclusions of the work are summarized.

Although the thesis is organized and written well and presents original research results, which I found interesting, I meet a problem of careful reading due to small fonts used for main text and figures. In fact, many times I had to use magnifying glass, see e.g. Figs. 17 (page 57) or 74 (page 105). Otherwise the number of minor errors, inaccuracies or linguistic mistakes is very small.

Specific comments

Let me point out a few points that I would like the Candidate to discuss during the defense:

page 20: Various types of defect should be distinguished while writing transition metal oxides formulas. There is an important difference between e.g. "NiO_x" and "$Ni_{1-x}O$". This point is also of importance in the context of Ni^{3+} cations present on the surface, as discussed at page 79.

page 48: How was the metal capping agent removed after the grafting of metal nanoparticles on the support?

page 52: *"Screening consists is carrying out short reactions at given conditions"* Were the steady-states reached during these measurements? How long does it take for the system to reach the steady-state conditions?

page 58: In Fig. 18 and the corresponding text: "pore size 35.14 Å" and "BET 152.59 m^2/g". Could you please discuss the number of significant digits for these parameters?

page 61: Fig. 21. There are some conclusions drawn from the intensities of the IR absorption maxima. Could you please discuss what determines the intensity of the IR spectra?

page 64: Fig. 24 The XRD profiles should be indexed. What does the XRD of a used catalyst look like? (The deactivation is discussed further at page 72).

page 75: The model for molecular modeling Ni clusters is certainly too small for a relevant discussion.

pages 78, 79 (Fig. 39 and Table 2): The TEM provides local information of the catalyst surface. Particle size distributions based on TEM observations are needed for NPs size evaluation. Especially, that as discussed further at p.86, “size of Ni nanoparticles is an important factor” and that the reaction is “structure sensitive”. Additionally, since the particles are relatively small the *Williamson-Hall* analysis may be more adequate here than the Scherer dependence.

Minor comments and typos:

page 56: Indexes in Al_2O_3, cm^{-1}

page 61/62 “Surface distribution of Ni species …is presented in Fig. 22” There is no surface distribution in Fig. 22 but XPS results.

page 65, 67: I was waiting for the possible reaction pathways (e.g. Scheme 2 and 3) from the beginning. It would be much more convenient for the reader if the schemes are shown in the Introduction.

page 102 “green chemistry principals” should be “green chemistry principles”.

page 103 “in comprison” should be “in comparison”.

The aim of this thesis was ambitious: “*to develop a versatile strategy for continuous flow chemoselective hydrogenation of α,β-unsaturated aldehydes in liquid phase*”. This the Candidate has achieved as summarized in chapter 5.5. In my opinion the Candidate correctly highlights the contribution of the thesis, and also emphasizes some ideas for future experimentation. It is clear the Candidate has a comprehensive understanding of the context of his work. In a broader perspective the obtained scientific results will lead to the intensification of technological processes by reducing the productions costs and chemical waste, in-line with the guidelines of green chemistry.

Conclusion

The PhD thesis by Damian Giziński represents a great deal of work. It is well written, and the obtained results are valuable. I really appreciate the Candidate's expertise in the field of synthesis, materials characterization and catalysts testing. The research it describes is of the international standard. The results were published in six original papers in catalytic journals. This thesis is ready to be defended orally and certainly meets the requirements laid down in the Act of 14 March 2003 on Academic Degrees and Academic Title and Degrees and Title in Art (*Dziennik Ustaw* No. 65, item 595) for the degree of Ph.D.