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Referee's Report
of the PhD Thesis of Mr. Damian Giziński

done in the Institute of Physical Chemistry
Polish Academy of Sciences
Warsaw, Poland

under the supervision of Jacinto Sá, PhD, DSc, Assoc. Prof. IPC PAS

The PhD Thesis of Mr. Damian Giziński entitled:

"Liquid-phase chemoselective flow hydrogenation over resin supported catalysts for synthesis of industrially relevant chemicals"

contains 120 pages, including: cover page with the title, acknowledgements, information about financial support, abstract (in English and Polish), contents list, main part of the thesis (introduction, literature background, aim of the studies, experimental section, results and discussion), list of scientific publications co-authored by Mr. D. Giziński as well as list of his scientific presentations, and finally bibliography used in the text body (179 items). Presented material is illustrated by tables, figures, schemes, and equations. In a brief summary it can be presented as follows:

Table 1. Statistic of the evaluated Thesis.

	Number of			
Chapter	equations	figures	tables	schemes
1. Introduction	-	-	-	-
2. Literature background	8	10	-	1
3. Aim of studies	-	-	-	-
4. Experimental section	1	6	1	-
5. Results and discussion	-	58	2	8
Total	**9**	**74**	**3**	**9**

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The research undertaken by Mr. D. Giziński concerns an important problem that lies in the area of scientific and practical interests. As the author wrote in the introduction of his thesis: " …*flow catalysis, is a 'green' and sustainable platform for new developments in chemical industry*". This is in line with the objectives that were outlined more than 30 years ago in the report of the World Commission on Environment and Development, chaired by Norwegian politician Mrs. Gro Harlem Brundtland.

Literature background is a well elaborated compact review with 156 references. This part of the work is read with a great pleasure, and any additional information relating to the issues addressed in the text can be found in well-cited literature. Skillful presentation of a number of information on various closely related issues, on the one hand, caused the reviewer's recognition, and on the other one left some shortage. It is justified, the PhD student will be able to argue during public defense. In my opinion, certainly there was no short (4-5 sentences) summary of the literature background as a whole.

The aim of the studies was to develop a versatile and thorough strategy for continuous flow chemoselective hydrogenation of α,β – unsaturated aldehydes in liquid phase, and to attain that the course of the research was divided into consecutive stages presented on page 46.

Results and discussion is followed by the experimental section, which is an integral part of the conducted experiments. There were presented materials and chemical reagents used, preparation of studied systems, as well as applied research methods including carried out tests. In most cases, the supplier of reagents and the degree of their purity were not given.

An analysis of this part of the work raises the question, whether all of the described activities have been carried out by a PhD student (e.g.: physicochemical characteristics, i.e. XPS, TEM, TGA, FT-IR, etc.). There is no mention of the participation of other people, so it can be considered that it was in fact.

Mentioned earlier the aim of work was the determinant of all the research carried out by the Mr. D. Giziński. The experimental material was presented and discussed in a systematic way. The discussion of the results was not limited only to own observations and conclusions, but also the quoted literature was included. The individual sections of the presented material end with a short summary. In addition, a general summary is posted on page 109. The rich experimental material and interpretation of the presented results do not raise any objections.

After analyzing the material presented in the thesis I fully agree with the statement in the final paragraph of the reviewed work: " … *flow chemistry is a perfect technique for process intensification listed as a one of the most important prospects for new generation chemical manufacturing*".

Some comments about the work itself. It is advisable to list all abbreviations used in the text at the beginning of the work. It greatly facilitates the tracking of the presented content. The following abbreviations were used in the thesis:

acac – acetyl acetonate
ATR – attenuated total reflection
CCD - charge-coupled device
CFD – Computational Fluid Dynamics
CNF – carbon nanofiber
CPN - nitrogen-doped porous carbon material
DBU – 1,8-diazabicyclo[5.4.0]undec-7-ene
DHC - dihydrocitronellal
DMPSi – poly(dimethyl)silane

EDS - energy-dispersive X-ray spectroscopy
FEG – field emission gun
FFT – fast Fourier transform
FID – flame-ionization detector
FT-IR – Fourier transform infrared
FWHM – full width at half maximum
HAADF - high-angle annular dark-field
HIV - Human Immunodeficiency Virus
HPLC – High Performance Liquid Chromatography
HPS – hyperbranched polystyrene
HR-TEM – high-resolution transmission electron microscopy
LDH – layered double hydoxide
MCM-41 – Mobil Catalytic Material-41
MOF - metal-organic framework (materials)
NBS – *N*-bromosuccinimide
NP – nanoparticle
PEG - poly(ethylene glycol)
PXRD – powder X-ray diffraction
SBA-15 - Santa Barbara Amorphous-15
SMSI – strong metal-support interaction
SSA – spherical sector analyzer
TEM – transmission electron microscopy
TGA – thermogravimetric analysis
TG/SDTA – thermogravimetric/single differential thermal analysis
TOF – turn-over frequency
TOPO – trioctylphosphine oxide
TPH - temperature-programmed hydrogenation
XAS - X-ray absorption spectroscopy
XOS – X-ray optics system
XPS – X-ray photoelectron spectroscopy
XRF – X-ray fluorescence

Most of them have been explained in the text of the work. However, some which are marked in yellow do not have clarification. Below there are listed some imperfections, which have been noted in the text (selected examples).

- Page 11 (4th line from the bottom) the abbreviation used should be TOF*s* instead of TOF.
- Page 56 (7th line from the bottom) – is min-1 and should be min^{-1} (superscript).
- Page 56 (6th line from the bottom) – is Al2O3 and should be Al_2O_3 (subscripts).
- Page 56 (2nd line from the bottom) – is cm-1 and should be cm^{-1} (superscript).
- Page 61, Fig. 21. No Y axis description (intensity probably in the arbitrary units).
- Page 64, Fig. 24. No Y axis description (intensity probably in the arbitrary units).
- Page 77, Fig. 38. No Y axis description (intensity probably in the arbitrary units).
- Page 90, Fig. 56. No Y axis description (intensity probably in the arbitrary units).
- Page 91, Fig. 57. No Y axis description (intensity probably in the arbitrary units).
- Formulas included in the text of the work are not provided with successive incidental numbers (pp: 29-31, 37, 54).
- According to the valid nomenclature, the oxidation state of an element is written after its name (symbol) without the use of spaces (e.g.: p.49, not palladium (II) but palladium(II)).
- Nickel in compounds usually occurs on the second, and less frequently on the third oxidation stage. In the text appears contradictory information. On page 47 (10th line from the bottom) it is written: "… *nickel (III) acetyloacetonate* ", and on the same page (5th line from the bottom) the following statement appears: "… *Ni(acac)$_2$* …". Could you be so kind to clarify it?

The author has used for graphical presentation figures and schemes. What was the reason of such division? Is it a big difference between graphical content presented in scheme 1 (p. 11) and figure 11 (p. 47)? Moreover, schemes are presented in some figures (e.g.: Fig. 9, 10 and 13).

Finally, the thesis is finished with the summary. At this point someone could expect conclusions strongly correlated with the aim of studies presented on page 46. I believe that during public defense of the thesis this point will appear (I mean main conclusions).

I declare that the above remarks do not undermine my **positive assessment** of the dissertation of Mr. Damian Giziński. The work was prepared very carefully, both from the editing and the graphic side.

A wide spectrum of applied research techniques forced the PhD student to move in various fields and disciplines of knowledge and technology. Catalytic tests complemented the performed physicochemical analyzes.

Part of the thanks at the beginning of the work clearly indicates that Mr. D. Giziński appreciates the advantages and the need for the teamwork.

Mr. D. Giziński is a co-author of six scientific papers and one book chapter (please see list included below).

Scientific papers co-authored by D. Giziński (according to the publication date).

1. A. Śrębowata, I.I. Kamińska, **D. Giziński**, D. Wideł, J. Oszczudłowski, *Remarkable effect of soft-templating synthesis procedure on catalytic properties of mesoporous carbon supported Ni in hydrodechlorination of trichloroetthylene in liquid phase*, *Catal. Today*, **251** (2015) 60-65; DOI: 10.1016/j.cattod.2014.11.005 (IF: 4,312).
2. C. Paun, **D. Giziński**, M. Zienkiewicz-Machnik, D. Banaś, A. Kubala-Kukuś, J. Sá, *p-Nitrophenol flow hydrogenation with nano-Cu_2O grafted on polymeric resin*, *Catal. Commun.,* **92** (2017) 61-64; DOI: 10.1016/j.catcom.2017.01.003 (IF: 3,389).
3. I. Goszewska, **D. Giziński**, M. Zienkiewicz-Machnik, D. Lisovytskiy, K. Nikiforov, J. Masternak, A. Śrębowata, J. Sá, *A novel nano-palladium catalyst for continuous-flow chemoselective hydrogenation reactions*, *Catal. Commun.,* **94** (2017) 65-68; DOI: 10.1016/j.catcom.2017.02.014 (IF: 3,389).
4. **D. Giziński**, I. Goszewska, M. Zieliński, D. Lisovytskiy, K. Nikiforov, J. Masternak, M. Zienkiewicz-Machnik, A. Śrębowata, J. Sá, *Chemoselective flow hydrogenation of α,β – unsaturated aldehyde with nano-nickel*, *Catal. Commun.,* **98** (2017) 17-21; DOI: 10.1016/j.catcom.2017.04.048 (IF: 3,389).
5. M. Zienkiewicz-Machnik, I. Goszewska, A. Śrębowata, A. Kubas, **D. Giziński**, G. Słowik, K. Matus, D. Lisovytskiy, M. Pisarek, J. Sá, *Tuning nano-nickel selectivity with tin in flow hydrogenation of 6-methyl-5- hepten-2-one by surface organometallic chemistry modification*, *Catal. Today*, **308** (2018) 38-44; DOI: 10.1016/j.cattod.2017.08.062 (IF: 4,667).
6. **D. Giziński**, W. Błachucki, A. Śrębowata, M. Zienkiewicz-Machnik, I. Goszewska, A. Kubas, D. Lisovytskiy, M. Pisarek, J. Szlachetko, J. Sá, *On-the-fly catalyst acceretion and screening in chemoselective flow hydrogenation*, *ChemCatChem*, **10** (2018) 3641-3646; DOI: 10.1002/cctc.201800581 (IF: 4,674).

Co-author in the book chapter

D. Giziński, J. Sá, *Hydrogenation by copper catalysts*, in: *Hydrogenation with low-cost transition metals* (J. Sá and A. Śrębowata, Eds.), Chapt. III (ISBN: 978-113874743-2), CRC Press, Boca Raton, 2017, pp 79-117 (DOI: 10.1201/b19156).

It ought to be mentioned that papers denoted above by numbers 2 to 6 are strongly connected with the referred thesis. This are leading scientific journals with international circulation associated with heterogeneous catalysis Moreover, D. Giziński was a leading co-author of four oral and eight poster presentations delivered during national and international conferences.

Bearing in mind the high quality of the reviewed dissertation and the fact that some of the results have already been published, I believe that it should be **awarded** taking into account that other internal conditions related to the distinction of doctoral dissertations at the Institute of Physical Chemistry of the Polish Academy of Sciences are met.

Summing up the assessment of the doctoral dissertation of Mr. Damian Giziński, it is necessary to emphasize the value and significance of the experimental results obtained, with the possibility of their further adaptation to practical solutions.

According to article 13 of the Act from 14th March 2003 on degrees and academic title as well as degrees and title in the field of art (Journal of Laws from 2003, No. 65, item 595, as amended) in item 6:

"*The doctoral dissertation should be accompanied by an abstract in English, and the doctoral dissertation prepared in a foreign language has also a summary in Polish*".

The reviewed dissertation has summary in Polish (p. 6).

I declare that the doctoral dissertation by Mr. Damian Giziński is in accordance with the regulation of the Ministry of Science and Higher Education of October 3, 2014 (Journal of Laws, item 1323) and art. 13 of the Act of 14 March 2003 on degrees and academic title as well as degrees and title in the field of art (Journal of Laws of 2003, No. 65, item 595, as amended) corresponds to the requirements set out in the above-mentioned Acts. Therefore, I propose to the Scientific Council of the Institute of Physical Chemistry Polish Academy of Sciences in Warsaw for the admission of Damian Giziński to the next stages of the doctoral thesis.
At the same time, as a reviewer of the dissertation, I submit a formal motion: the doctoral thesis deserves an **award**.

J. Ryczkowski