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Szczecin, 2016-09-05

**Review Report on PhD Thesis of Sylwia TURCZYNIAK, M.Sc.,**
**entitled**
**"Surface composition of cobalt catalysts for steam reforming of ethanol"**
prepared base on invitation letter from the Dean of the Faculty of Chemistry of Maria Curie-Skłodowska University (UMCS) in Lublin –Professor Wladyslaw Janusz, Ph.D., D.Sc. (771/WCHD/16, 01.07.2016)
and base on invitation letter from the Vice-Présidente, recherche et formation doctorale, Université de Strasbourg – Catherine Florentz, 30.06.2016)

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## Choice of topic

Taking into account a depletion of fossil fuels, there are strong needs to look for alternative energy sources. Hydrogen is undoubtedly the best energy source, the most efficient one and friendly for environment, although methods of hydrogen production are often energy demanding and not so clean. There are still a lot of challenges in the area of production, storage and transport of hydrogen.

One of the prospective hydrogen production methods is ESR (ethanol steam reforming). When bioethanol is a raw material for ESR, the process can fulfil all demanding environmental criteria imposed by EU.

The efficiency of the ESR strongly depends on the quality of catalysts applied in the process. Cobalt would be a suitable candidate, being less expensive than noble metals, however it would be first necessary to minimize some of its disadvantages, as a tendency to coking and/or to sintering.

With regard to the facts outlined above, I am of the opinion that the topic of Sylwia Turczyniak's doctoral thesis, titled "Surface composition of cobalt catalysts for steam

reforming of ethanol", is ideally aligned with the latest trends in contemporary materials science and energy issues.

## Aim and scope

The aim of the work was to study surface composition of cobalt catalysts applied to ESR process, in order to minimize such disadvantages as coking or sintering.

Two kinds of supports were used in the thesis – ceria and zirconia, each of them in the nano or micro form. The loading of cobalt was in the range of 8-9 wt.%. Some catalysts were promoted with potassium (2 wt.%).

The catalysts were analysed using a whole spectrum of modern experimental techniques, including X-ray powder diffraction, X-ray fluorescence, mass spectroscopy, atomic force microscopy, low temperature nitrogen adsorption, hydrogen chemisorption as well as X-ray photoelectron spectroscopy *ex situ* and *in situ*.

## Presentation

The reviewed thesis of Sylwia Turczyniak, M.Sc., consists of 277 pages. The thesis is written in English, and it has been very diligently edited.

The list of abbreviations at the beginning of the thesis is a good idea, useful for the reader.

The structure of the thesis is a traditional one - there is a part containing a literature review (39 pages) and the experimental part of 167 pages. Nevertheless, despite of this subdivision, the structure of the thesis is not so traditional, because it is composed of individual chapters, which are written as independent papers, it means each chapter is provided with its own abstract, content (introduction, experimental, results and discussion), conclusions and references.

In spite of the six chapters-papers the thesis contains executive summaries at the beginning (in English, French and Polish) as well as summary and general conclusions (in English) at the end. Additionally, there are short résumés in English and French at the very end of the thesis. As a result, there is some redundant repetition with all these summaries, because the text of the executive summary at the beginning is very similar to the conclusive summary at the end, including the figures.

To avoid the repetition, the executive summary at the beginning should be much shorter, like an abstract, an overview of the thesis. It should be like a brief, concise appetizer for a reader who is trying to decide whether or not to read the whole thesis. It should correspond to the "elevator pitch" in the area of management. The idea of an "elevator pitch" (or statement) is related to a situation of an accidental (or intended) meeting of a proposer with a very important person in the elevator. As the elevator ride is rather short, a proposer

disposes only of a timespan of 0.5 - 2 minutes for a conversation, which should be interesting enough to convince the decision maker about his excellent idea or project.

In our case a short abstract at the beginning should be attractive enough to encourage the reader to study the whole thesis or, at least, the conclusive summary at the end, where the most interesting findings should be presented.

**Content**

The introduction of the thesis is about hydrogen as an energy carrier and about bioethanol as a hydrogen source. Main goals of the doctoral thesis are addressed here as well, but they are presented twice in the thesis, because the goals mentioned in the Executive Summary are almost identical. The numbering of the same goals is different in the Executive Summary and in the Introduction, and then my remarks here below refer to the numbering applied in the Executive Summary.

The goals of the thesis are very important, they should be precise, specific, measurable and well ordered, and it is not always the case in that thesis.

The goal (iv) is included in the goal (i). The content of the goal (vii) should be added to the goal (iii) (reaction conditions). Concerning the goals (vi) and (viii), there is no more question of overlapping, these goals are just identical. The two last goals expressed as “providing new data in order to shed a light into ESR...“and “supplementing currently available knowledge” should be deleted, as too general, not specific, neither measurable.

There are also duplications concerning figures in the thesis, some figures in executive summary and in final summary are identical - Fig.1 is the same, Fig.4 in the Ex Sum is identical to Fig.2 in the final one, and Fig.5 – identical to Fig.4, respectively.

The notion “dispersion of cobalt (22,5 and 42,3) in the abstract should be better expressed as crystallite size of cobalt or particle size of cobalt.

Some remarks concern only the abstract written in Polish, as the translation to Polish is not always precise. For example, in the capture of Fig.2, the partial pressure is called “częściowe” and in another part of the Abstract – as “cząstkowe”. To avoid this confusion it would be better to call it “parcjalne”. In the same figure capture the partial pressure is expressed in mbar and the total pressure – in atm. The same unit of pressure should be applied in all the dissertation. In the same capture “stężenie grup” should be used instead of “ilość grup”. “Stan utlenienia” in conclusions of the Abstract should be replaced by “stopień utlenienia” and the sentence “zaadsorbowanych na powierzchni cząstek zawierających tlen” – by “grup zawierających tlen”, as in the English Abstract “species” are used, and not “particles”.

The theoretical part of the thesis is composed of one chapter only, titled “Hydrogen production via catalytic ethanol steam reforming”. In this chapter at first the kinetics and

thermodynamics of steam reforming of ethanol is presented. A subsequent subsection concerns literature relating to the state of art of catalysts based on noble metals (rhodium, ruthenium, platinum, iridium, palladium) deposited on various supports. The main role of the active metal in these catalysts is to facilitate C-C bond cleavage and rhodium is the most active to this regard. The final subsection in this part concerns the literature on transition metals (Co, Ni and Cu), as an alternative solution, much less expensive than noble metals. Cobalt is the most promising among them and its catalytic activity strongly depends on its dispersion (particle size and support morphology). Alkali metals promotion is reported to increase the catalytic resistance against coking.

The list of references in the literature part of the thesis contains 205 positions. The chapter is well written and the literature studies are thoroughly done, however some general conclusions are missing of this part. It would be useful to underline, what has been poorly investigated up to now and what is still missing, and then – what is worthy to be studied within this thesis.

The first chapter in the experimental part is devoted to the effect of the surface state on the catalytic properties of the $Co/CeO_2$ systems in the ethanol steam reforming. The information about surface state was acquired using *in situ* and *ex situ* XPS studies under the pressure of 0.2 to 20 mbar. The proposed reaction paths of ESR reaction over $Co/CeO_2$ catalysts in various pressure regimes are shown in this chapter. At the lowest pressure metallic cobalt and partially reduced $CeO_2$ was found, favourable for CO and $H_2$ production.

In the subsequent Chapter 3 the effect of reactants' ratio, of the cobalt and support particles size and of the promoter (potassium) on the surface state and selectivity of cobalt catalysts supported on ceria is discussed. Oxidation state of cobalt under reaction conditions depends on the reactants ratio and it increases with the water extent. However, this effect is damped by potassium presence, which influences as well the oxidation state of ceria. The presence of oxygen containing surface species is favourable not only for the catalyst activity but also for the prevention against coking.

Chapter 4 is devoted to the time-dependence of $Co/CeO_2$ surface states and in Chapters 5 and 6 the cobalt catalysts supported on zirconia are described. As was in the case of ceria-supported catalysts, particle size of cobalt and of the support, as well as the presence of oxygen-containing groups are important for ESR process. In the case of zirconia catalysts a promotion with potassium also inhibits coke formation.

Even if the thesis is organised in separate chapters-papers, some of them about ceria, other on zirconia, the differences and similarities between both supports are thoroughly discussed in the last part of the thesis – Summary and general conclusions.

**Overall assessment**

The doctoral thesis written by Sylwia Turczyniak contains very interesting experimental results, described in a logical and ordered manner in the form of separate papers.

The author has fully attained the goal of the work, providing an exhaustive study of the behaviour of ceria and zirconia-supported cobalt catalysts in the ESR process.

Praise should be given to the application of XPS studies not only *ex situ*, but also *in situ,* together with mass spectrometer on line, enabling to monitor simultaneously the surface states of the catalysts and the products leaving the reactor.

In summary, since the reviewed doctoral thesis of Sylwia Turczyniak, M.Sc., in my opinion fulfils the requirements of the *Act on academic and artistic degrees and titles*, I propose to the Council of the Faculty of Chemistry of Maria Curie-Skłodowska University that it be admitted to the further stages of the doctoral process. This thesis is ready to be defended orally, in front of respective committee.

Moreover, in view of the high quality of the thesis itself and taking into account the list of publications by Sylwia Turczyniak, I would like to propose to the Council of the Faculty of Chemistry of Maria Curie-Skłodowska University that a distinction will be awarded for this thesis.