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# Review Report on the PhD thesis submitted to Maria Curie-Skłodowska University in Lublin and University of Strasbourg

Author: Sylwia Turczyniak MSc

Title: "Surface composition of cobalt catalysts for steam reforming of ethanol"

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

## Project background

Nowadays the global energy demand of our world mostly includes the use of fossil fuels, nonrenewable and unclean energy sources. However, both scientists and practitioners consider hydrogen as an alternative fuel to support energy development due to its cleanness, renewability and high combustion efficiency. Traditional large scale industrial production of hydrogen, mainly for ammonia and hydrocarbon (Fischer–Tropsch) synthesis as well as refinery processes, is based on classic reforming of natural gas. Recently, however, the interest in development of technologies for converting renewable oxygenated hydrocarbons from biomass for hydrogen production can be clearly noticed. This is economically fully justified due to an increase of the global price of natural gas: the price has tripled in the past two decades in most parts of the world. As renewable hydrogen energy can be generated through catalytic ethanol steam reforming, the development of this process technology is considered as an important challenge for fundamental and applied catalysis in the 21st century. Ethanol steam reforming is an endothermic reaction and thus it requires heat to produce hydrogen. Therefore, in order to minimize the energy necessary for the process the development of an efficient catalyst plays a key role here.

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The PhD thesis of Sylwia Turczyniak is devoted to investigations of cobalt-based catalysts for ethanol steam reforming. Several important issues affecting the catalyst performance are addressed with the focus on the relationship between the composition-structure-morphology-activity. Thus, this thesis addresses the highly relevant and vital areas of current catalytic research.

**General description of the thesis**

The submitted thesis presents investigations on the preparation, characterization and catalytic performance evaluation of the synthesized catalytic materials ($Co/CeO_2$, $Co/ZrO_2$) in the steam reforming of ethanol. In general, the performance of cobalt-supported catalysts is affected by several factors with the most important being: metal dispersion, metal–support interaction, cobalt oxidation state, poisoning - all of them are addressed in the PhD thesis.

The dissertation comprises 272 pages (plus Annexes with the scientific outcome of the Author) and does not follow the classic structure of a PhD thesis in science. It begins with abstracts (in English, French and Polish) and an introduction to the subject, which directly leads to a list of several main goals of the thesis.

Part I consists in a literature review and has a logical partition and includes the fundamentals of the steam reforming process and a description of noble metal and transition metal based catalysts. The literature for this part is carefully referenced (205 references) and a comprehensive bibliography contains all the relevant papers for the discussed field. It is worth mentioning here that most of the references are from the last decade, showing the topical issues. This part is well written and provides a very good background for understanding the rest of the thesis.

The main part of the thesis – Part II experimental – consists of five chapters (Chapters 2-6), each addressing a specific scientific problem. All of them exhibit the same structure and are divided into sections, which are typical for scientific papers: introduction, experimental, discussion, conclusions and references. The advantage of such a structure is that the chapters, consisting of integral parts, can be read and analyzed separately. However, a disadvantage appears, in that some portions of

information found in the introductions, experimental sections and discussions are repeated (not mentioning references).

In the final section the general conclusions of the work are summarized. The thesis is prepared in good editing standard. All the figures are carefully prepared and clearly presented. The language is comprehensive and coherent while errors and inaccuracies are relatively rare.

**Specific comments**

Title

The title of the thesis “Surface composition of cobalt catalysts for steam reforming of ethanol” seems to be too specific and sounds like a title for one of the tables. I understand that the XPS was the principal technique used in the thesis, however, I have found much more in the thesis than the surface compositions alone.

Experimental

For all the investigated systems both characterization and activity tests results are presented and correlations between surface state/composition and performance are provided. The characterization of the catalysts by physical methods including: XRD, XPS, XAS, BET, TEM, TPR, etc. represent accurate studies and lead to plausible and internally consistent conclusions about chemical composition, structure, morphology, nature of active states and surface species. Although the results are sometimes difficult to understand, the candidate does well to sort out those which are univocal and those which are more tricky to interpret.

Concerning the experimental part of the thesis I would like the candidate to answer the following minor points during the defense:

1. For some catalysts the surface composition sums up to 100%, whereas for others it does not (e.g. compare the data from Tables in pages 173, 213, 234, 261 etc.). Could you please explain the reason? Quantitative analysis of the XPS data can strongly depend on the surface model applied. How was it done for the presented data? What I found missing in this context is a general model of the investigated catalytic surfaces, covering the geometrical aspects of the

active phase surface coverage and mutual location of the components etc. For example as indicated in page 206 the crystallites of the cobalt phase can be smaller or bigger than that of its supports. It thus implies that in some cases we deal rather with composites than with supported catalysts.

2. As mention in several places in the text it is difficult to characterize potassium surface species in the complex catalytic system. However, in many places the "$KCO_3$" or "K-O" species are denoted. What kind of surface structures does the Author have in mind? Also the possibility of potassium migration is mentioned. At elevated temperatures a more stable thermodynamically state would be favored. Does the Author expect different surface locations of the potassium promoter depending on the calcination temperature?

3. The catalysts were investigated by TEM. Can one extract any information on the cobalt crystallites morphology such as aspect ratio or exposed crystallographic planes? The specific surface topography may substantially influence the catalytic results. Also the mutual location of cobalt and potassium on the surface certainly plays a key role here.

4. For relevant comparison of the catalytic performance, besides conversion and selectivity, one should compare kinetic parameters for the catalysts such as reaction rates, rate constants, activation energies or, as more relevant, TOFs. Is it possible to evaluate their values from the performed catalytic tests?

In general, the presented results seem to be reliable and well documented, although, as always in cutting edge research, the interpretation and discussion can be extended and more in-depth. This is, however, the common inherent feature of all the experimental work in catalysis. I would like to emphasize that the studies concern a broad area of research and their main value consists in the detailed description of the obtained results. Thus, further work in the field can be easily planned. As the most valuable, in my opinion, is the revelation of the dynamic nature of the catalytic surface. This is exactly where the state-of-the-art modern catalytic research aims at.

The summary and general conclusions.

This chapter is short and to the point. The main goals of this thesis were quite extended and ambitious (page 48). They have been achieved to a large extent as demonstrated in this chapter. The Author correctly highlights the contribution of the thesis, and also notices its limitations, showing clearly that the PhD student has a comprehensive understanding of the context of her work. Maybe an overview of all the investigated catalysts in a table or in a graphical representation would be a good idea here.

**Final evaluation statement**

This thesis represents a great deal of work. The results are well presented and their interpretation is at a high scientific level. I really appreciate the candidate expertise in the field of materials characterization and catalysts testing. The research it describes is of the international standard. This thesis is ready to be defended orally and certainly meets the requirements laid down for the degree of Ph.D. in chemistry by the statutes in the Journal of Laws of the Republic of Poland (*Dziennik Ustaw,*14 October 2014).

Andrzej Kotarba