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Report on the **manuscript entitled**

Ru/TiO_2-based catalysts for the hydrogenation of levulinic acid using formic acid as internal hydrogen source"

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To obtain a PhD degree from Lodz University of Technology and Université de Strasbourg.

The PhD research of Joanna Wojciechowska was conducted under international joint supervision of Prof. A. Ruppert and Dr N. Keller. The thesis submitted involves a study on the development of active and selective catalysts supported on titania for the one-pot hydrogenation of levulinic acid (a biomass-derived platform molecule) to γ-valerolactone, using internal source of hydrogen from formic acid (an equimolar co-product of production of levulinic acid).

The thesis is divided in 7 main chapters including a conclusion and perspectives.

After a general introduction, the **first Chapter** of about 45 pages concerns a literature review on the thesis topic. It starts with a short general overview of biomass as an alternative to fossil fuels. Then, it describes the production of levulinic acid and some of the many applications of levulinic acid and γ-valerolactone (GVL). Since many of the routes of transformation of levulinic acid actually involve GVL only one figure for selected pathways to value-added fuels and chemicals could have been shown for both platform molecules. A detailed literature overview of the catalytic systems for each of the two reactions under consideration (hydrogenation of levulinic acid and dehydrogenation of formic acid) is given, before giving different examples performing both reactions in similar reaction conditions in gas or liquid phase. The role of the support , the important role of basic sites, and the effect of Ru particle size in the studied reactions are highlighted in the following important paragraphs. The chapter ends with the description of the catalyst system to be explored in this work, *viz.* TiO_2-supported metallic catalysts by photodeposition. This literature review chapter is very well-documented. A little critiscism would be the numbering of the references who appear a few times in the chapter with different numbers.

The **second Chapter** of about 12 pages gives a concise overview of the support and Ru-catalysts preparation, characterization techniques, the experimental set-up for the liquid- and gas-phase experiments and analytical methods to analyse the reaction mixtures. The technique of measure of Total Organic Carbon (TOC) mentioned in Chapter 4 should also have been described. The information provided will allow someone skilled in the art to reproduce the experimental studies described in the thesis.

The **third Chapter** (7 pages) describes experimental studies on the characterization of TiO_2-based supports. Titanium oxide supports modified with different calcium contents (1-20wt%) and prepared using the sol-gel method were thoroughly characterized by X-ray diffraction and N_2 physisorption. It was demonstrated that introduction of calcium results in a distortion of TiO_2 lattice, an amorphisation, and the formation of a calcium titanate phase, resulting in a decrease in the crystallite size and a increase of the BET surface area. The measure of the isoelectric point suggests the formation of basic sites at the support surface for Ca-modified materials. TEM and SEM images complete the observations.

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In **Chapter 4** (27 pages), a very complete experimental and mechanistic study of the preparation of Ru-catalysts by photodeposition is discussed in great details. The experimental work reported in this chapter is abundant, highly dispersed nanoparticles are obtained, and systematic interpretation of the observed results is given. It includes the effect of the nature of the Ru precursor (chloride or acetylacetonate) on the Ru loading, the characterization of the as-prepared catalysts by TEM and XPS techniques, the control of the homogeneous growth of Ru particle size by adjusting the time of irradiation, the scale-up to 1 g of the 5wt%Ru/TiO_2 catalyst without losing the Ru dispersion. Among the interesting results, the influence and the pH of the precursor solution on the efficiency of the loading of the metal is noteworthy; it has been well analysed taking into account the speciation of ruthenium chloride species as a function of pH.

The hydrogenation of levulinic acid with formic acid as internal source of hydrogen is described in **Chapter 5** (18 pages). The Ca-modified materials prepared by wet impregnation or by photodeposition method were further characterized by TPR, CO-FTIR and TOF-SIMS analysis and screened in the one-pot reaction. This chapter also contains extensive characterization and testing of the catalysts to evidence the influence of the different features of the materials. With introduction of calcium, for both sets of catalysts, there is stronger interaction of Ru with the support, the strenght of CO adsorption is lowered, basicity is increased, and consequently the catalytic activity is improved. The photodeposition method providing much smaller size Ru nanoparticles furtherimproves the catalytic activity compared with the impregnation method. Enhanced activity of the Ca-modified catalysts and of the photodeposition method were further demonstrated in each separate reaction. Some data on the experimental accuracy would have been a plus since sometimes deviation between levulinic conversion and GVL yield represent up to 10%.

The results for the formic acid decomposition in gas phase using the catalysts prepared by impregnation and photodeposition are provided in **Chapter 6.** The interest of Ca-modified titania supports has also been confirmed, owing to the reduction of the intrinsic activity of the support forming CO and the basicity of the support facilitating the dehydrogenation reaction.

Chapter 7 ends the dissertation with a short conclusion and relevant perspective section.

The dissertation, written in English, is well structured and easy to read. The thesis work is a very good training in research because of the amount and variety of the experimental work and interpretation involved. The work conducted to many interesting results which were well reported and accurately analysed. The research has been published recently in good peer reviewed journals in Catalysis (ChemSusChem, Catalysis Today) and a third one is under review in a Material journal (Materials). In addition, the research has been presented at various scientific conferences.

As a conclusion, by the quality of the research described in this thesis and the innovative character of the results, that was much appreciated by the referee, it appears that Joanna Wojciechowska masters the topic and I strongly recommend that she can defend the work to obtain the degree of Doktor Nauk Chemicznych Chemia and Docteur en Chimie.

In my opinion, the reviewed thesis fulfills all requirements stated in Polish Law on Higher Education, in Article 13 of the Act of 14 March 2003 (Journal of Laws, No 65, item 595, with amendments

Villeurbanne, November 19, 2018

M Besson

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