Ph.D. thesis review.

Candidate: Swaraj Rashmi Pradhan.

Thesis title: *Nanoengineering of Thin Layers Of Semiconductor Photocatalysts In A Microreactor Environment For Lignin-Based Model Compounds Valorization.*

A thesis submitted for the degree of Doctor of Philosophy in the field of Chemical Sciences was prepared within the International Doctoral Studies in Chemistry of the Institute of Physical Chemistry (IPC), Polish Academy of Sciences (PAS), Warsaw (Poland) by Swaraj Rashmi Pradhan. The work was supervised by Juan Carlos Colmenares (Assoc. Prof. IPC, PAS).

In general, as a previous comment related to the structure of the thesis, it was correctly written (ordered in different parts, schemes, acknowledgements, etc. being the content written in the part of "*Table of Contents*"). So, it could be correctly read, by order, understood and finally evaluated.

The "*List of Publications*" (pages 6 and 7) includes important finished publications in prestigious international scientific journals, a patent and other important participations of the author. All these publications were found in their respective web location and examinated. High-quality research works were found.

The abstract (pages 8 and 9) includes a summary of the research work. The synthesis of novel thin layers (TiO_2, ZnO) with the adding of Fe, Cu, and Co was carried out. The synthesis of nanoparticles modified with metals via the sol-gel method was included. The catalysts were characterized by N_2 physisorption, X-ray diffraction analysis, UV-Vis diffuse reflectance spectroscopy, etc. The doping of titania with metals for the application in heterogeneous photocatalysis improved the visible light response of the TiO_2. High conversions were found (lignin-based compounds, benzyl alcohol oxidation) with good and interesting yields to the suitable products (aldehydes for example). As written correctly at the end of the abstract: *The findings offer an insight into the ligand-to-metal charge transfer (LMCT) complex formation, which was identified to be the main reason for the activity of synthesized catalysts under visible light.*

The *Table of Contents* and *Acronyms and Abbreviations* were controlled and were correctly structured giving enough and correct information about the content of the work.

Chapter 1.

The introduction contains enough and interesting information about the valorization of lignin being the figures 1 and 2 really useful for the understanding of the topic.

The author clarified about the advantages of using a micro-flow reactor compared to the batch system. The role of the sonication was also clarified and justified. In addition, as an important research point, the use of non-expensive metals (non-noble ones) in the catalysts led to a final cost-effective catalyst which many possibilities in photocatalysis. So, in this chapter, the research work was justified and reasoned in a correct way. As written in the point 1.3, the chapter 1 *introduces the background to this research topic, with specific focus on the*

research objectives and hypothesis addressed in the doctoral work. This last sentence is adequate.

Chapter 2

This chapter an useful source of information for the learning of other interested researchers/engineers/general public/etc. This chapter contains a work published (Molecules 24 (2019) 3315; doi:10.3390/molecules24183315). The Graphical Abstract is an adequate summary of the work. The entire review is an useful introduction to understand the reason and to have a good background for realizing the PhD dissertation-work. It was correctly structured and clear including a comprehensive literature review of microflow reactors and ultrasound approaches. The state of art methods adopted for the TiO_2 immobilization onto the surface of a microreactor were discussed correctly.

Chapter 3

This chapter is about the design and development of TiO_2 coated microflow reactor for photocatalytic partial oxidation of benzyl alcohol. The work was already published (Molecular Catalysis 486 (**2020**) 110884; doi:10.1016/j.mcat.2020.110884).

A photocatalytic microreactor was developed including the deposition of the catalyst on the internal surface of the microreactor. The catalyst was synthesized by using ultrasound-assisted TiO_2 deposition on the inner walls of a perfluoroalkoxyalkane microtube. The deposition experiments were carried out with commercial and sol-gel synthesized TiO_2. The oxidation of benzyl alcohol in flow was tested.

The experimental part described the materials, tests, synthesis and characterization parts with enough detail to understand the next part of the work (results and discussion).

Table 3.1 included the conversion and selectivity from benzyl alcohol to benzaldehyde.

An environmentally friendly process was used to coat the inner walls of a microtube with a thin layer of photoactive TiO_2 for the selective photocatalytic partial oxidation of a lignin-based model compound of benzyl alcohol to benzaldehyde without the use of oxidants.

The utilization of ultrasonication for the coating process implied a very high specific surface area (284 m^2/ g) for a metal oxide-based material, almost five times higher than that of commercial P25 material. This special synthesis also implied the different type of structure of TiO_2 (brookite, anatase, rutile).

In general, the work was written correctly and no fails were found. The work could be used by academics and industry. An offering of a quite more detailed scaling up of this reactor could improve the expectations to use this reactor in industry. However, it is a difficult task to evaluate the scaling up of a photocatalytic reactor.

Chapter 4

The work written in this chapter was also published in Catalysis Communications 162 (2022) 106375; doi: 10.1016/j.catcom.2021.106375. Thus, the work was reviewed and then published in a prestigious international scientific journal.

The work was revised part by part:

In the abstract, the information of the research was summarized exposing the catalyst used, the type of catalytic reaction and the main result. The catalyst was doped with different

metals. The Fe doped catalyst was the most active. It was correctly written and clearly understood.

In the introduction part, the information, background of the work was exposed generally for the learning and understanding of the readers, being an useful tool for the next understanding of the completed work. From the basis to the purpose of the work.

The experimental part contains enough information about the materials, tests and characterizations.

TiO_2 photocatalysts were also doped with different metals (Cu, Co, and Fe) having higher catalytic activity when the metal was included in the material. The use of a microflow reactor implied a higher yield to the suitable oxidation reaction compared to the use of a batch reactor. The use of Fe implies the use of a cheap and available metal.

In general, this work was done by using cost-effective catalyst by using a novel reactor and methodology. This reaction is an useful source of knowledge for researchers and industry based in the lignin-based compounds conversions. The benefits are clear from the research, academic and industrial point of view.

In Fig. 25 (page 78), the results are represented clearly, being the catalyst doped with Fe the most active having a good result even comparing with literature being also a novel procedure, test and catalyst.

Chapter 5

This part of the research was published in an impact journal. The work is about the use of TiO_2 catalysts (modified) for the valorization of lignin model based compounds. The catalyst activity was improved by the using of bimetallic systems (Fe-Au, Cu-Au). Au metal was

selected according to expecting higher conversions and taking into account the information provided by the literature as written in the introduction part. Details of the experiments, characterization and tests were written in the experimental part.

The use of a third or more metals should be considered, at least for future experiments by the research group and author.

Fig. 28 (page 87) includes information about the conversion rate, presenting interesting and high conversion and selectivity of the oxidation of benzyl alcohol to aldehyde type products. XRD, porosity studies are really useful for the understanding of the overall process. TEM images and other studies were useful to interprete how the active sites were involved in the reaction and distributed on the catalyst support. Figure 33 in page 55 was especially interesting *SEM and optical microscope image of sol-gel synthesized bimetallic TiO_2 and after deposition in PFA microreactor.* In general, the explanation, interpretation of the characterization part involving the results of the catalytic tests was clear, correct and useful for other researchers and industry. An important new result was obtained to understand the activation mechanism of the catalyst under light: the LMCT complex formation of TiO_2 with the methoxy (OCH_3) and OH groups.

Chapter 6 – Research Summary

In this part, a summary of the overall work was included. This part is usable as one scheme for the understanding of the work. An important part, for each chapter and the work were the hypotheses exposed (representing challenging results):

Hypothesis 1: Photocatalytic activity of the catalyst can be improved for lignin-based model compounds (benzyl alcohol, BnOH) oxidation in microflow over the batch system with better product yield.

This hypothesis is correct, the results of a batch reactor and microflow reactor (created in Polad) are in agreement with the hypothesis.

Hypothesis 2: Using ultrasound for surface modification can further help in better deposition of catalyst onto the wall of the PFA tube.

The hypothesis is in agreement with the experimental results. The conditions parameters of the reactor were optimized (length of tube, ultrasonic power, and time of deposition for coating of catalyst and photocatalytic). As written by the author: *the higher availability of the active sites in this wall-coated microreactor helped in better conversion.*

Hypothesis 3: Introduction of transition metal (metal-containing; e.g., Cu, Fe, Co) and co-catalytic amount of noble metal (bimetal containing; e.g., Cu, Fe with Au) to improve the photocatalytic activity of the synthesized catalysts.

The introduction of transition metal and noble metal implied the catalytic activity. All the results were obtained in agreement with the hypothesis.

Hypothesis 4: Alcohol can be chemosorbed over TiO_2 and form a visible light-active ligand-to-metal charge transfer (LMCT)-complex involving the methoxy (OCH3) and hydroxy (OH) group of alcohols with TiO_2.

This information will be useful for next scientific works by the authors or other researchers who will continue with similar scientific topics implying a key mechanism to optimize the catalytic activity which could also help to the industry to the valorization of lignin based raw materials.

Addition information was included, useful for the understanding of the reactor and processeses. Table I.9 could be added with some more quality of the image. Anyway its content is enough readable.

Concluding remarks

The dissertation, scientific explanation and details in the work are of a high quality, correctly and clearly written. The thesis fulfills the criteria for PhD dissertation for the Polish normative (Article 187 of the Act of July 20, 2018 Law on Higher Education and Science). The candidate should continue with the next steps of the PhD process.

Regarding to the previous comments, I would recommend the awarding of Swaraj Rashmi Pradhan for the academic degree of PhD with the maximum distinction.

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