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Review report on the PhD thesis of Swaraj Rashimi Pradham entitled „Nano-engineering of thin layers of semiconductor photocatalysts in a microreactor environment for lignin-based model compounds valorization."

The dissertation presented for defence by Mrs Swaraj Rashimi Pradham is an interesting contribution to the development of sustainable processes of lignin valorization through oxidative depolymerization to produce value-added chemicals. The major challenge is to enhance the reactivity and selectivity of the chemical reactions. In this regard, the photocatalytic process has been proposed, emphasizing the work on the synthesis and immobilization of photocatalytic materials and the application of fluidic microreactors in selective photooxidation reactions. Several important issues affecting the photocatalyst performance and microreactors capability to perform photooxidation reactions are addressed with a focus on the development of photocatalytic systems, synthesis of semiconductor materials active under UV-vis light and their immobilization on the internal surface of perfluoroalkoxyalkane microtubes of the photoreactor. Photomicroreactors have the potential to overcome the difficulties associated with conventional batch photocatalytic reactors. Thus, this thesis addresses the highly relevant and vital areas of current photocatalytic research.

The presented doctoral dissertation was conducted under the supervision of Professor Juan Carlos Colmenares Quintero at the Institute of Physical Chemistry, Polish Academy of Sciences in Warsaw, and it correlates well with the research activities carried out successfully in this team.

The reviewed PhD thesis is well-structured and divided into five coherent chapters. It is organized as a collection of four scientific articles published in international journals. The IF of these works range from 3.27 to 5.06, and the total IF is equal to 16.63. The PhD student is the first author of all of them. The publications included in the dissertation were reviewed by experts, and their high scientific level was already confirmed.

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The PhD dissertation has 124 pages and is written in English. It consists a list of scientific activities, summaries in Polish and English, a list of acronyms and abbreviations, the introduction, theoretical background, research hypothesis and objectives, organization of the thesis, future outlook, references and attachments in the form of reprints of articles selected as the basis for PhD procedure, as well as statements of co-authors of these publications. Therefore, this PhD dissertation meets the formal requirements. The reader is introduced to the subject of the thesis by the Chapter 1 - “Introduction”. This chapter consists of 15 pages and provides a good background for understanding the research problem. The scope of the PhD thesis is mainly focused on (1) preparation of thin layers of photocatalyst by ultrasound technique on the internal wall of fluoropolymer microtube reactor for selective oxidation of lignin-based model compounds, (2) evaluation of the photocatalytic activity in batch and microflow system in reaction of benzyl alcohol oxidation, and (3) understanding the effect of TiO_2 modification with transition metal species and the role of surface hydroxy (OH) groups of TiO_2 in LMCT-mediated visible light activation of TiO_2.

According to Art. 187 of the Act of 20 July 2018, The Law on Higher Education and Science: “The subject matter of the doctoral dissertation shall be an original solution to a scientific problem or in terms of the application of results of own scientific research in the economic or social sphere, or an original artistic achievement”. In this regard, I am not convinced that it is justified to include a review publication in the monothematic cycle of publications. In my opinion, the review article on “Designing microflow reactors for photocatalysis using sonochemistry” provides an overview of the current state of knowledge and therefore, should be a part of the research background presented in Chapter 1, not a part of the results presenting the scientific achievements of the PhD candidate within the dissertation.

The core research work of the PhD thesis can be found in the third, fourth and fifth chapters. The scientific novelty presented in this dissertation undoubtedly lies in developing a simple ultrasound-assisted deposition method for the immobilization of photocatalysts on the internal surface microtubes of the photoreactor ([P2] - described in Chapter 3). This microreactor was used for the selective oxidation of benzyl alcohol towards benzaldehyde. It is worth emphasizing that the novelty of research in this field is confirmed by the patent application on “A flow microreactor system and the way of conducting photocatalytic processes using it” (P.430411, 2019), co-authored by the Candidate.

Light source is one of the most important components in photocatalytic systems, which through the variation of energy and intensity of photons, can influence the reactivity and selectivity of the photocatalytic reactions, tune the properties of the photocatalyst, and alter the reaction mechanism. Therefore, the synthesis and application of photocatalysts that would be active at the entire visible light spectrum were key points in developing sustainable photochemical processes within the reviewed doctoral dissertation of Mrs Swaraj Rashimi Pradham described in publications [P3] and [P4] described in Chapters 4 and 5. In publication 3, to enhance the photocatalytic activity modification with Fe, Cu, and Co of TiO_2 inside fluoropolymer-based microcapillaries was proposed for the oxidation of benzyl alcohol under UV-visible light irradiation. Furthermore, the photocatalytic conversion of benzyl alcohol in the batch and microflow reactors for selected photocatalysts was compared.

The research work on improving the activity and selectivity of the photocatalyst was continued, and the results are described in publication 4, with a focus on the comparison of selective oxidation in batch and microfluidic reactors for TiO_2 modified with bimetallic Cu-Au and Fe-Au photocatalysts. It was found that the addition of a second metal markedly improved the selectivity of benzyl alcohol oxidation towards benzaldehyde.

Taking into account the obtained results and discussion as the most valuable in the present work, I would like to highlight the following:

1. Development of ultrasound-assisted deposition method for the immobilization of photocatalysts on the internal surface microtubes of the photoreactor;
2. Successful application of microfluidic and batch photocatalytic systems to valorize lignin-based model compounds by exploiting photocatalysts with high activity and selectivity under UV and vis light;
3. Demonstrating the effect of TiO_2 modification with mono- and bimetallic particles on benzyl alcohol conversion and benzyl aldehyde selectivity
4. Demonstrating the effect of the ligand-to-metal charge transfer by the formation of the complex between the methoxy and hydroxy groups of alcohol and TiO_2 on the activation photocatalyst under visible light.

The specific questions and remarks addressed to the doctoral dissertation are given below.

1. What is the opinion of the PhD student about the repeatability of the photooxidation reaction in the microfluidic system using the same layer of the photocatalyst?

2. Despite the improved conversion rate observed for all the photocatalysts in microflow photocatalysis for TiO_2 modified with metal species, higher selectivity towards benzaldehyde in a batch system was noticed. Has the Candidate compared light intensity in both photocatalytic systems and radiation distribution inside the reactors? Have you observed any abrasion of the photocatalyst layer or microreactor clogging during the oxidation processes? Whether the photocatalyst content was different in both systems?
3. In the entire text of the dissertation, the word *catalyst* with respect to the active materials should be replaced with the word *photocatalyst* regarding the described results of photocatalytic selective oxidation of benzyl alcohol to benzaldehyde.
4. I would like to ask the PhD student to comment on the method of TiO_2 modification (surface or volume) described in Chapters 4-5. Doping of TiO_2 suggests the replacement of ions in the crystal lattice (or other changes in the crystalline lattice) but not obtaining semiconductors with deposited metallic species on the surface.

Summarizing, the reviewed doctoral dissertation concerns important and current topics in the preparation, characterization and application of TiO_2-based photocatalysts for selective oxidation of benzyl alcohol in microflow and batch systems under UV and vis light. The method of research, its execution, the form of presenting the results and their analysis and discussion prove the high scientific and research maturity of Mrs Swaraj Rashimi Pradham. In this regard, in my opinion, her doctoral dissertation meets all conditions specified in Art. 187 of the Law on Higher Education and Science in Poland of July 20, 2018 (in Polish: Prawo o szkolnictwie wyższym i nauce, Dz.U. z 2018 r. poz. 1668 ze zm.) and I request the Scientific Council at the Institute of Physical Chemistry of the Polish Academy of Sciences to admit the PhD student to further stages of doctoral dissertation defense.

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