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Review of PhD thesis written by Miss Ayesha Khan entitled

" *Titania-based heterogeneous photocatalysis for the selective oxidation of biomass-derived platform chemicals*".

The subject of PhD dissertation, which was undertaken by M.Sc. Ayesha Khan is very interesting and brings some new insights on the utilization of biomass towards gain of some value-added products. The PhD student in the scientific approach applied photocatalytic process for conversion of some biomass derived products such as hydroxymethylfurfural (HMF) and benzyl alcohol (BnOH) to the industrially meaning compounds: 2,5-diformylfuran (DFF) and benzaldehyde (Bnald), respectively. In the introduction the fundamentals of the photocatalysis have been discussed, high attention was focused on the properties of titanium dioxide, which is still the most commonly used photocatalyst in many areas of applications. Presentation of the state of art in the subject related to the selective oxidation of HMF and BnOH have been carefully performed, including mechanisms of their transformation and factors affecting both, selectivity and conversion degree to the preferred products. The PhD student in a very logical way conducted the discussion on the properties of TiO_2 towards extending its activity with utilization of solar light. Application of TiO_2 with using visible light has a great meaning for obtaining high selectivity in the photocatalytic reactions to the defined products. Contrary to this, under UV light irradiation, there is an abundance formation of hydroxyl radicals, which expose high oxidation potential and non-selective reactivity with organic compounds.

M.Sc. Ayesha Khan based on the literature survey formulated two general assumptions referring to the photocatalytic oxidation of HMF and BnOH. The overall target was focused on the preparation of titania nanocomposite with enhanced absorption of the visible light. In the first attitude the PhD student assumed, that 5-hydroxymethyl furfural could adsorb on the titania surface to form a LMCT (ligand-to-metal charge transfer) complex, which could act as a

sensitiser and enabled the selective oxidation of HMF to DFF under visible light. It was stated, that the presence of hydroxyl groups in HMF and their interaction with titania surface had a great impact on the sensitization of titania via LMCT complex formation. Additionally, high surface area of titania could increase the number of active sites available for HMF adsorption. To verify this hypothesis, Ms. Ayesha decided to conduct a series of reaction with titania-LMCT complex having different amount of hydroxyl groups and did fluorination of titania to replace hydroxyl groups with fluoric ions. By applying different analytical techniques, such as Raman and FTIR Spectroscopies, XPS, UV-Vis/DR Spectroscopy and others tried to elaborate mechanism of HMF selective oxidation to DFF.

In the second research hypothesis, PhD student was focused on the preparation of nanocomposite, consisted of chitosan-lignin biopolymer and TiO_2. It was stated, that formulation of composite containing chitosan with lignin would bring some unique properties, which in combination with TiO_2 could be utilized for TiO_2 photosensitisation under visible light and selective oxidation of BnOH do Bnald. Additional the role of chitosan in doping nitrogen to TiO_2 and increase its visible light response was investigated. The proper methods of materials characterization were used, such as N_2 physisorption, XRD, Raman, FTIR and UV-Vis/DR Spectroscopies and XPS.

Arrangement of the dissertation is a classical, it consists of abstract, introduction, research hypothesis, experimental part with following presentation of the obtained results and discussion. Finally there are conclusions, references and appendix. At the beginning PhD student also demonstrated the list of published papers and funding obtained for realisation of this research work.

Presentation of the obtained results is clear, all the conclusions are validated by the obtained results from the performed measurements. Conducted discussion on the obtained results is very logical and substantive correct.

All the figures and tables are readable, however some of them could be improved, because sometimes the used font inside the figure is very small and too many graphs are loaded into the one diagram.

Presented research work by M.Sc. Ayesha Khan is an original and introduces some new attitudes to photocatalysis operated under visible light. Although, in most cases the quantum yield of the photocatalytic processes carried out under visible light will be less efficient than under UV, high selectivity to the preferable reaction products could state a great advantage in course of using visible light.

M.Sc. Ayesha Khan proposed two solution for driven visible light photocatalysis: preparation of LMCT complex and organic composite with TiO_2, which expose absorption of visible light. Both solutions gave positive results. I would like to applause Ms. Ayesha Khan for elaboration the mechanism of HMF conversion to DFF through LMCT complex and very good interpretation of the data obtained from the analytical measurements. I appreciate also high impact of Ms. Ayesha research work related to the explanation the visible light activity of the composite consisted from biopolymer (chitosan mixed with lignin) and TiO_2. I have also a question to this part of work. Did you observe any adsorption of benzyl alcohol on the surface of composite T/CL? In Table 7, Entry 29 there is written, that any conversion of benzyl alcohol wasn't noted. Should it be understood, that any transformation of BnOH to Bnald did not occur or it was not observed any change in the initial concentration of BnOH at the presence of T/CL in a dark? I am interested in the impact of the adsorption of BnOH on the surface of T/CL complex on its photocatalytic conversion. Could you explain this issue during your PhD defense?

In general I greatly appreciate the research work performed by M.Sc. Ayesha Khan, which was introduced in this dissertation and her scientific achievements. Ms. Ayesha is a co-author of 4 published papers, one more has been already accepted and another was submitted to the review. All the papers are published in very prestigious journals with high impact factor, such as: Applied Catalysis B with IF=19.503, ChemSusChem (IF=8.928) or ACS Sustainable Chem. Eng. (IF=5.95). Ms. Ayesha is 4 times the first author in these published papers and undoubtedly had a great contribution in the composing of the manuscripts.

To sum up I state, that submitted for evaluation dissertation written by M.Sc. Ayesha Khan meets the criteria contained in the article 187 of Act "The Law of Higher Education and Science" issued in July 20, 2018 year in Poland, so I apply to The Scientific Council of the Institute of Physical Chemistry, Polish Academy of Sciences in Warsaw for permission of PhD student to follow the further stage of the doctoral defence.

Moreover, in my opinion the dissertation submitted by M.Sc. Ayesha Khan should be distinguished and I submit a request to The Scientific Council of the Institute of Physical Chemistry, Polish Academy of Sciences in Warsaw to consider possibility of distinguish this dissertation.

The substantial reasons are as follows:

- originality of the research work
- very good interpretation of the obtained results
- high quality scientific discussion

- demonstration new possibilities of the photocatalytic processes conducted under visible light towards obtaining some valuable chemicals from biomass with high selectivity
- appreciable research published output