UNIVERSIDAD D CÓRDOBA

Departamento de Química Orgánica
Facultad de Ciencias

Cordoba 28 October 2021

EVALUATION THESIS DISSERTATION, AYESHA KHAN MSc

I am pleased to provide my comments after examination of the thesis entitled "**Titania-based heterogeneous photocatalysis for the selective oxidation of biomass-derived platform chemicals**" presented by Ayesha Khan MSc as PhD candidate.

The manuscript has a very good structure in terms of kind-of-chapters (four plus one including the conclusions and future perspectives together with some appendices) and content, dealing with the relevant concept of titania-based systems for photocatalytic oxidations (benzyl alcohol and HMF).

The English is very good generally speaking (although it could benefit from some polishing of minor corrections in the final version, a few typos can be found in text and references) and the whole writing is overall clear and easy to understand.

The general introduction sets the thesis in context and provides an excellent starting point on the topic of Titania photocatalysts (including composites and doping) as well as conversion of biomass-derived platform molecules (benzyl alcohol, HMF) into valuable

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chemicals. This chapter is backed up by a highly comprehensive literature revision on the aforementioned topics (207 references). The chapter also provides an overview from different mechanisms to general considerations and focusing on the design of titania-based photocatalysts for various photo-oxidations.

The main goals of this doctoral Thesis, in line with the principles of sustainable and green chemistry as well as research hypotheses (for the design of photocatalysts and biomass conversion) have been clearly defined after the Introduction, right before the experimental section.

The experimental section provides a significant body of data related to synthesis of materials (at least five types of titania-based systems) and sample characterization as well as reaction conditions for the investigated photocatalytic experiments. A large number of photocatalytic tests have been performed and catalytic activity and stability results obtained were compiled in a good number of Tables and Figures (mostly in the Results and discussion section) as part of this whole thesis.

Last, but not least, the Results and discussion section deals with two separate parts 1) on the LMCT-sensitization of titania and photocatalytic conversion of HMF, including relevant (and not so extended) calculations on apparent quantum yields and a plausible reaction mechanism and 2) on the design of titania/chitosan-lignin nanocomposites for

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benzyl alcohol selective photo-oxidation including apparent quantum yield calculations and stability and reusability experiments. While the first part is largely innovative and results are of high relevance and quality, the second part (still relevant) has only certain innovative elements since the conversion of benzyl alcohol has been extensively investigated in recent years and only moderate activity is obtained for the visible light conversion of benzyl alcohol (results need to be improved). In any case, the obtained results have been well explained and supported by nice images and Tables that overall showcase an excellent work performed by the PhD candidate.

The manuscript ends with a conclusions and future perspective section which reads well but perhaps could have been better to have a more compact writing (based on bullet points) also for the perspective and further research which is rather short.

Overall, this Thesis stands out in the amount and quality of work that has been performed by the candidate in a multidisciplinary project. The work ranges from technological (photocatalysis) and characterization aspects to photocatalytic testing and analysis of the reaction mixtures. This type of work can only be completed in a center that is well equipped and has experience in house in catalyst characterization and catalyst screening.

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In addition to these, there is a list of publications coauthored by the student (5 excellent published papers, one more pending publication in an international journal), highlighting the contributions to the scientific community, with results that have been already validated by peer experts in the topic).

In conclusion, this is an excellent scientific conducted research that has required relevant efforts from the candidate, and consequently recommended for a PhD degree subjected to successful completion of the final examination/defense. The doctoral dissertation meets the conditions specified in Article 187 of the Act of July 20, 2018 Law on Higher Education and Science (Journal of Laws of 2018, item 1668, as amended). Additionally, based on the overall quality of work as well as published results (almost everything including 5 publications in the top scientific journals in the field), the reviewed work deserves distinction from the point of view of this evaluator. Most results for the Thesis stand out as top in the field (as recognized by peers in the evaluation of published work).

With very best wishes for the applicant and her future PhD defense

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