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Candidate: Abdul Qayyum, M.Sc.
Thesis Title: Titania-based photocatalysts prepared by sonication in understanding the selective oxidation of lignin-inspired molecules to phenolics.

Reviewer's Report:

The candidate has embarked on a major endeavor to address the predominant limitations of known material Titania namely the fast recombination of photogenerated electron-hole pairs, low porosity, and an indiscriminate photoreactivity that limits its potential appliances for selective catalytic transformations. Interestingly, ultrasound (US), an alternative energy activation tactic, has been astutely deployed to synthesize novel titania-centered photocatalysts to circumvent the above-mentioned weaknesses. The ensued nanomaterials have been assessed and exploited for the selective catalytic conversion of lignin-based exemplary entities. The assorted chemical and physical effects like de-passivation, formation of hydroxyl free radicals and increased mass transfer aspects could be easily realized using this strategy; higher localized temperature and pressure being attainable due to cavitation phenomenon. The research study concluded that deployment of ultrasound at optimized amplitude and frequency for the duration of the synthesis can bring about the formation of preferred products via highly selective redox photocatalytic operation. The sonophotocatalytic investigations disclosed that among various fabricated samples, 22kHz-3 displayed superior selective sonophotocatalytic conversion of 2-phenoxy-1-phenylethanol (PP-ol) than a simple photocatalytic procedure; highest photocatalytic conversion of benzyl alcohol (75 %) to benzaldehyde (67 %) was discerned relative to all other US-aided fabricated photocatalysts. Interestingly, this recyclable catalyst could be redeployed five times without its noticeable leaching, an important attribute for sustainability.

The thesis is clearly organized among five chapters; traditional arrangement of the dissertation, comprising an abstract both, in English and Polish, overview, research proposition,

investigational segment with ensuing report on the acquired conclusions and discussion. Finally, there are additional items like future perspective, conclusions, and references in that order. At the commencement, the candidate research scholar has presented particulars of support gained for the realization of this investigation, the list of articles published, list of abbreviations and units used throughout.

The appearance of the achieved outcomes is well-defined, each and every one of the deductions are authenticated by the attained end results from the performed measurements; deliberations on the secured results is rational and noticeably accurate. All the tables and figures are legible, though some of them could be tweaked, this reviewer could identify few misspelled words (e.g., 'photocatalyst' on page xvi).

The opening chapter offers the introduction to the research investigation where the usage of titania and ultrasound-assisted protocols are presented among the discussed heterogeneous catalysts and details pertaining to lignin valorization (Chapter 1). The next chapter 2 presents the underlying hypotheses of the study (four in total) and their association among the corresponding aims and its linkage to the opening topic in chapter 1. However, being related, the first three hypothesis could have been combined. Chapter 2 offers details regarding the usage of different frequencies and amplitude and the photocatalytic selective alteration of β-O-4 linkage bearing lignin-centered diaromatic entities to the equivalent high value phenolics. This includes the impact of calcination on the photocatalytic operation and crystallinity aimed for greener synthesis strategy. In Chapter 3, the research scholar explains details of various catalysts prepared including their physicochemical descriptions followed by the photocatalytic activity assessments.

Chapter 4 is the main component of the thesis that covers almost all the experimental evidences, detailed descriptions and discussion pertaining to the performed work. Besides the deployment of ultrasound in the synthesis of the titania catalyst, this tactic was also explored not only for the selective oxidation of benzyl alcohol but also for the 2-phenoxy-1-phenylethanol (PP-ol). I wish the candidate could have identified this abbreviation in the text of the thesis besides the initially offered list of abbreviation at the outset; reader has to hunt for this PP-ol abbreviation otherwise. The outcomes of the sonophotocatalytic activity for the identified active catalyst, 22kHz-3, revealed a 46 % conversion of PP-ol, which is inferior to the conversion (57 %) exhibited by regular photocatalytic process. However, the 46% yield of the aimed product, Ph-CHO, attained was better than the 42% yield realized from the photocatalysis alone (6 h). The vital message has been the 96% of the aromatic balance, which is higher than the 85% aromatic balance (84.8 %)

acquired in photocatalytic activity. Interestingly, this increment in the aromatic balance implied the reduction of side reaction thus diminishing the realization of potential byproducts, which often lead to non-selective mineralization of the aromatics.

The final abbreviated chapter 5 offers the summary of aforementioned endeavors and future perspectives on this research problem. Essentially, the conclusion of the sonophotocatalytic studies has been that the 22kHz-3 sample exhibited higher sonophotocatalytic selective rupture of Cα-Cβ bond of PP-ol culminating in increased aromaticity of the reaction relative to the general photocatalytic studies. The plausible mechanism could be established by conducting an array of photocatalytic trials via the addition of $AgNO_3$, KI, *t*-BtOH and BQ as e^-, h^+, OH and $O_2^{\bullet-}$ scavengers, respectively which affirmed the presence of photogenerated h + to be the main reactive species. The greener aspects of the whole operation could be identified when the introduced method with catalyst, secured via ultrasound-assisted protocol without calcination, displayed higher photocatalytic selective conversion of PP-ol to the corresponding products, thus saving on energy consumption.

The rationale for suggesting future research in this domain included exploration of other metal oxides including composites utilizing less demanding (low energy) sonication, possibly using the abundant sunlight. The premise to utilize real-world lignin-centered waste from paper and pulp industry is an enticing suggestion, which if coupled with other options such as coated catalyst on the inner walls of the microreactor in a continuous flow set-up, could pay gratifying dividends.

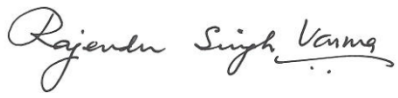
During the PhD defense, the candidate may be asked to clarify or amply the details pertaining to:

(i) Optical properties of photocatalysts (for instance, principles, how to measure, key interpretation, as they relate to photocatalysis);
(ii) Crystallographic details (for example, principle, calculation, etc.); and
(iii) Analytical methods for the reaction assessments (like, GC, GC-MS).

To recapitulate, I state that the dissertation presented for evaluation as written by Abdul Qayyum M.Sc. meets the standards encompassed in Article 187 of the Act of July 20, 2018 Law on Higher Education and Science (Journal of Laws of 2023, item 742, as amended) in Poland, hence the Scientific Council of the Institute of Physical Chemistry, Polish Academy of Sciences in Warsaw, is requested for approval of PhD candidate to adhere to the next phase of the doctoral defense.

Furthermore, in my judgement the submitted thesis by Abdul Qayyum, M.Sc. ought to be considered in distinguished category. The strong reasoning for that is apparent from the six papers published by Abdul Qayyum in good journals, and equal number of presentations in international meetings. Besides, the ample discussion and the rationale interpretation of the results and proposed exploratory future possibilities are commendable efforts and hence I invite the Scientific Council of the Institute of Physical Chemistry, Polish Academy of Sciences in Warsaw to deliberate option of bestowing 'distinguish' stature to this thesis.

Signed: Rajender S. Varma



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