Poitiers, January 24th, 2024

Object: report on the PhD manuscript of M. Abdul Qayyum

To whom may it concern,

M. Abdul Qayyum reports a PhD manuscript titled "*Titania-based photocatalysts prepared by sonication in understanding the selective oxidation of lignin-inspired molecules to phenolics*" to get the doctor diploma from Warsaw-4-PhD School in Natural and BioMedical Sciences at the Institute of Physical Chemistry, Polish Academy of Sciences.

In his manuscript, M. Abdul Qayyum reports in a very comprehensive way the main scientific results he got during his PhD supervised by Prof J. C. Colmenares Quintero. The PhD work of M. Abdul Qayyum concerns the exploration of ultrasound for the synthesis of TiO_2-based photocatalysts, which were then assessed in the photocatalytic oxidation of aromatic alcohols. Oxidation of benzyl alcohol to benzaldehyde was first used as a model reaction to assess the catalytic performances of the as-prepared photocatalysts and also to compare them with TiO_2 photocatalysts prepared by a more conventional route. Later, M. Abdul Qayyum selected the best photocatalyst, in terms of activity and selectivity, to investigate a more challenging reaction, *i.e*. the oxidation of a model lignin, a reaction for which innovation is expected. During the writing of his PhD manuscript, M. Abdul Qayyum has followed a clear scientific strategy. First of all, the impact of different ultrasonic parameters, in particular the frequency and the amplitude, on the morphology, the porosity, the basicity, the surface water coverage or hydroxylation, band gap, among many other photocatalyst features, have been investigated in details using various equipment (XRD, XPS, microscopy, etc.). From this study, M. Abdul Qayyum showed that a TiO_2 prepared at 22 kHz and with an amplitude of 30 µm

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yielded the best photocatalysts in terms of activity and selectivity. This TiO_2 prepared by ultrasound even surpassed the catalytic performances of a commercial photocatalyst such as P25 for instance. Although different structural and textural aspects may explain this superior catalytic performance, the amorphous nature and the very low amount of anatase phase in the sonochemically-prepared TiO_2 is more likely to be responsible for this observation. The recyclability of sonochemically-prepared TiO_2 photocatalysts has been also successfully demonstrated, thus validating the preparation method explored by M. Abdul Qayyum. If the impact of ultrasound on the activity of sonochemically-prepared TiO_2 is clear and well described, impact on the reaction selectivity is however less obvious to understand, but this remark does not change the scientific quality of the work.

The manuscript follows a clear scientific line and is divided into four main sections.

The first section is an introduction on biomass followed by a brief state of the art on the preparation of photocatalysts, with a focus on TiO_2 materials, and sonochemistry which is at the heart of the work. This part is helpful for the reader, in particular to understand the scientific strategy followed by M. Abdul Qayyum and the positioning of the work within the state of the art.

The second section demonstrates that utilization of a low amplitude during ultrasonic preparation of TiO_2 leads to materials with a high porosity, pore volume and surface area, features which have been linked to the catalytic performances. This section led M. Abdul Qayyum to select an amplitude of 30 µm (at 22 kHz) as an optimal value to get a TiO_2 with the best catalytic performances (assessed in the oxidation of benzyl alcohol to benzaldehyde).

In a third section, effect of the frequency was investigated, going from 22 to 80 kHz. As a general trend, increasing the frequency led to a decrease in the textural properties of the TiO_2 material, a result also linked with a decrease in the catalytic performances. Hence, 22 kHz was selected as the optimum frequency for the preparation of TiO_2. Here again, whatever the applied frequency, increasing the amplitude was found detrimental for the catalytic performances of sonochemically-prepared TiO_2. This result was also confirmed by increasing again the frequency to 500 kHz.

Finally, in a last section, the best preparation method (*i.e.* 22 kHz, 30 µm amplitude) was selected to explore the photocatalytic performances of TiO_2 in the selective cleavage of Cα-Cβ bond of PP-ol, a model of lignin. By means of counter experiments, in particular using different scavengers, M. Abdul Qayyum demonstrated that the photogenerated h+ are more likely to be the main reactive species involved in the reaction mechanism.

In conclusion, it makes no doubt for me that M. Abdul Qayyum did a work of a high quality, which has opened very promising perspectives. He demonstrated that he was able to manage a research project, to address the correct scientific questions and to work in a scientifically logical way. Beside a solid scientific expertise acquired in the field of ultrasound and photocatalysis, he used a lot of characterization methods which will be undoubtedly useful for his future career. In my opinion, M. Abdul Qayyum gathers all the scientific qualities to become a doctor and, for all these reasons, I give a favorable opinion for the defense of his PhD work.

Feel free to contact me if you need any additional information,

Sincerely,

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