Rebuttals on the comments made on our manuscript entitled "Comparative catalytic performance study of 12-tungstophosphoric heteropoly acid supported on mesoporous supports for biodiesel production from unrefined green seed canola oil"

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The authors thank the Reviewers for excellent comments on the manuscript. The itemized response to each comment is given below and the manuscript is modified accordingly. These modifications helped to improve the quality of the manuscript. The discussion added to the manuscript are based on the Reviewers' comments and are highlighted in the rebuttals below.

Reviewer Comments:

Reviewer 2;

1. The authors tried to improve their manuscript and new references have been added. However, the characterization of the acidic properties is still very lacking and the manuscript cannot be accepted in the current form. The quality of figures 6 (a, c) is very poor, the signals are really noisy.

Our response: Regarding the acidic properties, the total acidic quantity (µmol/g) of the catalysts were determined using NH3-TPD analysis. The Pyridine-FTIR was used to indicate the presence of both types of acidic sites (Bronsted and Lewis), however, it was a qualitative analysis in our case as we do not have access to the quantitative analysis equipment to determine the amount of Bronsted and Lewis acidity. Similar procedures were used by Hoo et al. [34], and Sudhakar et al. [35] to determine and discuss catalysts' acidity.

[34] P. Y. Hoo and A. Z. Abdullah, "Direct synthesis of mesoporous 12-tungstophosphoric acid SBA-15 catalyst for selective esterification of glycerol and lauric acid to monolaurate," Chem. Eng. J., vol. 250, pp. 274–287, 2014, doi: 10.1016/j.cej.2014.04.016.

[35] P. Sudhakar and A. Pandurangan, "Heteropolyacid (H3PW12O40)-impregnated mesoporous KIT-6 catalyst for green synthesis of bio-diesel using transesterification of non-edible neem oil," Mater. Renew. Sustain. Energy, vol. 8, no. 4, pp. 1–11, 2019, doi: 10.1007/s40243-019-0160-1.

Figure 6 is removed due to the poor quality, however, the analysis of total acidity of the support materials and catalysts using NH3-TPD are given in Table 3 in the revised manuscript (please see lines 271-279 on pages 10 and 11), which is given below:

Based on the TPD results (Table 3), the acidity amount of γ-Al_2O_3, MAP and MAS were obtained 795 µmol/g, 1015, and 922 µmol/g, respectively. HPW immobilization on support materials led to an acidity increase of 9.5 % for HPW/MAS and 5.8 % for HPW/MAP. Accordingly, HPW/MAS represented higher acidity related to the HPW/MAP and HPW/γ-Al_2O_3. The acidity of HPW supported catalysts were also analyzed after the first recovery from the reaction which indicated no significant decrease in their acidity for HPW/γ-Al_2O_3 (< 5%), HPW/MAP (< 1%), HPW/MAS (< 3%) [32, 39].

Table 3. Acidity of support materials and HPW supported catalysts obtained from NH_3-TPD.

Catalyst	Total acidity (µmol/g)	100-300 °C	300-500°C	500-600°C
γ-Al_2O_3	922	354	429	139
HPW/γ-Al_2O_3	913	328	480	105
R*- HPW/γ-Al_2O_3	876	332	453	91
MAP	795 ± 8	283	220	292
HPW/MAP	841	245	348	248
R*-HPW/MAP	835	292	302	241
MAS	1015 ± 16	270	276	469
HPW/MAS	1111 ± 13	466	448	196
R*-HPW/MAS	1082	449	565	68

*R-Recovered.

[32] P. Y. Hoo and A. Z. Abdullah, "Direct synthesis of mesoporous 12-tungstophosphoric acid SBA-15 catalyst for selective esterification of glycerol and lauric acid to monolaurate," Chem. Eng. J., vol. 250, pp. 274–287, 2014, doi: 10.1016/j.cej.2014.04.016.

[39] D. P. Sawant, A. Vinu, N. E. Jacob, F. Lefebvre, and S. B. Halligudi, "Formation of nanosized zirconia-supported 12-tungstophosphoric acid in mesoporous silica SBA-15: A stable and versatile solid acid catalyst for benzylation of phenol," J. Catal., vol. 235, no. 2, pp. 341–352, 2005, doi: 10.1016/j.jcat.2005.08.010.

2. The authors revised the experimental part, specifing that :"the spectrum for the desorption of NH3 was recorded with TCD with temperature rise from100°C to 700°C for the evaluation of the NH3 desorbed and total acidity" but the signals are stopped at 600 °C. On the other hand considering that supported HPWs have been calcined at 450 °C, a TPD process at temperature > 450 °C doesn't make a sense, unless the authors investigate the thermal stability of their samples at T > 450 °C.

Our response: We thank the Reviewer for this comment. The thermal stability of the catalysts were determined using TGA showing that supported catalysts are stable up to 600 °C. Based on this, the calcination was only carried out at 450 °C, however due to the stability of catalyst up to 600°C, TPD analysis was carried out in the range of 100°C to 600 °C. Maximum temperature for TPD is changed to 600 °C, which was previously mentioned 700 °C by mistake (Please see lines 263 and 270 on page 10).

3. Other point: XRD patterns are very poor, except that one for HPW. Please, register again and correct the strange behaviour at 2 theta < 10°.

Our response: We determined the structure of the catalysts in wide angle during XRD study in the range of $10° < 2\theta < 90°$, and scanning of $2\theta < 10°$ was not considered.