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5-Hydroxy Methyfurfural (5-HMF) Production From Biomass Through Heterogeneous Catalysis Based On Heteropolyacids

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Heteropolyacids, which are inexpensive and non-toxic strong acids, have been studied as homogeneous catalysts. However, the possibility of supporting them for use as heterogeneous catalysts has been rarely explored. In this work, a series of materials based on 12-tungstophosphoric heteropolyacid heterogenized on zirconia and niobia were prepared and applied as heterogeneous acid catalysts in the valorization of glucose, fructose and real wastewater obtained from beer production. The composites, synthesized under mild conditions, contained homogeneously well-dispersed Keggin clusters for both niobium-containing and zirconium-containing samples when prepared hydrothermally. The calcination of the samples compromised the heteropolyacid cluster in the Zr-containing catalyst decreasing its overall acidity. The catalysts gave good conversions of glucose and fructose, reaching 51 and 68 %, respectively. A conversion of almost 100 % was obtained for the brewery wastewater. However, the selectivity to 5-HMF was very low in all cases. This result has been attributed to the high acidity of the solids leading to overreaction of the desired product to form humins. An optimization of the reaction conditions was performed via a Design of Experiment (DoE) approach in the presence of the material that maintained intact the Keggin HPA structure upon heterogenization. The optimized parameters for the catalytic reaction realized in 25 mL reactor charged with a solution o glucose 6 g/L were a temperature of 180 °C for 5 h in the presence of a catalyst amount of 25 mg.

* 1. Introduction

Biomasses are renewable resources with great potentialities. Bio-based molecules derived from biomasses are therefore of great interest and recent research has focused on the sustainable production of platform molecules, which can be used for obtaining fuels or biomaterials. One of the most interesting platform chemicals derived from biomass is 5-Hydroxymethylfurfural (5-HMF). This is one of the chemical bio-compound, different from petroleum-derived ones, with the highest added value and is generally obtained from lignocellulosic biomasses through acid catalysis. It is defined as platform molecule because it is the precursor of several compounds for the chemical industry and may source polymeric materials such as polyesters, polyamides and polyurethane (Chang et al. 2021). The 5-HMF molecule can be obtained from biomass in a three step process: i) hydrolysis of complex sugars into monomers ii) isomerization of glucose to fructose iii) dehydration of fructose to 5-HMF. The last two processes are schematized in Figure 1.

Figure 1. Reaction scheme for the production of 5-HMF from hexoses in the presence of a heterogeneous acid catalyst, with Lewis and Brønsted acid sites. The scheme also shows the formation of side products.

In general, dehydration reactions are achieved with strong acidic catalysts such as H2SO4 or HCl; however, the use of heterogeneous solid acid catalysts is by far desirable for practical reasons. Heterogeneous catalysts would represent a valid solution since they are easily separated from the reaction mixture by filtration and therefore can be conveniently reused. Acidic catalysts as Nb2O5 or NbOPO4 efficiently promote biomass transformation to 5-HMF by a dehydration process of the monomeric hexoses derived from, for instance microalgae (Lima at al. 2023) or olive mill waste fractions (Lima at al. 2024). The isomerization of glucose to fructose is catalyzed by the Lewis acid sites located on the surface of the heterogeneous catalyst, then the dehydration reaction of fructose to 5-HMF takes place by virtue of the Brønsted acid sites of the solid catalyst as shown in Scheme 1. Regrettably, it is arduous to avoid side reactions that reduce the selectivity to 5-HMF (Agarwal et al. 2018). The use of organic solvents has been found to enhance the effectiveness of the process; however, the catalytic system becomes costly and environmentally unfriendly. Besides, glucose is strongly hydrophilic and the glucose coming from the hydrolysis of cellulose or polysaccharides contains water and thus, from this perspective, water is the most desirable, low-cost and echo-friendly, solvent for glucose conversion.

Metal oxides as Nb2O5 or ZrO2 are abundant and non-toxic materials displaying on their surface both Brønsted (BAS) and Lewis acid sites (LAS) as schematized in Figure 2(A). Both are well known as acidic catalysts, particularly Nb2O5 (Nowak, 1999) so these features can be exploited to simultaneously isomerize glucose to fructose (by LAS) and dehydrate fructose to 5-HMF (by BAS). In addition, we can also consider a less well-known metal oxide material, i.e. nanosized transition metal oxygen clusters, also called polyoxometalates (POMs), a very wide family of species including heteropolyacids (HPAs). Heteropolyacids are inexpensive and non-toxic strong acids. They are classified by taking into account the geometry of the heteropoly anion that confers to the structure strong Brønsted acidity and redox properties (Mizuno, 1998). Heteropolyacids (HPAs) have been extensively used as catalysts and particularly in dehydration reactions due to their strong acidity (Marcì et al. 2014). One of the most used HPAs in catalysis is the Keggin cluster, a polyanion with formula [PW12O40]3-, composed of a globe-like cluster whose diameter is ca. 1.0 nm (Okuhara et al. 1996). Figure 2 (B) depicts the primary very stable structure of the Keggin anion cluster [XM12040]3-. Among the different Keggin-type heteropolyacids, 12-tungstophosphoric acid H3PW12O40 is the most widely studied for acid catalysis as it possesses the highest Brønsted acidity among all the Keggin clusters. In this case, the primary structure is formed by a central PO4 tetrahedron surrounded by 12 WO6 octahedra as depicted in Figure 2(B). The coordination of the clusters, due to their relatively large size, gives rise to a secondary structure that confers the solid superacidity (see groups H5O2+ in figure 2(B)). In spite of their solubility in polar reaction media, heteropoly acids have been widely used as insoluble solid acid catalysts for liquid-phase reactions when supported suitably (Corma 1997).



Figure 2. Schematical representation of the surface of the metal (M) oxides used as heterogeneous catalysts showing the Brønsted and Lewis acidic sites on their surface; (B) Structure of the cluster of the Keggin anion [XM12040]3- along with the coordination of the anions in the HPA nanosized catalyst.

In this work, with the aim of obtaining 5-HMF from biomass, we have prepared, characterized and used two metal oxides Nb2O5 or ZrO2 that were further used as supports for the Keggin heteropolyacid H3PW12O40. The aim of the work is, by taking advantage of the acidic sites of these catalysts exposed to the solution containing sugars, performing isomerization and dehydration reactions aimed to obtain 5-HMF from glucose, fructose or real wastewaters provided by a brewery industry which contain great amount of polysaccharides, potentially good candidates to be valorized.

* 1. MATERIALS AND METHODS

*2.1. Preparation and characterization of the catalysts*

Two sets of catalysts were prepared using tungstophosphoric acid, H3PW12O40, (Aldrich 99.7%) labelled hereafter as PW12. It was heterogenized onto two home prepared oxides, Nb2O5 and ZrO2 by using an amount of PW12 corresponding to a 30% in weight of the metal oxide. The niobium-based solid was prepared from Ammonium Niobium Oxalate (ANbO) (NH4[NbO(C2O4)2]ꞏn H2O) via a hydrothermal process where 25 g of ANbO was dispersed in 70 mL of distilled water, then the suitable amount of PW12 was added to the ANbO solution. The obtained suspension was stirred for 0.5 h and then placed in a Teflon-sealed autoclave and heated to 180 °C for 3 days. The final powder was dried at 60 °C. The solid was labelled as PW12-Nb-A. A second strategy, skipping the hydrothermal treatment, was followed by using the same components to obtain a suspension containing ANbO and PW12, that after being stirred and dried was calcined at 350°C for 4 h. The catalyst thus obtained was labelled as PW12-Nb-350. For the ZrO2-based material, two composites were obtained with the same type of approach. Zirconium butoxide, Zr(OBut)4 (Aldrich), was used as Zr precursor. 50 mL of Zirconium butoxide was dispersed in 70 mL of ethanol containing 3 mL of HCl (35%). A solution of the appropriate amount of PW12 in ethanol was added to the resulting gel. It was stirred for 0.5 h and then hydrothermally treated as the previous Nb2O5 based material or calcined at 350 °C, resulting in solids labeled as PW12-Zr-A or PW12-Zr-350.

Bulk and surface characterizations were carried out in order to define the physicochemical properties of the powders. The crystalline structure of the samples was determined at room temperature by powder X-ray diffraction analysis. Scanning electron microscopy (SEM) was performed by using a FEI Quanta 200 ESEM microscope operating at 20 kV on specimens upon which a thin layer of gold had been evaporated. An electron microprobe used in an energy dispersive mode (EDX) was employed to obtain information on the actual elementary content present in the samples in order to evaluate the overall dispersion of the PW12 on the support. Specific surface area was determined in accordance with the BET method from the nitrogen adsorption-desorption isotherms. FTIR spectroscopy was useful to verify the preservation of the cluster structure after the heterogeneization of the PW12. The transformation of isopropanol to propylene was used a test reaction to study the acid character of the catalysts (Gervasini A. et al. 1991). The catalytic transformation of isopropanol was carried out in a 25 mL cylindrical Pyrex batch reactor provided with a silicon/teflon septum with 0.1 g of catalyst where N2 was fluxed for ca. 0.5 h. The liquid isopropanol (2 μl) was introduced and vaporized in the reactor to reach a concentration of 1 mM. The system was maintained at room temperature in dark conditions to achieve the adsorption equilibrium of the substrate on the catalyst surface, then it was heated at 120 °C into a static oven.

*2.2. Heterogeneous catalysis*

The heterogeneous catalysis was performed inside a stainless-steel autoclave (Tefic Biotech Co. 247 Limited, Xi’an, China). For each experimental run, 25 mg of catalyst (PW12-Nb-A, PW12-Nb-350, PW12-Zr-A or PW12-Zr-350) were added inside the reactor together with a 25 mL of aqueous solution containing 6 g/L of fructose or glucose or a real wastewater coming from beer production. In this last case, the sugar content of the solution was adjusted at 6 g/L. Before its use, the wastewater was filtered through cellulose acetate 0,45 µm syringe filters. The autoclave was immersed in a pre-heated oil bath at 160 °C for 3 hours. For one catalyst, PW12-Nb-350, further experimental runs were performed by using a Design of Experiment approach, by changing three parameters: temperature (from 160°C to 210°C), time (from 3 to 5,7 h) and amount of catalyst (from 0 to 100 mg). After the experiments, the reactor was cooled down for 20 min, and samples from each batch were filtered and analyzed by HPLC as explained previously (Lima et al. 2023). The results of the experimental runs were expressed as:

3. RESULTS AND DISCUSSION

**3.1. Characterization of the catalysts**

Diffractograms of the composites present a crystalline structure characterized by several diffraction peaks attributed to the Keggin PW12, whereas both Nb2O5 and ZrO2 resulted amorphous in agreement to previous observations for materials prepared in a similar manner both for Nb2O5 (Genco et al. 2025) and for ZrO2 (Alcañiz-Monge et al. 2018). The specific surface areas (SSA) of the composites are reported in Table 1. The composite materials studied by SEM evidenced a needle-shaped nanostructured morphology, with needles in the range size 6 to 10 nm, whereas for the calcined materials the structure slightly sintered, becoming more roundish particles whose size ranged between 25 and 30 nm. EDX analysis revealed in all the samples the presence of W from the HPA close to the nominal amount and resulting homogeneously distributed on the particles surface. The integrity of the heterogenized Keggin heteropolyacid structure was evaluated by FTIR analysis. The Keggin anion (PW12) give four characteristic transitions in the range 700-1200 cm-1, as seen in Figure 3. These bands have been assigned to the P-O stretching transition at 1080 cm-1, the stretching vibration of W=O at 992 cm-1 along with those at 898, and 810 cm-1 attributed to the corner and edge sharing W–O–W vibrations (Rocchiccioli-Deltcheff et al. 1983).



*Figure 3. FTIR spectrum of the prepared catalysts*, which helped in verifying the integrity of the heterogenized Keggin heteropolyacid structure.

There is no substantial shift in the vibrational positions attributed to the Keggin cluster on PW12-Nb-350 compared to those in pure PW12, while a distortion of the cluster was observed for the hydrothermally prepared sample, PW12-Nb-A, as evidenced by the shift on the specific vibrations of the Keggin anion (Figure 3(A)). The ZrO2-based composites (Figure 3(B)) showed a significant distortion of the heteropolyacid cluster in the PW12-Zr-A sample, evidenced by the shift of the characteristic bands. Remarkably, no evidence of the Keggin cluster is present on the FTIR spectrum of the PW12-Zr-350, indicating the complete compromise of its structure.

As mentioned, the acidity of the catalysts surface is an important parameter influencing the activity of the catalysts. The dehydration of 2-propanol forming propene is catalysed by an acid site. Dehydration to propene is considered a good measure of acidic properties of the catalyst surface (Gervasini, et al. 1991). The catalytic 2-propanol dehydration forming propene by using supported Keggin heteropolyacid highlights the acidity of the Keggin contained catalysts. Preliminary experiments indicated that after an equilibration time (ca. 30 min.) at room temperature in dark conditions, 2-propanol was partially adsorbed on the surface of all the catalysts used in this work. Under these conditions the extent of 2-propanol adsorption was ca. 80 % for all of the solids. After the adsorption/desorption equilibrium was reached, the temperature insight the reactor was increased up to 120°C and the catalytic experiments started and lasted 2 h. The formation of propene, as well as low amount of propanone and diisopropyl ether, was detectable. One important peculiarity of heteropolyacids is that the catalytic reaction occurs in a pseudo liquid phase formed inside their bulk where the acidic Brønsted sites are present (see the tertiary structure of HPAs in Figure 2 (B)). Polar molecules, such as 2-propanol, are very soluble in the pseudo liquid phase and therefore it is appropriate to follow the evolution of propene which is not soluble in the polar pseudo liquid phase. The amount of propene formed is indicative of the degree of acidity of the catalyst and provides an idea of the relative acidity of the catalysts used in this work. It was measured in the batch reactor atmosphere after the 2 hours catalytic dehydration reaction of 2-propanol and is reported in Table 1.

*Table 1: Specific surface area and propene amount after the 2-propanol catalytic dehydration at 120 °C in the presence of 0.1 g of solid catalyst.*

|  |  |  |
| --- | --- | --- |
| Catalyst | SSA [m2∙g-1] | Propene obtained from 2-propanol dehydration [mM] |
| PW12-Nb2O5-A | 190 | 1.4 10-2 |
| PW12-Nb2O5-350 | 115 | 2.5 10-2 |
| PW12-ZrO2-A | 175 | 6.3 10-3 |
| PW12-ZrO2-350 | 89 | 1.1 10-3 |

3.2 Catalytic reactivity for glucose, fructose and beer wastewater to obtain 5-HMF

The activity of the different catalysts was tested by using three different substrates: fructose, glucose and a real wastewater solution coming from beer manufacturing, as shown in Table 2. Even though there were some differences in the yields and selectivities obtained, they were generally low and below 1%. On the contrary, conversions reached values up to the 97 %. Dehydration of fructose is easier than that of glucose which requires an isomerization step where Lewis acid groups are needed. The high conversion of brewery wastewater can be related to the high amount of easy-to-dehydrate sugars present in the mixture. The very low selectivity and yield to 5-HMF observed for all the catalysts can be related to the acidity of the solids that can resulted very high for the reaction. Indeed, a strong acidity of the catalyst favors the overreaction forming condensation product and humins (see Figure 1); indeed, after the reaction the catalysts appear covered by a black-brown layer of carbonaceous species. This fact suggests to reduce the amount on HPA in the next preparation of the composites.

*Table 2: Reactivity of the tested catalyst by using as reagent glucose, fructose or a real beer wastewater. The reactions were conducted at 160 °C for 3 hours with 25 mg of catalyst. A single trial for condition was conducted.*

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Substrate | Catalyst | Conversion | Selectivity\_HMF | y\_HMF |
| Fructose | PW12-Nb-A | 68% | 0.98% | 0.66% |
| Fructose | PW12-Nb-350 | 63% | 0.79% | 0.50% |
| Fructose | PW12-Zr-A | 61% | 0.93% | 0.56% |
| Fructose | PW12-Zr-350 | 58% | 0.85% | 0.50% |
| Glucose | PW12-Nb-A | 57% | 0.74% | 0.42% |
| Glucose | PW12-Nb-350 | 51% | 0.69% | 0.35% |
| Glucose | PW12-Zr-A | 54% | 0.68% | 0.37% |
| Glucose | PW12-Zr-350 | 51% | 0.68% | 0.35% |
| Beer wastewater | PW12-Nb-A | 97% | 0.36% | 0.35% |
| Beer wastewater | PW12-Nb-350 | 95% | 0.37% | 0.35% |
| Beer wastewater | PW12-Zr-A | 96% | 0.20% | 0.19% |
| Beer wastewater | PW12-Zr-350 | 96% | 0.02% | 0.02% |

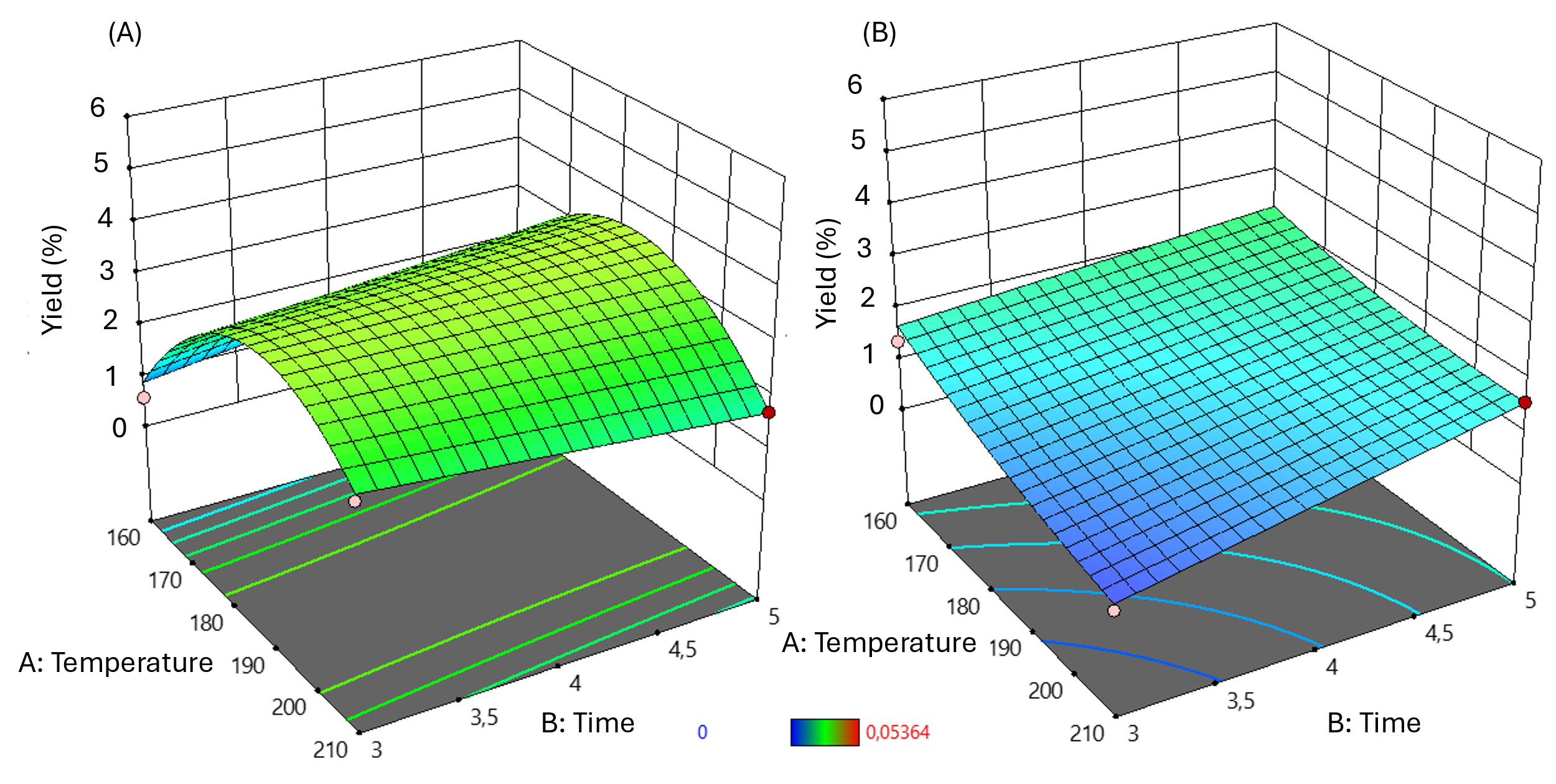
Taking into account the characterization of the four prepared samples, and in particular the fact that the cluster structure of the heteropolyacid remains unchanged only in the solid PW12-Nb-350, also considering the values of specific surface area and relative acidity of the catalysts, the PW12-Nb-350 sample was chosen as representative of this set of materials to perform a Design of Experiment (DoE) in order to analyze the effects of the operating parameters on the reaction yield to obtain 5-HMF. The starting solution was glucose at the concentration of 6 g/L. DoE is a statistical technique used to optimize complex processes by analyzing relationships between input variables and responses, making it valuable for improving efficiency and performance in various processes. To describe the results in terms of 5-HMF yields, we found a significant reduced cubic model with a R2 of 0,95. The response surfaces which describe the variation in yields by modifying the operational variables are reported in Figure 4.

Figure 4. *Response surface of the yield to 5-HMF as a function of Temperature and Time with (A) 25 mg of catalyst* PW12-Nb-350 *and (B) 100 mg of catalyst starting from a glucose solution 6 g/L. Colours of points determine the yield percentage to 5-HMF in the experimental responses.*

The yields are generally higher when using the lower amount of catalyst (25 mg) as shown in Figure 4 (A). Furthermore, the best temperature appears to be around 180°C, while the time makes a slight improvement at 5 hours compared to shorter durations. The quantity of catalyst is the parameter which most strongly influences the final yield, decreasing it when added in high amounts. These results can be explained by the fact that more extreme conditions, such as high temperatures and large amounts of catalyst for long reaction times, can lead to the disappearance of the desired product due to two distinct phenomena: the hydration of 5-HMF to levulinic and formic acid that occurs in water and the polymerization of 5-HMF together with unreacted sugars to insoluble products called humins. The high conversions together with the low yields are consistent with the fact that the reaction proceeds beyond 5-HMF. Possibly a lower acidity of the material would help to improve the selectivity and yield although the conversions would be lower.

* 1. Conclusions

Acidic composite catalyst containing the Keggin heteropolyacid H3PW12O40 in amorphous structures of Nb2O5 and ZrO2 has been prepared, characterised and used as heterogeneous catalysts for the conversion of fructose, glucose and beer wastewater into 5-HMF. The conversions of the sugars aqueous solutions were in the range 50 to almost 100% albeit the yields were in any case ca. 1 %. An optimization of the catalytic reaction parameters, temperature and time were addressed by a Design of Experiment model resulting that high temperatures, large amounts of catalyst for long reaction times gives rise to the overreaction of the desired product 5-HMF to form insoluble humins. The strong acidity of the materials can account for the low yield obtained also under the best operational conditions, i.e. 25 mg of catalyst for 5 hours at 180 °C. This work demonstrates the feasibility of using acid composite catalyst containing heteropolyacids. Future works will address the optimization of the catalyst in order to achieve higher yields of conversion.

References

Agarwal B., Kailasam K., Sangwan R.S., Elumalai S., 2018, Traversing the history of solid catalysts for heterogeneous synthesis of 5-hydroxymethylfurfural from carbohydrate sugars: A review, Renew. Sust. Energy Rev. 82, 2408–2425.

Alcañiz-Monge J., El Bakkali B., Trautwein G., Reinoso S. 2018, Zirconia-supported tungstophosphoric heteropolyacid as heterogeneous acid catalyst for biodiesel production, App. Catal. B 224, 194-203

Corma A. Solid acid catalysts, 1997, Curr. Op. Solid State Mater. Sci. 2, 63-75

García-López, E.I., Marcì, G., Krivtsov I., Casado Espina J., Liotta L.F., Serrano A. 2019, Local Structure of Supported Keggin and Wells-Dawson Heteropolyacids and Its Influence on the Catalytic Activity. J. Phys. Chem. C 123, 19513-19527.

Genco A., García-López E.I., Megna B., Ania C., Marcì G.,2025, Nb2O5 based photocatalysts for efficient generation of H2 by Photoreforming of aqueous solutions of ethanol, Catal.Today, 447, 11514.

Gervasini, A.; Auroux, A. Acidity and basicity of metal oxide surfaces II. Determination by catalytic decomposition of isopropanol. J. Catal. 1991, 131, 190-198.

Hochan Chang H., Gilcher E.B., Huber G.W., Dumesic J.A. 2021, Synthesis of performance-advantaged polyurethanes and polyesters from biomass-derived monomers by aldol-condensation of 5-hydroxymethyl furfural and hydrogenation, Green Chem., 2021,23, 4355-4364.

Lima S., Ricotta T., García-López E.I., Liotta L.F., Villar-Rodil S., Li Puma G., Marcì G., Scargiali F., 2024, Valorization of olive mill waste fractions and production of furfural and 5-hydroxymethylfurfural by heterogeneous catalysis over Nb2O5, NbOPO4 and TiO2-PO4 catalysts, Chem. Eng. J. 497, 154654

Lima S., García-López E.I., Adawy A., Marcì G., Scargiali F. 2023, Valorisation of Chlorella sp. biomass in 5-HMF through a two-step conversion in the presence of Nb2O5 and NbOPO4 and optimisation through reactive extraction, Chem. Eng. J. 471, 144583

Marcì M., García-López E.I., Palmisano L. 2014, Heteropolyacid‐based materials as heterogeneous photocatalysts, Eur. J. Inorg. Chem. 2014, 21-35.

Mizuno N., Misono M.,1998, Heterogeneous Catalysis. Chem. Rev. 98, 199-218.

Nowak I., Ziolek M. 1999, Niobium Compounds: Preparation, Characterization, and Application in Heterogeneous Catalysis, Chem. Rev. 99, 3603–3624.

Okuhara T., Mizuno N., Misono M., 1996, Catalytic chemistry of heteropoly compounds, Adv. Catal. 41, 113-252.

Rocchiccioli-Deltcheff C., Fournier M., Franck R., Thouvenot R. 1983, Vibrational investigations of polyoxometalates. 2. Evidence for anion-anion interactions in molybdenum(VI) and tungsten(VI) compounds related to the Keggin structure. Inorg. Chem. 22, 207-216