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Preyssler heteropolyacids in the self-etherification of 5-hydroxymethylfurfural to 5,5’(oxy-bis(methylene))bis-2-furfural (OBMF) under mild reaction conditions

Alexander. Páez[a], Hugo A. Rojas[a], Omar Portilla[a], Gabriel Sathicq[b], Carlos A. M. Afonso[c], Gustavo P. Romanelli[a] and José J. Martínez*[a]

Abstract: The synthesis of 5,5’(oxy-bis(methylene))bis-2-furfural (OBMF) from 5-hydroxymethylfurfural (5-HMF) was studied using bulk and alumina-supported Preyssler heteropolyacids. The formation of OBMF was related to the amount of Brønsted acid sites, the lowest yield to OBMF being obtained with supported heteropolyacids. However, the Lewis acidity of HPA supported on Al₂O₃ favored the formation of 2,5-dimethylfurane. The effects of solvent, catalyst loading, temperature and reaction time on the selectivity to OBMF from 5-HMF were studied in order to optimize OBMF production using bulk Preyssler heteropolyacids; a yield of 84 % to OBMF was obtained at 5 h and 343 K. These results demonstrate that bulk Preyssler heteropolyacid is a good candidate for OBMF synthesis under mild reaction conditions.

Introduction

5-Hydroxymethylfurfural (5-HMF) is considered as a promising construction block that can be transformed into different compounds such as biofuels, monomers in plastic industries, and pharmaceutical ingredients.[1] Among these compounds, 5,5’(oxy-bis(methylene))bis-2-furfural (OBMF) has been used as a precursor for the synthesis of compounds with antiviral activity[2] and some imine-based polymers with high thermal and electrical conductivity.[3] However, the conventional synthesis of OBMF by etherification of 5-HMF (Scheme. 1) involves elevated temperatures (≥373 K), anhydrous conditions, long reaction times, and homogeneous catalysts. Conventionally, the catalyst used has been p-toluenesulfonic acid. Using this catalyst, Musau et al., reported a 58% yield to OBMF.[4] Likewise, Chundury et al., reported a 75% yield, this slight increase being due to the use of anhydrous phosphorus pentoxide as water scavenger.[5] Although OBMF can also be synthesized by a conventional Williamson reaction between 5-HMF and 5-(chloromethyl)-2-furfural, only a 43% yield was obtained.[6] Indeed, these methodologies generate large amounts of residues and by-products.

![Scheme 1. Schematic representation of the synthesis of OBMF](image)

To achieve a green process and improve the yields of OBMF, the use of acid solids has been assayed. A good example is the work of Casanova et al., who used structured micro and mesoporous aluminosilicate solids in the synthesis of OBMF from HMF.[7] They concluded that Al-MCM-41 affords a yield close to 99% as a result of suitable acidity, small diffusion constraint, and good adsorption property. However, the reaction was carried out at elevated temperatures (≤ 373 K) using trifluorotoluene (TFT) as solvent. Similarly, Wang et al., investigated the selective etherification of 5-HMF to OBMF with oxide graphene as catalyst (GO), obtaining 87% yield to OBMF.[8] But this yield was only reached using CH₃Cl₂ as solvent at 400 K and 8 h of reaction; moreover, it was necessary to use a water removal trap. Likewise, Milki et al., obtained a high yield to OBMF (96%) using Amberlyst 15 in a combined process of ultrasonic conditions and reflux.[9] In fact, these results are interesting because only under reflux conditions a 50% yield was obtained. Recently, similar yields to OBMF (96%) were obtained by Shinde et al., with a Sn catalyst supported on montmorillonite but this yield was only reached with the elimination of water, which favors OBMF formation.[10] Recently, Amarasekara et al., obtained OBMF from fructose with 76% yield using acid resin as catalyst and dimethylsulfoxide as solvent at 383 K.[11] Also, the OBMF was oxidized to 5,5’-[oxybis(methylene)]bis[2-furanocarboxylic acid] (OBFC), obtaining as principal product the dimer of FDCA.

In summary, the production of OBMF is directly related to the presence of Brønsted acid sites and the elimination of water, so Preyssler heteropolyacids (HPA’s) should suitable to be used in this reaction. These solids have attracted special attention due to their low toxicity, high thermal and hydrolytic stability throughout a wide pH range (0-12), strong Brønsted acidity (14 H⁺), low corrosiveness, and high oxidation potential.[12] Preyssler HPA’s present a D₅₆₈ symmetry and are composed of five PW₁₀O₄₂ units of Keggin anion and a sodium ion located within the structure.[13] In addition, the solids have been used as eco-friendly catalysts in different organic reactions because of...
their different acidity and oxido-reduction properties. In fact, our research groups have studied distinct reactions using this type of solid and found that the easy preparation of Preyssler solids and their low cost would allow them to be used as catalysts in biorefinery industries.

To improve the yield of OBMF by the etherification of 5-HMF under mild reaction conditions, we studied bulk and alumina-supported Preyssler heteropolyacids. The heteropolyacids present a low surface area and for this reason are generally deposited on different supports. However, the heteropolyacid-support interaction depends on the type of support employed, since the dispersion of protons differs depending on the characteristics of the oxide used, for example, on alumina more active surface protons of the heteropolyacid than SiO2 are available. Thus, in this study alumina was chosen as support of Preyssler heteropolyacids.

To the best of our knowledge, this is the first application of bulk and alumina-supported Preyssler heteropolyacid in the synthesis of OBMF under mild reaction conditions. The effects of solvent, temperature, catalyst loading and reaction time on the selectivity to OBMF from 5-HMF have been carefully studied using bulk Preyssler heteropolyacid.

Results and Discussion

Catalyst characterization

The ATR-FTIR spectra in the range of 1200 cm\(^{-1}\) to 800 cm\(^{-1}\) of bulk and supported heteropolyacids showed bands attributed to Preyssler structure, mainly P-O (1115 cm\(^{-1}\), 1085 cm\(^{-1}\) and, 1024 cm\(^{-1}\)), W=O (956 cm\(^{-1}\)) and W-O-W (898 cm\(^{-1}\)). However, for the heteropolyacids supported on Al2O3 the bands showed (the IR spectral of the solids is shown in the Supporting Information, Figure. S.1) a shift to lower wavenumbers related to the interaction of the heteropolyanion with hydroxyl groups of the support.

The textural properties are summarized in Table 1. The heteropolyacids have low surface areas characteristic of this type of solids. The N\(_2\) adsorption isotherms of the supported catalysts are shown in Figure 1. Al2O3 presented a type-II isotherm according to IUPAC classification. Although the impregnation of the Preyssler heteropolyacid on Al2O3 decreases its surface area and slightly modifies the pore size and pore volume due to pore blocking by HPA particles, the mesoporous structure still remains, as can be seen by hysteresis buckle.

![Figure 1. N2 adsorption isotherms of the supported Preyssler heteropolyacids](image)

![Figure 2. DTG curves of bulk Preyssler and supported heteropolyacids. (a) Preyssler, (b) Preyssler-Mo, (c) Preyssler/Al2O3, (d) Preyssler-Mo/Al2O3](image)

**Table 1. Textural properties of bulk and supported Preyssler heteropolyacids.**

| Catalyst                | S\(_{BET}\) (m\(^2\)/g) | Pore volume (cm\(^3\)/g) | Pore size (nm) |
|-------------------------|--------------------------|---------------------------|----------------|
| Preyssler               | 10<                      | -                         | -              |
| Preyssler/Al2O3         | 176                      | 0.3                       | 6.5            |
| Preyssler-Mo/Al2O3      | 167                      | 0.3                       | 6.4            |
| Al2O3                   | 195                      | 0.4                       | 6.5            |

Fig. 2 displays the DTG curves of bulk and supported heteropolyacids. Three characteristic signals are observed in the DTG of the solids studied. The first signal in the range of 290 K to 415 K can be attributed to the physically adsorbed water. The second signal between 410 K and 540 K can be associated with loss of crystallization water. Finally, the third signal is the decomposition of the heteropolyanion structure in its corresponding oxides, which takes place after 500 K. However, the Preyssler structure begins to decompose from 373 K, and after 573 K the heteropolyanion structure collapses almost entirely. This phenomenon is observed with the HPA supported on Al2O3, due to the interaction of the acid sites of HPA with basic sites of Al2O3.

**Fig. 3 displays the TPD-NH3 profiles of the solids studied.** Desorption of ammonia in the HPA showed sites of distinct nature. It has been reported that the weak-acid sites appear at below 573 K, moderate strength acid sites are characteristic in the range of 573 K to 723 K, and signals in temperatures higher than 723 K are associated with strong acid sites. However, the interpretation of TPD analysis should be carefully performed, since the Preyssler heteropolyacid begins to decompose from 373 K, and the signal in 590 K by Preyssler-Mo (blank) can be...
attributed to decomposition of the structure, as can be seen in Figure 3 f. Thus, the signal at low temperature (540 K) could be attributed to decomposition of NH₄⁺ species that are bonded to oxygen atoms in one HPA or between two neighboring HPAs, respectively. The other signals could also be ascribed to the decomposition of NH₄⁺ species forming other acidic species (possibly Keggin units) that could contribute to the sample acidity. Besides, the stability of the structure is affected by the presence of another heteroatom (Mo) or when heteropolyacid is supported on Al₂O₃, as can be clearly observed in Figure 3.

![Figure 3. NH₃-TPD profiles of Preyssler catalysts. (a) Preyssler, (b) Preyssler-Mo, (c) Preyssler/Al₂O₃, (d) Preyssler-Mo/Al₂O₃ and (e) Al₂O₃ and (f) Preyssler-Mo (Blank)](image)

The nature of acid sites was investigated with pyridine adsorption by using FTIR spectroscopy. The results are shown in Figure 4. In the Preyssler heteropolyacid the band near 1487 cm⁻¹ is related to strong Brönsted-Lewis sites. Lewis acid sites are associated with bands at 1539 cm⁻¹. The band at 1635 cm⁻¹ corresponds to Brönsted acid sites. Other bands at 1592 cm⁻¹ correspond to pyridine physisorbed on Al₂O₃. The integration of the distinct bands is shown in Table 2. The results indicated that Brönsted sites not were observed in HPA supported on Al₂O₃; however, this could be explained by the lower amount of HPA deposited on the support or possibly by the neutralization of the strongest protons of pure heteropolyacid with the basic sites of the support.

![Figure 4. FTIR spectra of pyridine adsorption on Preyssler catalysts. (a) Preyssler, (b) Preyssler-Mo, (c) Preyssler/Al₂O₃, (d) Preyssler-Mo/Al₂O₃ and (e) Al₂O₃.](image)

### Table 2. Integration of the distinct bands shown in the Py-FTIR and initial electrode potential determined by potentiometric titration.

| Catalyst     | Bₘ (%) | Lₐ (%) | L-Bₘ (%) | IEP (V) |
|--------------|--------|--------|----------|---------|
| Preyssler    | 52     | 22     | 26       | 779     |
| Preyssler Mo | 52     | 22     | 26       | 530     |
| Preyssler/Al₂O₃ | 1.4  | 86     | 12.6     | -27     |
| Preyssler-Mo/Al₂O₃ | 3   | 85     | 12       | 18      |
| Al₂O₃        | 0      | 92     | 8        | -0.4    |

Abbreviations: Bₘ: Brönsted acid sites, Lₐ: Lewis acid sites, L-Bₘ: Brönsted-Lewis acid sites, IEP: initial electrode potential.

To confirm the Brönsted acidity, potentiometric titrations of bulk and supported heteropolyacids were performed (Figure 5). The initial electrode potential (V), which is related to the maximum acid strength of the sites, is listed Table 2. It can be seen that the Preyssler HPA is more acidic than the Preyssler-Mo HPA; however, when supported on Al₂O₃, the Preyssler-Mo/Al₂O₃ is the more acidic and the Preyssler/Al₂O₃ has lower acidity, even compared with the support only. This could be related to the proton mobility when the HPA is supported, which in part depends on the negative charge distribution in the heteropolyanion oxygens and the electrostatic interaction of the HPA with -OH surface groups of the support, i.e., a lower interaction of Preyssler-Mo with the alumina surface causes a higher strength acidity and possibly a lower thermal stability (DTG results).

![Figure 5. Potentiometric titration curves of supported Preyssler heteropolyacid (a) Preyssler/Al₂O₃, (b) Preyssler-Mo/Al₂O₃ and (c) Al₂O₃.](image)

### Catalytic studies

The etherification of 5-HMF to OBMF was initially studied in solvent-free conditions using bulk and alumina-supported heteropolyacids with the aim of selecting the best catalyst to optimize the reaction conditions. Table 3 lists the results obtained at 2 h of reaction using 0.26 mmol of 5-HMF and 10 mg of bulk and alumina-supported Preyssler heteropolyacids. The order of activity in terms of conversion (α), selectivity (ΣOBMF) and yield (YOBMF and YDFF) is Preyssler > Preyssler-Mo > Preyssler-Mo/Al₂O₃ > Preyssler/Al₂O₃. The highest conversion was obtained using the bulk solids. The incorporation of Mo to
the structure of the heteropolyacid decreases the conversion but maintains the selectivity. The etherification is a Brønsted acid-catalyzed reaction. Thus, the conversion is directly related to the Brønsted acidity obtained. The heteropolyacids supported on \(Al_2O_3\) present lower Brønsted acidity and consequently, a lower conversion of 5-HMF and poor selectivity to OBMF. The blank experiments using only \(Al_2O_3\) as catalyst showed no activity, which means that some Brønsted acid sites of the heteropolyacid were incorporated in \(Al_2O_3\). When the results of activity are compared with specific activity (\(\text{Mmol} \ \text{g}_{\text{Preyssler}}^{-1} \ \text{s}^{-1}\)) it can be observed that the supported heteropolyacids present a higher activity (Table 3). However, the Lewis acidity and lower Brønsted acidity of the supported heteropolyacids is not enough to catalyze the etherification of 5-HMF to OBMF; instead, it can induce the formation of other compounds such as 2,5-diformylfuran (DFF). We argued that the formation of DFF is probably due to the redox potential of the heteropolyacids that favors the aerobic oxidation of 5-HMF, similarly as occurs in other heteropolyacids. It has been demonstrated by theoretical studies that 5-HMF oxidation to DFF using Keggin heteropolyacids occurs with the interaction of terminal oxygen atoms (Ot) and the bridged oxygen atoms (Ob) of the \([\text{PMo}_{12}O_{40}]^{3-}\) species, where the hydrogen atoms of the hydroxyl group migrate to Ot and the hydrogen atom of the -CH₂ migrate to Ob via a five-membered complex, this molecular complex containing the DFF molecule [26]. Thus, a similar mechanism can be followed with the Preyssler heteropolyacids by the formation of DFF in aerobic conditions.

### Table 3. Activity results at 2 h of reaction of etherification of 5-HMF using bulk Preyssler and supported on \(Al_2O_3\) heteropolyacids.

| Catalyst       | \(\alpha\) (%) | \(S_{\text{OBF}}\) (%) | \(Y_{\text{OBF}}\) (%) | \(Y_{\text{HMF}}\) (%) | \(\text{Mmol} \ \text{g}_{\text{Preyssler}}^{-1} \ \text{s}^{-1}\) |
|---------------|----------------|------------------------|------------------------|------------------------|-------------------------------------------------|
| Preyssler     | 53             | 92                     | 49                     | 4                     | 2.2                                             |
| PreysslerMo   | 49             | 95                     | 5                      | 47                   | 2.1                                             |
| Preyssler/Al₂O₃ | 9              | 43                     | 57                     | 4                    | 13.6                                            |
| PreysslerMo/Al₂O₃ | 14         | 58                     | 42                     | 8                    | 6.6                                             |
| Al₂O₃        | 5              | 0                      | 0                      | 0                    | 0                                               |

Reaction conditions: 10 mg catalyst, 0.26 mmol of 5-HMF, 313 K, solvent toluene, at 2 h of reaction. \(\alpha\): conversion; \(S_{\text{OBF}}\): selectivity to OBMF; \(Y_{\text{OBF}}\) and \(Y_{\text{HMF}}\): Yield; \(\mu\text{mol}_{\text{OBF}} \ \text{g}_{\text{Preyssler}}^{-1} \ \text{s}^{-1}\): specific activity of 5-HMF per gram of catalyst and time.

A plausible mechanism for the etherification of 5-HMF to OBMF with bulk Preyssler catalyst is shown in Scheme 2. The first stage involves the protonation of the group of 5-HMF by the availability of the protons of \(\text{H}_4\text{[NaP}_2\text{W}_{12}\text{O}_{40}]^{10}\) HPA. This protonated hydroxyl group promotes the by another 5-HMF molecule via nucleophilic bimolecular substitution (SN₂), followed by water molecule elimination. The final stage is the release of water generating a cation stabilized by liberation of a proton of HPA, giving the OBMF as main product and recovering the catalyst.

### Scheme 2. Plausible mechanism for the formation of OBMF.

#### Optimization of reaction conditions

The recovery of catalysts is more difficult using free solvent conditions; to improve the results we studied the solvent effect using the Preyssler heteropolyacid. The results are shown in Table 4. Aprotic solvents such as toluene favor the conversion of 5-HMF but with lower selectivity to OBMF; this result is probably ascribed to the alklylation reaction activated by the aromatic ring of toluene. Similar results were described by Wang et al. [9] The coupling of alcohols to ethers on the catalyst surface usually proceeds by formation of an oxonium ion that is attacked by a second alcohol molecule via nucleophilic bimolecular substitution (SN₂). We studied the solvent effect using other polar aprotic solvents that favor the SN₂ mechanism and that do not solubilize the bulk Preyssler heteropolyacid for an easy catalyst recovery. Higher selectivities to OBMF are obtained with the use of polar aprotic solvents. Thus, the best solvent is dichloromethane because it is less able to solvate the oxonium ion. Casanova et al., reported a conversion of 81% and \(S_{\text{OBF}}\) of 99% using zeolites and trifluorotoluene as solvent at 373 K at 2 h of reaction [9]. Our results show that it is possible to obtain OBMF using \(\text{CH}_2\text{Cl}_2\) with less drastic conditions using the Preyssler heteropolyacid.

### Table 4. Effect of solvent on the etherification of 5-HMF to OBMF with Preyssler heteropolyacid.

| Solvent      | \(\alpha\) (%) | \(S_{\text{OBF}}\) (%) | \(Y_{\text{OBF}}\) (%) | \(Y_{\text{HMF}}\) (%) |
|--------------|----------------|------------------------|------------------------|------------------------|
| Dichloromethane | 53             | 98                     | 52                     | 2                      |
| Toluene      | 21             | 83                     | 17                     | 17                     |
| Dioxane      | 13             | 97                     | 12                     | 3                      |
| Toluene      | 52             | 60                     | 31                     | 40                     |

Reaction conditions: 20 mg catalyst, 0.26 mmol of 5-HMF, 313 K, 0.5 mL solvent, and 2 h of reaction. \(\alpha\): conversion; \(S_{\text{OBF}}\): selectivity to OBMF; \(Y_{\text{OBF}}\) and \(Y_{\text{HMF}}\): Yield to OBMF; \(S_{\text{OBF}}\): Selectivity to others.

To verify the absence of mass transfer limitations, the effect of Preyssler heteropolyacid loading on the etherification of 5-HMF was studied. In the absence of external mass transfer resistance,
the rate of reaction should be proportional to the catalyst loading. As can be seen in Figure 6, there is a linear trend in the conversion with an increase of the catalyst mass used, which is due to the proportional increase in the number of active sites. Besides, the Weisz–Prater criterion was employed to assess the influence of intraparticle diffusion resistance (see Supporting Information, Figure. S.2). Table 5 shows the Weisz-Prater values at distinct temperatures studied and mass used. In all cases, the calculated value of CWP is less than 1. Hence, there was no intraparticle diffusion resistance.

![Figure 6](image)

**Figure 6.** Effect of catalyst loading on 5-HMF conversion with Preyssler heteropolyacid. Reaction conditions: 0.26 mmol of 5-HMF, 313 K, 0.5 mL of CH₂Cl₂ and 2 h.

The effect of reaction temperature on Preyssler heteropolyacid was also studied in the range of 313 K to 373 K (Figure 7). This range of temperature was chosen considering the properties of solvent and the thermal stability of the solid. The 5-HMF conversion increased with reaction temperature; however, the selectivity to OBMF was not affected by the temperature.

![Figure 7](image)

**Figure 7.** Effect of temperature on 5-HMF conversion with Preyssler heteropolyacid. Reaction conditions: Catalyst 20 mg, 0.26 mmol of 5-HMF, 0.5 mL CH₂Cl₂ and 2 h.

![Figure 8](image)

**Figure 8.** Effect of reaction time on the etherification of HMF to OBMF. Reaction conditions: Catalyst 20 mg, 0.26 mmol of 5-HMF, 343 K, and 0.5 mL CH₂Cl₂.

The catalyst reusability was studied four times, including the use of fresh catalyst (Figure 9). After each run the catalyst was filtered, washed with dichloromethane, dried, and weighed before its use in the next batch. Although the catalyst was washed after filtration to remove all the adsorbed reactants and products, there was still a possibility of retention of a small amount of adsorbed reactants and product species, which might cause the blockage of active sites of the Preyssler heteropolyacid. After of the first reuse, the spent solid was analyzed by FTIR (See supporting Information, Figure. S.3). The IR spectrum showed a decrease in the characteristic signals of the Preyssler HPAs and new bands at 1667 cm⁻¹, 1514 cm⁻¹, 1022 cm⁻¹ and, 767 cm⁻¹. These new bands could be associated with adsorbed reactants or products on the catalyst surface. These are apparent factors for the loss in activity that have been taken into account because no fresh catalyst was added to the reaction mixture to maintain the same catalyst loading during reusability tests. Also, it cannot be excluded/ruled out that the decrease in the activity of Preyssler HPAs is associated with the loss of the solid structure. During the four cycles, the conversion of 5-HMF decreased to 50%, but the selectivity toward OBMF remained at 95%.

| Temperature (K) | Viscosity CH₂Cl₂ (cP) | Bulk Diffusivity (Dₛₛₛ) | Weisz-Prater criterion (Nₛₛₚ) |
|----------------|----------------------|--------------------------|-------------------------------|
| 313            | 0.38                 | 4.90 × 10⁻¹              | 2.64 × 10⁻⁸                  |
| 343            | 0.28                 | 6.09 × 10⁻⁷              | 3.29 × 10⁻⁸                  |
| 373            | 0.22                 | 8.33 × 10⁻⁸              | 4.50 × 10⁻⁸                  |

Abbreviations: temperature (T), viscosity CH₂Cl₂ (Vₛₛ), bulk diffusivity (Dₛₛₛ), effective diffusivity (Dₑₛₛ) and Weisz-Prater criterion (Nₛₛₚ).
Figure 9. Catalyst recycling experiment. Reaction conditions: Catalyst 20 mg, 0.26 mmol of 5-HMF, 343 K, 0.5 mL CH₂Cl₂ and 5 h of reaction.

Conclusions

The etherification of 5-HMF was favored by the higher Brønsted acidity; thus the order of activity was Preyssler > Preyssler-Mo > Preyssler Mo/Al₂O₃ - Preyssler/Al₂O₃. The interaction of Preyssler heteropolyacids with the hydroxyl groups on the Al₂O₃ surface decreases the acidity of the heteropolyacid, its thermal stability, and consequently, these solids present less activity in the etherification of 5-HMF. The formation of 2,5-dimethylfuran could be attributed to the interaction of 5-HMF with Preyssler species; however, the results showed poor conversions. The production of OBMF was optimized using bulk Preyssler heteropolyacid, obtaining a selectivity of 95% with 85% of conversion of 5-HMF at 5 h and 343 K.

Experimental Section

All solvents and reagents were purchased from Aldrich-Sigma and used without further purification. 5-Hydroxyethylfurufural (≥99%), sodium tungstate dihydrate (≥99%), sodium molybdate dihydrate (≥99%), phosphoric acid (85%), potassium chloride, dichloromethane (reactive grade), toluene (99.9%), tetrahydrofuran (≥99%), pyridine (99.8%) were employed.

IR spectra were obtained with a Nicolet iS50 spectrometer by the ATR method. IR spectra were processed with a resolution of 4 cm⁻¹ and a spectral range of 4000 cm⁻¹ – 400 cm⁻¹. The textual properties of the solids were obtained by N₂ adsorption–desorption isotherms measured at 77 K in Micromeritics ASAP 2020 equipment. Samples were previously evacuated at 423 K for 12 h. The BET method was used to calculate the total surface area of the samples.

The thermogravimetric analysis was performed using a Setaram thermobalance. Sixty mg of the solids was placed in an alumina crucible and heated at a rate of 5 K min⁻¹ up to 850 K, under an atmosphere of N₂ flowing at 20 cm³ min⁻¹.

TPD-NH₃ analyses were performed in a Micromeritics AutoChem II 2920. Prior to the adsorption of NH₃, the samples were preheated at 473 K in He flow (20 mL min⁻¹) for 1 h. Ammonia (20 mL min⁻¹) was then pulsed into the reactor every minute at room temperature under a flow of He (5 mL min⁻¹), until the acid sites were saturated with ammonia. The physisorbed ammonia was removed by evacuating the catalyst sample at 373 K for 1 h. The desorption of NH₃ began at 373 K with a heating rate of 278 K min⁻¹ to reach 1000 K under a helium flow at 10 mL min⁻¹.

The nature of acid sites was studied by pyridine (Pyr) adsorption followed by FTIR. Infrared spectra were collected using Nicolet iS50 equipment with an in situ diffuse reflectance cell (Hänsch, Praying Mantis). For the determination of acid sites, the samples were heated at 423 K with a helium flow at 50 mL min⁻¹ for 1 h and then were gradually cooled down to room temperature, and reference spectra of the solid were collected. Then pyridine adsorption was performed for 1 h. After desorption, the pyridine was gradually removed by evacuation with a helium flow (30 mL min⁻¹) at different temperatures, and the spectrum of the sample was collected (120 scans and resolution of 2 cm⁻¹).

The potentiometric titration was performed using 0.05 mL of n-butylamine (0.1 N) in acetonitrile. This solution was added to 0.1 g of solid using acetonitrile as solvent, and stirred for 3 h. Later, the suspension was titrated with the same base, at 0.05 mL min⁻¹. The electrode potential variation was measured with an Instrumentalia S. R. L. digital pH meter, using a double junction electrode.

The quantification and identification of products was carried out using a Varian 3400 gas chromatograph equipped with both a flame ionization detector (FID) and a Varian 2000 mass spectrometer (MS). Reaction products were analyzed with a DB1 column. He as carrier, and using the following conditions: oven temperature, 353 K (hold 2 min.) to 573 K and 10 K min⁻¹ (hold 6 min.); detector, FID at 493 K. Conversions and selectivities were determined by the relative peak area of substrates and products using a normalization method. The retention times by DFF, HMF and OBMF were 4.61 min, 8 min and 18.5 min respectively.

Catalyst preparation

The Preyssler salt, K₄[NaP₂W₁₀O₃₉]·nH₂O, was prepared from Na₂WO₄·2H₂O according to a reported method. In a typical experiment Na₂WO₄·2H₂O (30 g, 0.09 mol) was dissolved boiling water (20 mL), and concentrated phosphoric acid (H₃PO₄) was poured carefully into the solution (27 g, 0.27 mol). Then, the mixture was refluxed for 24 h, and concentrated nitric acid (1 mL) was added to the solution. Preyssler salt was precipitated by adding KCl (10 g, 0.13 mol). The K₄[NaP₂W₁₀O₃₉]·nH₂O was converted to the corresponding acid H₄[NaP₂W₉O₃₆] (Preyssler) by passing it through a Dowex-50W-X8 ion-exchange column.

The Preyssler heteropolyacid H₄[NaP₂W₉O₃₆] (Preyssler-Mo) was synthesized following a literature method. The method for the synthesis of Preyssler-Mo was similar to that of Preyssler HPA. Briefly, Na₂WO₄·2H₂O (23 g, 0.07 mol) and Na₂MoO₄·2H₂O (2 g, 8.3 mmol) were dissolved in water (20 mL) and mixed at 333 K for 30 min. Then, H₃PO₄ (27 mL) was added, and the solution was refluxed for 24 h. The solution was cooled to room temperature, and KCl (10 g, 0.13 mol) dissolved in H₂O (30 mL) was added with vigorous stirring for 30 min. The solid was obtained by crystallization in warm water (70 mL) and then was cooled down to room temperature, obtaining yellow crystals corresponding to K₄[NaP₂W₉MoO₃₉]. This salt was converted to its corresponding acid H₄[NaP₂W₉MoO₃₉] by passing it through a column filled with Dowex-50W-X8 ion-exchange resin.

The Al₂O₃ support (Catalox SBA 200) was used as received without any pretreatment. The support was impregnated with the Preyssler heteropolyacid to get a 10 wt% HPA content. In a typical experiment,
bulk Preyssler heteropolyacid (0.3 g) was diluted in water (6 mL), and the solution was added to 3 g of support. The obtained mixture was stirred at 950 rpm for 3 h at room temperature. The resulting paste was dried under vacuum at room temperature for 18 h. The materials were labeled as Preyssler/Al₂O₃ and Preyssler-Mo/Al₂O₃.

**Catalytic experiments**

To select the catalyst with the best catalytic performance, the etherification of 5-HMF in solvent-free conditions was studied using 5-HMF (0.033 g, 0.26 mmol) and catalyst (10 mg) under open air. The reaction mixture was maintained at 373 K and 400 rpm for 2 h. The effects of solvent (CH₃OH, THF, dioxane, and toluene), catalyst loading (5 mg to 20 mg) and reaction temperature (313 K to 373 K) were evaluated to optimize the reaction conditions with the catalyst selected. Briefly, the catalyst was added to a solution of 5-HMF (0.033 g, 0.26 mmol) and solvent (0.5 mL). The reaction was maintained at the desired temperature under constant agitation and reflux. The reaction was stopped at the desired time, and the catalyst was recovered by filtration. The solvent was removed on a rota-evaporator, and the products were purified by column chromatography over silica gel using a mixture of hexane and ethyl acetate (1:1). For the reusability, the catalyst after each run was filtered, washed with dichloromethane (3 x 5 mL), dried, and weighed before its use in the next batch.

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The self-etherification of 5-HMF was studied using Preyssler heteropolyacids (HPA). The formation of OBMF was related to the amount of Brönsted acid sites. The Lewis acidity of HPA/Al₂O₃ favored the formation of 2,5-dimethylfuran. A yield of 84% of OBMF at 5 h and 343 K was obtained under optimized conditions.