In this paper, we have described a novel route to produce 5-hydroxymethylfurfural (HMF), a valuable platform molecule obtained from biomass. Metal-exchanged Keggin heteropolyacid salts were used as catalysts, in microwave-assisted reactions carried out in a water-ethyl acetate biphasic system. To avoid the use of homogenous Brønsted acid catalysts, which are corrosive and difficult to be reused, we have exchanged the protons of the Keggin heteropolyacids with transition metal cations. These salts were evaluated in the fructose dehydration, being the Cu$_{3/2}$PW$_{12}$O$_{40}$ the most active and selective catalyst, achieving 81% of HMF yield, after 15 min reaction at 413 K under microwave irradiation. The effects of metal cation, anion or heteropolyanion present in the catalyst were evaluated. The greatest efficiency of the Cu$_{3/2}$PW$_{12}$O$_{40}$ was attributed to its high Lewis acidic strength which allows its coordinates with the water molecules, consequently generating H$_3$O$^+$ ions in the reaction medium. In addition, after assessing reactions of fructose dehydration in the presence of other Copper salts [i.e., CuCl$_2$ or Cu(NO$_3$)$_2$], we conclude the anion plays too a key role. The higher softness of phosphotungstic anion should stabilize protonate intermediates better than chloride or nitrate anions, favouring this way the reaction. Finally, although the catalyst has been soluble, it was easily reused by removing the aqueous phase and adding a new load of the substrate dissolved in ethyl acetate. The runs were successfully repeated without the loss of activity of the catalyst.

**Abstract**

In this paper, we have described a novel route to produce 5-hydroxymethylfurfural (HMF), a valuable platform molecule obtained from biomass. Metal-exchanged Keggin heteropolyacid salts were used as catalysts, in microwave-assisted reactions carried out in a water-ethyl acetate biphasic system. To avoid the use of homogenous Brønsted acid catalysts, which are corrosive and difficult to be reused, we have exchanged the protons of the Keggin heteropolyacids with transition metal cations. These salts were evaluated in the fructose dehydration, being the Cu$_{3/2}$PW$_{12}$O$_{40}$ the most active and selective catalyst, achieving 81% of HMF yield, after 15 min reaction at 413 K under microwave irradiation. The effects of metal cation, anion or heteropolyanion present in the catalyst were evaluated. The greatest efficiency of the Cu$_{3/2}$PW$_{12}$O$_{40}$ was attributed to its high Lewis acidic strength which allows its coordinates with the water molecules, consequently generating H$_3$O$^+$ ions in the reaction medium. In addition, after assessing reactions of fructose dehydration in the presence of other Copper salts [i.e., CuCl$_2$ or Cu(NO$_3$)$_2$], we conclude the anion plays too a key role. The higher softness of phosphotungstic anion should stabilize protonate intermediates better than chloride or nitrate anions, favouring this way the reaction. Finally, although the catalyst has been soluble, it was easily reused by removing the aqueous phase and adding a new load of the substrate dissolved in ethyl acetate. The runs were successfully repeated without the loss of activity of the catalyst.
Graphical abstract

Introduction

The required reduction of the dependence on fossil-based products has stimulated the search for renewable raw materials, which can be transformed into biofuels and or high-value-added chemicals in processes with low environmental impacts (Mika et al. 2018; Hassan et al. 2021; Besson et al. 2014). In this sense, biomass-derived feedstocks rise as the best alternative to provide substitutes to the petrochemical origin products. Abundant and renewable biomass resources can be converted to platform molecules, which can be used to generate fine chemicals or biofuels (David et al. 2019; Castro and Fernandes 2021; Brar et al. 2014; Corma Canos et al. 2007).

Among them, 5-hydroxymethylfurfural (HMF) is one of the “top 10” biobased chemicals named by the U.S. Department of Energy as a platform for value-added products. HMF deserves to be highlighted due to the numerous applications of its derivatives, such as bio-polymers, medicines, and personal care products (Yu and Tsang 2017; Putten et al. 2013). It can be obtained through acid-catalyzed dehydration of carbohydrates. Further conversion leads to biofuels, fuel additives, agrochemicals, pharmaceuticals, resins, and polyesters, among other useful products (Kong et al. 2020; Rosatella et al. 2011; Deng and Amarasekara 2021).

Although a plethora of catalytic systems has already been explored to synthesize HMF, there are still many challenges to be overcome before they become environmentally and economically viable (Takagaki et al. 2012; Abdelaziz et al. 2020). Particularly, finding an efficient, inexpensive, and environmentally friendly organic solvent to extract the HMF has been a goal pursued (Esteban et al. 2020). Dimethyl sulfoxide has been used in numerous works, with excellent yields, but its separation from HMF is a difficult procedure, due to its high boiling point (462 K) (Despax et al. 2014; Paiva Silva et al. 2019). Ionic liquid-based systems are also explored, but there are still several challenges to making these systems economically and environmentally feasible processes for HMF production, since they are expensive, viscous, toxic, and require a laborious synthesis (Cao et al. 2011). Some authors have attempted to convert carbohydrates to HMF in water, but the formation of humins due to condensation of HMF molecules, and the side-reaction of rehydration of the furan ring leading to the formation of levulinic acid can compromise the selectivity of the reaction. Therefore, the use of biphasic systems is an attractive alternative; the conversion of carbohydrate to HMF occurs in the aqueous phase and it can be instantly extracted to another phase, preventing parallel reactions, and eliminating purification steps (Román-Leshkov et al. 2006; Tang
et al. 2017; Saha and Abu-Omar 2014). The organic solvent that composes the biphasic system should be easily recycled and reused, for instance, through simple distillation. In addition, the isolation of the HMF must be efficient. The presence of impurity can difficult the industrial use of HMF, for instance, in the manufacture of adhesives.

Keggin-type heteropolyacids (HPAs) are widely exploited catalysts in acid-catalyzed reactions (Silva et al. 2015; Gonçalves et al. 2012; Vilanculo 2021; Silva and Liberto 2016). Recently, they have been successfully used in the conversion processes of biomass-derived platform molecules into high value-added products (Teixeira et al. 2020; Vilanculo et al. 2020). Similarly, Keggin HPAs have been also used as catalysts to convert hexoses into platform molecules. For instance, phosphotungstic acid, the strongest Bronsted acid among the Keggin heteropolyacids, has been used as a catalyst to produce HMF from different carbohydrates sources (Yang et al. 2012).

However, the low surface area and the solubility of Keggin HPAs in polar solvents lead to a laborious process of recovery. To circumvent this drawback, they have been supported or anchored on solid matrices such as mesoporous silica, or different mixtures of metal oxides (Huang et al. 2018; Liu et al. 2014; Lai et al. 2021; Kumari et al. 2018; Tang et al. 2019). The main challenge for solid-supported HPAs is to resist the leaching triggered by high medium polarity. An approach that has achieved noticeable results is the total or partial exchange of the protons belonging to the Keggin HPAs by large metal cations such as Potassium or Cesium (Silva et al. 2018, 2020; Srinivas et al. 2016; Batalha et al. 2020). This protons exchange transforms the heteropolyacid into insoluble salts which have been demonstrated to be highly efficient catalysts (Silva and Oliveira 2018).

When the metal cation that replaces the protons of HPAs is a Lewis acid likewise Sn(II), the activity of the catalyst may be considerably improved (Chaves et al. 2019; Silva et al. 2017, 2019a). Recently, Tin(II) silicotungstate was successfully used in the synthesis of alkyl levulinates from different carbohydrates (Pinheiro et al. 2019). However, in that work, the reaction was carried out with a conventional heating system at approximately 433 K, in a homogeneous phase (i.e., alkyl alcohol), hampering the step of products purification.

In this work, we evaluate the catalytic activity of metal exchanged HPA catalysts in the production of HMF in microwave-assisted (MW) reactions carried out in a water-ethyl acetate biphasic system. In this system, heteropoly salt remained soluble in water, because the cations selected have a small ionic radius. Since the characterization of the catalysts was previously published (Silva et al. 2016), the focus herein was mainly to evaluate the impacts of the main reaction variables on the HMF yield as well as to establish a mechanism that can explain the catalytic results.

**Experimental**

**Chemicals**

All reagents, solvents and analytical standards were acquired from commercial sources and used without previous treatment. The HPAs (i.e., $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot n\text{H}_2\text{O}$, $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot n\text{H}_2\text{O}$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}\cdot n\text{H}_2\text{O}$; (99.9 wt%)) were purchased from Sigma-Aldrich. All the metal salts, $\text{CrCl}_3\cdot 6\text{H}_2\text{O}$ (98 wt%), $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ (97 wt%), $\text{AlCl}_3\cdot 6\text{H}_2\text{O}$ (99.5 wt%), $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ (99 wt%), $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$ (99 wt%), $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ (98 wt%), and $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ (97 wt%) were acquired from Vetec.

**General procedure for the synthesis of heteropoly salts**

The general procedure for the synthesis of heteropoly salt catalysts exchanged with transition metals was carried out via heteropolyacid acid metathesis with a dilute solution of the metal chlorides, as described in the literature (Silva et al. 2016). Typically, an aqueous solution (30 mL) containing the HPA dissolved was prepared, and subsequently, it was slowly added to another solution containing the desired metal chloride in an adequate stoichiometric amount. The resulting solution was heated to 343 K and magnetically stirred for 3 h. Subsequently, the solution was evaporated releasing HCl and providing the solid salt, which was dried at 383 K for 3 h.

**Heteropoly salts characterization**

To check the success of synthesis, the catalysts were characterized by infrared spectroscopy analysis
(FT-IR/ATR Varian 660-IR spectrometer). To obtain the UV spectra (190–400 nm), we prepared a CH₃CN solution of the heteropolyacids or their metal-exchanged salts at 2×10⁻⁴ mol L⁻¹. The spectra were recorded using an AJX-6100 PC double beam Micronal spectrometer, fitted with Tungsten and Deuterium lamps, which provide radiation in the range of Visible and UV wavelengths, respectively. The spectra in the Visible region (400–760 nm) were obtained from concentrated solutions of HPAs (0.3–0.8 mol L⁻¹). All the spectra were recorded at room temperature using an AJX-6100 PC double beam Micronal spectrometer, fitted with Tungsten and Deuterium lamps to provide visible and UV wavelengths, respectively.

The measurements of the acidic strength of the catalysts were carried out through the measurement of the initial electrode potential (Bel, model W3B) in an acetonitrile solution containing the soluble heteropoly salt. Potentiometric titration was performed to estimate the number of acidic sites. The procedure was performed according to the work described by Pizzio et al. (2003). Typically, the catalyst (50 mg) was dissolved in CH₃CN (30 mL) and was magnetically stirred for 3 h at room temperature. Subsequently, the content was titrated with a solution of n-butylamine in CH₃CN (ca. 0.025 mol L⁻¹). These data sets are presented in the supplemental material (Figs. 1SM–11SM).

General procedure for the synthesis and quantification of HMF

In a Pyrex glass tube, fructose (0.25 mmol) was dissolved in an aqueous solution previously saturated with Sodium chloride (1.0 mL). To this solution, the heteropoly salt catalyst was added (10 mol%), followed by the addition of ethyl acetate (4.0 mL). This tube was sealed, then introduced microwave oven reactor (CEM Discovery microwave reactor), where the temperature was monitored through an internal probe. This reaction mixture was magnetically stirred and heated at 413 K for 17.5 min, using a maximum power of 75 W.

At the end of the reaction, the tube was removed from the reactor and the organic phase was separated from the aqueous phase. The residual water present in the organic phase was removed with anhydrous sodium sulfate. Then, it was filtered and transferred to a volumetric flask (5.0 mL), and its volume was checked with ethyl acetate. Finally, an aliquot (238 µL) of this solution was collected, and the volume was completed to 1.0 mL with ethyl acetate solution containing 1, 3, 5-trimethoxybenzene (TMB) as an internal standard (i.e., TMB, 1.312 mg mL⁻¹).

The quantification of HMF yield was performed by gas chromatography coupled to a mass spectrometer (Shimadzu GCMS-QP2010C Ultra fitted with an Ultra Alloy 5 column, 30 m, ID 0.25 mm). A calibration curve was obtained through analyses of standard solutions prepared in ethyl acetate, with concentrations of HMF varying from 0.25 to 2.0 mg mL⁻¹ and with an internal standard at 1.0 mg mL⁻¹. Helium was the gas carrier, and the chromatographic conditions were as follows: injector temperature (523 K); oven temperature; 313 K (2.0 min), with a ramp of 30 K/min to 493 K (maintained for 1.0 min).

Catalyst recycling

The catalyst recycling was performed using the aqueous phase of the reaction, which contains water, NaCl, and soluble heteropoly salt. The first run was carried out with the selected conditions (i.e., fructose (0.25 mmol), heteropoly salt catalyst (10 wt%), NaCl saturated water (1 mL) and ethyl acetate solution (4.0 mL). The sealed glass tube containing this mixture was heated (17.5 min) in a microwave reactor (413 K) and kept under magnetic stirring. At the end of this period, the system was cooled to room temperature and the ethyl acetate was removed. In that same
tube, a new charge of fructose (0.25 mmol) and ethyl acetate (4.0 mL) was added. This system was taken back to the microwave reactor and this procedure was repeated three more times.

Results and discussion

Characterization of heteropoly salts

The characterization of all the metal transition-exchanged catalysts used in this work was discussed in two previous papers. In the first one (da Silva et al. 2016), metal exchanged catalysts were used in glycerol esterification reactions (Silva et al. 2016). In the second one, Aluminum salts were used as catalysts in olefin oxidations (da Silva et al. 2019a, 2019b). In this present work, we carried out UV–Vis and infrared spectroscopy analyses, and acidity measurements. All the results are presented in the supplemental material (Figs. 1SM–9SM; Table 1SM) (Fig. 1).

The typical absorption bands of the Keggin anion of H₃PW₁₂O₄₀ appeared at 1080, 990, 890, and 790 cm⁻¹, and were assigned to the vibrations υₐₐₕ (P–Oₐ), υₐₐₕ (W–O₉), υₐₐₕ (W–O₉–W) and υₐₐₕ (W–O₉–W) bonds, respectively (Holclajtner-Antunović et al. 2010; Méndez et al. 2011). Figure 2 shows the Oxygen atoms and their localization in the Keggin anion structure (Silva and Oliveira 2018).

These bands appear practically at the same wave-numbers in the FT-IR spectra of meta-exchanged salts, indicating that the structure of the Keggin anion was preserved after the protons exchange. However, some of these bands, for instance, that at approximately 1000 cm⁻¹, were slightly shifted. This shift is a consequence of the strengthening or weakening of W–O₉–W bonds, triggered by the presence of metal cation in the neighbourhood of these Oxygen atoms. Depending on the metal cation, this band is shifted toward a higher or lower wavenumber if compared to the pristine H₃PW₁₂O₄₀. It is visible mainly in the infrared spectra of CrPW₁₂O₄₀ and AlPW₁₂O₄₀ salts. These data are in agreement with the previous works (Silva et al. 2016, 2019b).

The absence of splitting in-band attributed to the vibration of the P–O bond assures that no lacunar anion was formed and that the primary structure remained almost intact after the synthesis. The same was observed when silicotungstic acid had its protons exchanged by the same actions used herein (Silva and Rodrigues 2020).

The main absorption bands that are typical of Keggin heteropolyanions were also observed in the infrared spectra of all the metal-exchanged phosphotungstic acids, as unequivocally demonstrated a comparison of their spectra with the phosphotungstic acid (Fig. 1SM–3SM).

The UV spectra were recorded in the range of 200–750 nm, however, the main absorption bands only appeared within intervals of 190–325 nm (Fig. 3).

The UV spectra of these compounds display two characteristic absorption bands, attributed to the charge transfer from Oxygen atoms to Tungsten since that W atom has electronic configuration “d⁰” (Combs-Walker and Hill 1991). The first, with maximum absorption placed at a low wavenumber (ca. 190 nm) was assigned to the charge transfer from terminal Oxygen to Tungsten. This band was almost not affected by the presence of metal cations. Conversely,
a second absorption band, noticed around 260 nm was assigned to charge transfer from bridges Oxygen atoms to W atom (Mandal et al. 2003; Patel and Patel 2020). The maximum absorption was slightly toward red, mainly when in the presence of $M^{3+}$ cations (Fig. 3b).

In the supplemental material, we compared the UV–Vis spectra of three Keggin HPAs with Copper-exchanged salts (Figs. 4SM–9SM). The discussion of these spectra was placed also in the supplemental material. It is noteworthy that when metal-substituted polyoxometalates (POM) are synthesized by removing an MO unit (M=W, Mo), a lacunar catalyst is generated. When a metal cation is introduced into the Keggin anion structure, metal-substituted POM salts are obtained, which are also very active photocatalysts (i.e., $[PW_{11}M^{2+}O_{39}]^{5-}$, $M^{2+}$ = Mn, Fe, Co, Ni, Cu, Zn) (Liu et al. 2016). In the UV–Vis spectra of these types of doped-metal heteropoly salts, the presence of the transition metal ions in octahedral coordination leads to risen “d–d” transitions absorption bands, in the region from 450 to 780 nm (Li et al. 2018). However, comparatively to the charge transfer bands, “d–d” transitions lead to very weak absorption bands. Consequently, to detect these bands highly concentrated solutions were prepared and

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**Fig. 3** Comparison of UV spectra of phosphotungstic acid and their $M^{2+}$ (a) and $M^{3+}$ (b) metal exchanged salts

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**Fig. 4** Comparison of Visible spectra of phosphotungstic acid and their $M^{2+}$ (a) and $M^{3+}$ (b) metal exchanged salts
their UV–Vis spectra are shown in Fig. 4. Aiming for higher clarity, only the spectral region from 350 to 1000 nm was presented.

The absence of these bands in the spectra of phosphotungstic acid and their Aluminum phosphotungstate salt can be explained by the absence of “d” electrons. Conversely, the intensity and position depended on the metal cation. They were visible in the spectra of Ni\textsubscript{3/2}PW\textsubscript{12}O\textsubscript{40} (380–450 nm), Cr\textsubscript{3/2}PW\textsubscript{12}O\textsubscript{40} (530–650 nm), Cu\textsubscript{3/2}PW\textsubscript{12}O\textsubscript{40} (650–900 nm), Co\textsubscript{3/2}PW\textsubscript{12}O\textsubscript{40} (450–600 nm) (Kurajica et al. 2012; Youn et al. 2005; Mazari et al. 2010). The spectra of metal cations with d\textsuperscript{5} configuration (Mn\textsuperscript{2+} and Fe\textsuperscript{3+} ions) do not show bands with a detectable intensity.

The potentiometric titration curves of metal-exchanged phosphotungstate are presented in Fig. 5. According to Pizzio et al. (2003), the measurements of initial electrode potential (E\text{I}) provide the acidic strength of acid sites: E\text{I} > 100 mV (very strong acid sites), 0 < E\text{I} < 100 mV (strong acid sites), −100 < E\text{I} < 0 (weak acid sites), and E\text{I} < −100 mV (very weak acid sites). All the synthesized catalysts presented E\text{I} > 100 mV, indicating that they have very strong acid sites. However, they showed different values of E\text{I}, which can be ordered as follow: FePW\textsubscript{12}O\textsubscript{40} ≈ CrPW\textsubscript{12}O\textsubscript{40} > AlPW\textsubscript{12}O\textsubscript{40} > Co\textsubscript{3/2}PW\textsubscript{12}O\textsubscript{40} > Ni\textsubscript{3/2}PW\textsubscript{12}O\textsubscript{40} > Mn\textsubscript{3/2}PW\textsubscript{12}O\textsubscript{40}. As expected, the trivalent metal cations had the highest strength of acidity (Fig. 5).

All these catalysts have still Brønsted acidity since the Lewis metal cations can react with hydration water molecules present in the heteropolyanion. This can be confirmed by the absorption band placed at 1620 cm\textsuperscript{-1} wavenumber in the infrared spectra of these salts (Fig. 1). In the supplemental material, we showed the titration curves of Keggin heteropolyacids (Fig. 6SM). The titration curves can be found in Fig. 6SM in the supporting material. The titration curves of phosphotungstic acid and their AlPW\textsubscript{12}O\textsubscript{40} salt have a sharp decline after the addition of 0.8 mL of n-butylamine. Conversely, the other curves presented a different behaviour, some with a strong fall of potential at the beginning of titration (i.e., Ni\textsubscript{3/2}PW\textsubscript{12}O\textsubscript{40}, Mn\textsubscript{3/2}PW\textsubscript{12}O\textsubscript{40}, Cu\textsubscript{3/2}PW\textsubscript{12}O\textsubscript{40}, Co\textsubscript{3/2}PW\textsubscript{12}O\textsubscript{40}), and others with a more gradual diminishing in the E\text{I} value (i.e., CrPW\textsubscript{12}O\textsubscript{40}, FePW\textsubscript{12}O\textsubscript{40}). Nonetheless, all these curves presented two plateaus, suggesting the presence of sites with different acidity strengths. Literature has described that the presence of acidity in the neutral salts of Keggin HPAs is due to the coordination of metal cations to water molecules, which leads to a release of H\textsuperscript{+} ions. In addition, we previously demonstrated that the metal cations themselves can consume n-butylamine, due to the presence of empty orbitals.

When we compared the titration curves of Keggin HPAs with those of Copper exchanged salts (Figs. 6SM and 7SM), we conclude that this modification remarkably modifies the profile of curves; although the E\text{I} values have undergone a slight lowering (ca. 50 mV, at maximum), all the three curves presented two plateaus at different regions, after the
Cu(II) doping, suggesting that they now have acidity sites with different strength.

**Catalytic tests**

**Evaluation of different metal phosphotungstate catalysts on the conversion of fructose to HMF**

Initially, a screening aiming to verify the most active and selective catalyst in the conversion of fructose to HMF was performed. The main results are shown in Table 1. It is important to highlight that at this stage, the reaction conditions are not optimized to achieve the maximum yield. Our objective herein is to evaluate all the catalysts under the same conditions.

The HMF yields varied from 40 to 53%, with Cr and Cu phosphotungstate salts being the most efficient catalysts. Initially, we have expected that the catalysts with higher strength of acidity (i.e., with higher Ei values, Fig. 5) will reach the higher HMF yields.

Although the CrPW$_{12}$O$_{40}$ catalyst has presented a strong acidity and its reaction has achieved also a high HMF yield, the reactions in the presence of FePW$_{12}$O$_{40}$ or AlPW$_{12}$O$_{40}$ also showed high acidic strength, reached only lower yields (Table 1).

Surprisingly, Cu$_{3/2}$PW$_{12}$O$_{40}$ that had an Ei value almost equal to the Ei measured for AlPW$_{12}$O$_{40}$, suggesting that both have a similar acidic strength, achieved the highest yield. This suggests that probably the success of the reaction depends on other aspects that may be beyond the acidity strength of the catalysts. These results support the conclusion that although necessary, the Brønsted acidic strength should not be too strong, to prevent further rehydration of HMF. Consequently, the strongest acid will not necessarily be the best catalyst (Guo et al. 2018).

In addition, the appearance of a brown ring on the walls of the glass reactor verified the formation of humins, triggered by HMF polymerization.

It is noteworthy that this reaction occurs in an aqueous phase, therefore, we carried out pH measurements to verify the acidity of the reaction medium after adding the metal exchange salt catalyst (Table 2SM). The pH value of the solutions was 3.3 for AlPW$_{12}$O$_{40}$ and FePW$_{12}$O$_{40}$, which were partially soluble, and 3.2. for all the other soluble salts. These very close pH values are a consequence of the leveling effect of the water. The aqueous medium becomes acidic due to the hydrolysis of metal cations, which generate H$_3$O$^+$ cations (Eqs. 1 and 2).

\[
M^{n+} + nH_2O \rightleftharpoons [M(H_2O)_{n}]^{n+} \quad (1)
\]

\[
[M(H_2O)_{n}]^{n+} + H_2O \rightleftharpoons [M(H_2O)_{n-1}(OH)]^{(n+)-1} \quad (2)
\]

**Mechanistic insights**

It is natural to suppose that the protons should be the main players in these catalytic games and therefore act as the main active sites. Therefore, in Scheme 1 we propose a reaction pathway that can be useful to explain how they have risen into the reaction medium and how they can participate in steps that lead to the conversion of fructose to HMF. However, the Copper phosphotungstate has no protons.

The literature describes that transition metal salts can be hydrolyzed generating hydronium cations in aqueous solutions (Eqs. 1 and 2) (Silva et al. 2016, 2019b). We suppose that the same occurs with Copper phosphotungstate (Scheme 1). Afterwards, the reaction probably proceeds such as the typical Brønsted acid-catalyzed reactions (Scheme 1) (Putten et al. 2013).

### Table 1

| Catalyst | HMF yields (mol%) |
|----------|-------------------|
| AlPW$_{12}$O$_{40}$ | 43 |
| FePW$_{12}$O$_{40}$ | 40 |
| CrPW$_{12}$O$_{40}$ | 51 |
| Cu$_{3/2}$PW$_{12}$O$_{40}$ | 53 |
| Co$_{3/2}$PW$_{12}$O$_{40}$ | 45 |
| Ni$_{3/2}$PW$_{12}$O$_{40}$ | 46 |
| Mn$_{3/2}$PW$_{12}$O$_{40}$ | 46 |

Reaction conditions: fructose (0.25 mmol), catalyst (5 wt%), temperature (413 K), MW, biphasic system [AcOEt (4 mL)/NaCl saturated aqueous solution (1 mL)], time (10 min)

The humin formation was observed in the AlPW$_{12}$O$_{40}$, Ni$_{3/2}$PW$_{12}$O$_{40}$ or Mn$_{3/2}$PW$_{12}$O$_{40}$-catalyzed reactions.
The first step begins with the protonation of the hydroxyl bound to the anomeric carbon of fructose, followed by the loss of a water molecule, and the formation of the oxonium ion (intermediate I, Scheme 1). Subsequently, water removes β-hydrogen from the oxonium ion, forming an enol (intermediate II, Scheme 1) that is in tautomeric equilibrium (keto-enol) (intermediate III, Scheme 1). From the intermediate aldehyde, there is the protonation of a second hydroxyl (intermediate IV, Scheme 1), followed by the loss of another water molecule, leading to the formation of an α, β-unsaturated aldehyde (intermediate V, Scheme 1). Finally, the protonation of the secondary hydroxyl (intermediate VI, Scheme 1), followed by the loss of a water molecule and β-hydrogen from the carbon of aldehyde, leads to the formation of the HMF molecule (Scheme 1).

Gomes et al. (2017) previously evaluated the activity of soluble phosphotungstic acid or solid-supported such as MCM-41 silica mesoporous. Those authors concluded that although \( \text{H}_3\text{PW}_{12}\text{O}_{40}/\text{MCM-41} \) has been an efficient solid catalyst, it was less active than soluble acid (Gomes et al. 2017). They attributed this highest activity to the greatest strength of Brønsted acidity of HPA. Nonetheless, it is known that when a Lewis acidity site is introduced in the catalyst, a positive effect can occur. For instance, Lai et al. (2021) investigated the conversion of glucose to HMF and verified that the yield achieved in the presence of \( \text{Ag}_3\text{PW}_{12}\text{O}_{40} \) was higher than that in the presence of \( \text{H}_3\text{PW}_{12}\text{O}_{40} \) catalyst. Those authors attributed this effect to the Lewis acidity of \( \text{Ag}^+ \) cations, which favour the isomerization of glucose to fructose, and...
consequently the HMF formation. Herein, as we are starting from fructose, no isomerization is required.

Although the mechanism describes how the reaction occurs in the presence of $\text{H}_3\text{O}^+$ cations (Putten et al. 2013), it remains unclear how the Copper cations can directly participate in this reaction. Our pH measurements demonstrate that $\text{Cu}^{2+}$ cations participate in the generation of $\text{H}_3\text{O}^+$ cations. However, the metal cation itself may also play an essential role in the catalytic process, possibly, promoting the dehydration steps. Another possibility is that the Copper heteropoly salt minimizes the formation of humins from the polymerization of HMF, thereby increasing the yield. In addition, we suppose that bulky heteropolyanion act to stabilize the protonate intermediates formed during the reaction (Scheme 1).

Therefore, we will proceed with our investigation for a better understanding of this catalytic system. Although the $\text{CrPW}_{12}\text{O}_{40}$ has been also very active, due to the highest HMF yield achieved in $\text{Cu}_{3/2}\text{PW}_{12}\text{O}_{40}$-catalyzed reaction, it was selected to assess the effect of other reaction variables. Furthermore, Chromium is considered a highly toxic metal cation, and its use should be avoided. The Principles of Green Chemistry are favourable to the use of recyclable catalysts, and as we will demonstrate, the $\text{Cu}_{3/2}\text{PW}_{12}\text{O}_{40}$ can be easily recovered and reused.

**Effect of heteropolyanion on the activity of copper exchanged heteropolyacid salts on the conversion of fructose to HMF**

The fructose dehydration in a biphasic system was carried out in the presence of different HPAs, as well as in the presence of their Copper exchanged salts (Table 2). All the reactions were assisted by microwaves radiation.

Regardless of the Keggin anion, the Copper exchanged salts were always more efficient than their precursor acid. This means that the substitution of protons by Copper had a positive effect on the activity of the catalysts. Measurements of pH performed in the solution after the catalyst addition showed that likewise to the observed in the reactions with the other metal exchanged phosphotungstate salts the pH was always close to 3.2, except when $\text{Cu}_2\text{SiW}_{12}\text{O}_{40}$ was the catalyst.

Once more, it is demonstrated that the presence of Copper has a key influence, possibly more important than Brønsted acidity since the solutions

| Catalyst     | pH value$^a$ | HMF yields (mol%) |
|--------------|--------------|--------------------|
| $\text{H}_3\text{PW}_{12}\text{O}_{40}$ | 3.2          | 51                 |
| $\text{Cu}_{3/2}\text{PW}_{12}\text{O}_{40}$ | 3.2          | 53                 |
| $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ | 3.0          | 25                 |
| $\text{Cu}_{3/2}\text{PMo}_{12}\text{O}_{40}$ | 3.0          | 39                 |
| $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ | 3.4          | 50                 |
| $\text{Cu}_2\text{SiW}_{12}\text{O}_{40}$ | 4.2          | 51                 |

Reaction conditions: fructose (0.25 mmol), catalyst (5 wt%), temperature (413 K), MW irradiation, biphasic system [AcOEt (4 mL)/NaCl saturated aqueous solution (1 mL)], time (10 min)

Humin formation was observed in the $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ or $\text{Cu}_{3/2}\text{PMo}_{12}\text{O}_{40}$-catalyzed reactions

$^a$Measurements of pH were performed in water
with the same pH achieved different yields (i.e., Cu$_{3/2}$PMo$_{12}$O$_{40}$, 39% against Cu$_{3/2}$PW$_{12}$O$_{40}$, 53%). Moreover, the heteropolyanion should also have a significant role. In the reactions with equal Copper concentration, the runs in the presence of phosphotungstate or phosphomolydbdate salts reached different HMF yields (39 and 53%, respectively, Fig. 7). Probably, these heteropolyanions could act to stabilize the protonated intermediate formed throughout the process.

Evaluation of main reaction variables

To assess the influence of catalyst load (Fig. 7a), reaction time (Fig. 7b), and temperature (Fig. 7c), on the HMF yield, all the other reaction parameters were kept constant.

An increase in the amount of catalyst had a positive effect on the yield of HMF until 10 mol% (Fig. 7a). It can be assigned to the increase of active sites in solution due to higher catalyst concentration. For catalyst loads higher than this, no beneficial effect
was verified. It is possible that at these conditions the reaction equilibrium within the time interval evaluated has been achieved. Therefore, using 10 mol% of catalyst, the next step was investigating how the yield of HMF varies over time (Fig. 7b).

The HMF yield was gradually increasing when the reaction was carried through greater periods (Fig. 7b). However, the maximum yield was achieved in a time of 17.5 min of reaction. Reactions performed in longer periods lead to a lowering of the yield of HMF, probably due to its polymerization into humins.

Another important parameter is the temperature of the reaction. It was not possible to evaluate temperatures above 413 K due to limitations of the MW reactor because when doing experiments at 423 K the ethyl acetate (boiling point is 350 K) was lost, due to high pressure in the system.

Figure 7c displays the results of the reaction performed at three temperatures (393, 403 and 413 K), in the biphasic system containing the soluble catalyst. The yields considerably drop to 46% at 403 K and 10% at 393 K. Therefore, as the greatest yield was achieved at the highest temperature, it is evidence of the endothermic character of the reaction.

The composition of the biphasic system is an aspect that may drastically affect the reaction yield, mainly because the reaction occurs in the aqueous phase while the organic phase is used to extract the final product. To decrease the solubility of HMF in the aqueous solution and to favour its migration to the organic phase, the reaction can be carried out in saturated solutions using different salts. Different salts can distinctly affect the ionic strength of an aqueous solution and consequently impact the reaction yield. Figure 8 shows the HMF yields obtained in reactions with the aqueous phase saturated using different ionic compounds.

When no salt was used, only a poor yield of HMF was achieved (24%, Fig. 8). This result can be explained by the salting-out effect (Görgényi et al. 2006; Desai and Eisen 1966). When a solution is saturated with ions, the solubility of other solutes is compromised. These ions interact strongly with water molecules, through ion–dipole interactions, lowering the solubility of HMF in the aqueous medium. Consequently, this makes it migrate more efficiently to the extracting organic phase. This explains why all evaluated systems containing salts have a better yield for HMF since it is extracted more efficiently in their presence, thereby also avoiding parallel reactions that can occur in the aqueous phase (Esteban et al. 2020; Saha and Abu-Omar 2014).

In general, the best results are observed for systems with the salts NaCl (81%) and KCl (67%), which indicates a better HMF extraction efficiency for systems containing the cations Na⁺ and K⁺. Conversely, in the solution saturated with LiCl, only a 49% yield was reached. It is expected that cations with smaller radii will be more efficient to saturate this solution, and consequently, they can favours the HMF removal toward the organic phase.

The reactions carried out in solutions saturated with CaCl₂ or MgCl₂ achieved yields of 41% and 37%, respectively; the yields were lower and the formation of humins was observed. This lower yield can be assigned to greater ionic radius of cations Ca²⁺ and Mg²⁺, which require a higher water molecules number to be completely hydrated. The cation with a smaller hydration radius causes a higher salting-out effect, which leads to greater HMF extraction efficiency and, consequently, a lower occurrence of parallel reactions in the aqueous phase (Saha and Abu-Omar 2014; Görgényi et al. 2006). This effect was not observed when compared to the HMF yield of NaCl and LiCl.

The polarity of the organic phase as well as the intermolecular forces existent can favour the removal

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**Fig. 8** Effect of different salts present in the saturated aqueous solution on the HMF yield in Cu₃₀PW₁₂O₄₀-catalyzed fructose dehydration reactions. Reaction conditions: fructose (0.25 mmol), catalyst load (10 wt%), temperature (413 K), MW, biphasic system (AcOEt (4 mL)/saturated aqueous solution (1 mL)), time (17.5 min)
of HMF from the aqueous phase. This effect was investigated using the optimized conditions and different organic solvents. The main results are shown in Fig. 9.

The selection of the organic solvents used to compare with ethyl acetate was performed according to literature as follows: MIBK (Román-Leshkov et al. 2006; Lucas et al. 2020), acetonitrile (Wrigstedt et al. 2016), and tetrahydrofuran (Tang et al. 2017; Fang et al. 2018) (Fig. 9).

The reactions carried out with ethyl acetate as the organic phase continued to be that with the highest HMF yield (81%), followed by the acetonitrile (65%) and methyl isobutyl ketone (MIBK) ones (60%). Among the solvents tested, tetrahydrofuran was the worst extractor, reaching the poorest yield of (32%), which was also lower than the yield achieved in a system without the extraction phase (46%). The superior performance of ethyl acetate can be assigned to its lowest dielectric constant, and its low dipole moment (Table 4SM). Ethyl acetate can interact with HMF molecules through hydrogen bonds; their physical and chemical properties look to have a synergic effect that favours the extraction of these product molecules from an aqueous phase.

Finally, the possibility of reducing the volume of ethyl acetate used in the extraction was also evaluated. The extraction was done using different volumes (5.0, 4.0, 3.0, 2.0 and 1.0 mL, Fig. 10). It was found that a reduction of volume used to extract the HMF triggered a drop in yields. This can be explained by the limitation caused by decreasing the volume of the extracting phase, which restricts the amount of HMF extracted and this leads to parallel reactions in the reaction phase, such as HMF self-condensation reactions that produce humins (Lucas et al. 2020).
Catalyst recycling

Processes using a recyclable catalyst generate fewer effluents and residues and are more sustainable and viable, according to the principles of green chemistry (Sheldon 2017). In this sense, the recovery and reuse of the Cu_{3/2}PW_{12}O_{40} catalyst were evaluated using the optimized conditions. (10 mol% catalyst, 413 K, MW, 17.5 min, ethyl acetate/NaCl saturated aqueous solution (4:1 v/v). The recycling was carried out as described in the experimental section. At the end of the reaction, the organic phase was removed and a new charge of fructose and ethyl acetate (4 mL) were added to the aqueous phase containing the catalyst. Figure 11 shows the main results.

Thus, the aqueous phase and the catalyst were recycled for another four cycles (Fig. 11). The catalyst activity presented a minimum decline within the five successive cycles of reuse, and HMF yield decreased only from 81 to 77%.

Conclusions

In this work, we evaluated the activity of metal-exchanged Keggin heteropolyacid salts as catalysts to produce HMF in microwave-assisted reactions carried out in ethyl acetate-water biphasic system. Among the heteropolyacids and salts evaluated, Cu_{3/2}PW_{12}O_{40} was the most active and selective catalyst. The effects of the main variables of reaction were assessed. Among the solvents investigated, ethyl acetate was the best choice, due to the lowest dipole moment and low dielectric constant, which demonstrated to be more important than hydrogen bonds existing in other solvents. Sodium chloride promoted the most efficient salting-out effect. At the optimized conditions (ca. 413 K, Cu_{3/2}PW_{12}O_{40} (10 mol%), biphasic system (ethyl acetate/NaCl saturated aqueous solution 4:1 v/v), an HMF yield of 81% was achieved after 15 min MW irradiation. The best performance of Cu_{3/2}PW_{12}O_{40} is a consequence of the Lewis acidity of Cu^{2+}, which allows it to coordinate with the water molecules, consequently releasing H_3O^+ ions, as demonstrated by the pH measurements. These ions can promote fructose dehydration. However, comparing the superior performance of Cu_{3/2}PW_{12}O_{40} with those achieved by heteropolyacids or mineral Brønsted acids, we can conclude that a great amount of H_3O^+ ions can compromise the HMF yield, probably due to the rehydration of fructose or humins formation. A comparison with other metal salts allowed concluding that the Cu^{2+} cation plays an essential role in this reaction. Conversely, comparing the performance of different Copper salts, we can realize that the anion is also essential for the success of the catalyst. The Copper salts had different performances, being Cu_{3/2}PW_{12}O_{40} the best among them. This suggests that the heteropolyanion plays also an important role. We suppose that bulky heteropolyanion should act to stabilize the protonated species formed during the reaction. This work may bring a new application of polyoxometalate salts, in particular, Copper phosphotungstate, a recyclable, water-soluble, and less corrosive catalyst in modern biorefinery. It may open a new route where MW assisted reactions carried out in biphasic systems can make the industrial processes for biomass conversion more sustainable and green. The catalyst was easily reused after the removal of the organic phase and the addition of a new load of the substrate to the remaining aqueous phase that contains the catalyst. The high partition coefficient of reactants and products assure the efficiency of this biphasic process. The recyclability of metal salt catalyst is an aspect that minimizes the environmental impact of the process.

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Declarations

Conflict of interest None.

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