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Synthesis of 5-hydroxymethylfurfural from fructose catalyzed by phosphotungstic acid

Filipe N.D.C. Gomes[a], Fabiana M.T. Mendes[b], Mariana M.V.M. Souza[a],*

[a] *Escola de Química—Universidade Federal do Rio de Janeiro (UFRJ), Centro de Tecnologia, Bloco E, sala 206, CEP 21941-909 Rio de Janeiro/RJ, Brazil*
[b] *Instituto Nacional de Tecnologia, Divisão de Catálise e Processos Químicos, Av. Venezuela, 82, sala 110, CEP 20081-312 Rio de Janeiro/RJ, Brazil*

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ABSTRACT

The dehydration of fructose to 5-hydroxymethylfurfural (HMF) is a way to produce a very versatile intermediate of the green chemistry. Heteropolyacid compounds are acid catalysts with singular properties (strong acidity and well-defined structure). This paper aims to analyze the activity of phosphotungstic acid (HPW) and Cs-exchanged phosphotungstic acid (HCsPW) in HMF synthesis, as well as HPW supported on MCM-41. The reactions were conducted in a batch reactor, using dimethyl sulfoxide (DMSO) as solvent, for 2 h. The initial tests indicated that HMF is formed in the absence of catalyst, but in presence of the catalysts, the maximum yield to HMF is higher and achieved in less time. The HPW showed promising results, reaching 100% of fructose conversion and 92% of HMF yield, after 30 min of reaction at 120 °C, with a catalyst:fructose mass ratio of 1:10. However, this heteropolyacid is soluble in DMSO. Besides, the Cs-exchanged HPW resulted in a reduction in HMF yield, because of the reduction in solid acidity. HPW supported in MCM-41 (HPW/MCM) showed to be a good solid acid catalyst for the production of HMF from fructose; moreover, it can be recovered and reused. The variables evaluated for this catalyst were the reaction temperature (100, 120 and 140 °C) and the catalyst:fructose mass ratio (1:10; 1:30 and 1:50). The best results obtained for HPW/MCM were 100% of fructose conversion and 80% of HMF yield in 60 min, at 120 °C.

1. Introduction

The energy generation from biomass has been widely used in substitution of fossil fuels, such as using ethanol instead of gasoline. However, the use of biomass as an alternative to replace oil in the production of chemical supplies is walking in the slow steps. In this scenario, it is highlighted the production of furan derivatives. Such compounds can be obtained from biomass with properties equivalent to petrochemical derived ones, and thus are considered as fundamental building blocks for biorefineries. In particular, 5-hydroxymethylfurfural (HMF) is considered a key intermediate for the development of biomass-based products, because a series of compounds derives from it, like: organic acids (formic, levulinic and adipic), polymer precursors (furan 2, 5 dicarboxylic acid, 2-hydroxymethyl-furan) and biofuels (2-methylfuran, 2,5-dimethylfuran) [1,2].

Dehydration of carbohydrates, particularly fructose, in acid medium, as shown in Fig. 1, is the most promising way to produce HMF. However, this synthesis is complex due to the high instability of HMF; depending on the reaction conditions, there occur parallel reactions that lead HMF and fructose to soluble polymers and humins. In addition, HMF can be converted to levulinic and formic acids by rehydration resulting in yield loss [3,4].

The literature about dehydration of fructose to HMF is fairly extensive, with studies of the reaction mechanism, search for optimal synthesis conditions and also the market analysis. However, no catalytic system with potential for industrial application has been developed yet. Regarding this issue, there is a range of catalysts, reaction conditions and solvents that have been evaluated and the results provide a great understanding of how these variables influence the HMF synthesis.

Researches about reaction temperature and solvent used for fructose dehydration showed that temperatures from 120 to 180 °C and the water reducing content of the reaction system are ideal conditions to produce HMF. The fructose conversion is very low at low temperatures; however, at temperatures above 180 °C the degradation of HMF is favored. On the other hand, the water content directly influences the rehydration of the product to levulinic and formic acids [5,6].

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* Corresponding author.
E-mail address: mmattos@eq.ufrj.br (M.M.V.M. Souza).

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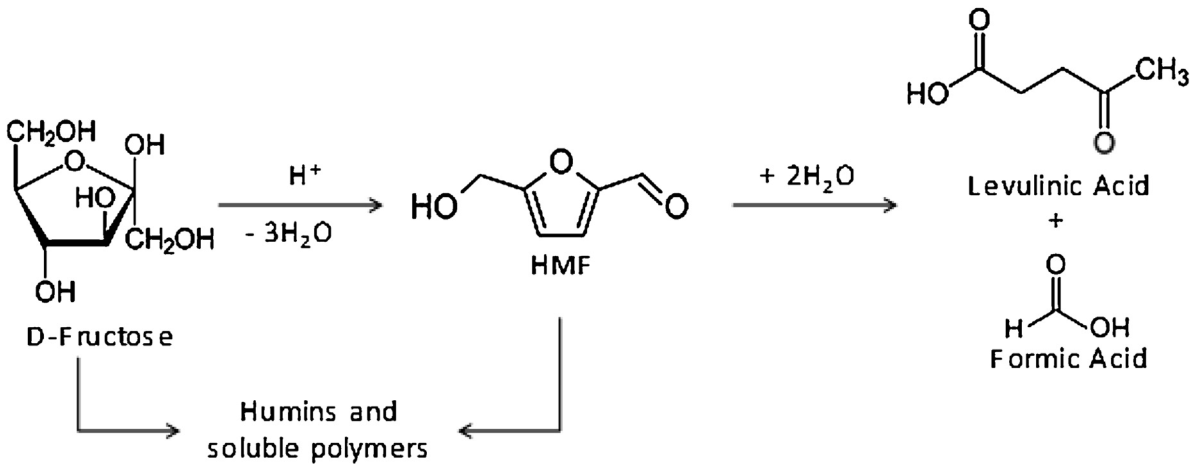

Fig. 1. Reaction scheme of fructose dehydration to HMF and parallel reactions.

A lot of system reactions have been studied and the biphasic and organic media have greater advantages for HMF production over aqueous medium. The continuous removal of the HMF into the organic phase provides the displacement of the reaction equilibrium for production of this compound, as well as prevents its rehydration and polymerization. Among the solvents used in the literature, compounds with four carbons (tetrahydrofuran and 1-butanol, for example) produce higher HMF yields [7–9]. However, DMSO (dimethyl sulfoxide) showed similar results to those solvents with four carbons [10,11]. Thus, its use as solvent is more attractive because the fructose is soluble in DMSO, unlike other organic solvents, reducing parallel reactions and the possibility of HMF oxidation in the same medium.

The acid strength of the catalysts (homogeneous or heterogeneous) is another variable that governs the HMF selectivity. The use of strong acids favors deprotonation of the hydroxyl groups present in the hexoses and therefore the parallel and rehydration reactions [5]. Thus, it was found that the use of moderate acids provides increased formation of HMF. Another factor that hinders the production of this furan derivative is the reaction time. The use of heterogeneous catalysts requires a longer reaction time for conversion of fructose and this can cause an increase in polymerization reactions of both substrates and products, which necessitates the continuous extraction of HMF from the reaction medium. In addition, the HMF yield also decreased with the increase of substrate or catalyst concentration [5–7].

The heteropolyacids (HPAs) of Keggin type are superacids, with a well-defined structure, consisting of a central cation (heteroatoms: P, As, Si, Ge, B etc.) and surrounded by polyanions. Due to their structural characteristics and heteroatoms, the acidity and other properties can vary considerably. In addition, the exchange of protons by other cations, such as Cs^+, can cause deep modifications in their properties [12–14]. Therefore, this class of compounds, which already has a wide application in catalysis, has a great potential for use in the HMF synthesis and its derivatives. Although the HPAs have high acidity, they present weak thermal stability, high solubility in polar solvents and low specific surface area ($<10\,m^2\,g^{-1}$), which can limit their use in several reactions. Because of that, HPAs supported over classical porous materials (e.g., mesoporous silica) are usually more effective for catalytic reactions [15–17].

There are few reports of the use of HPAs in HMF synthesis. The studies with pure phosphotungstic acid (HPW) and cesium-modified HPW – $H_3PW_{12}O_{40}$ and $H_{0.5}Cs_{2.5}PW_{12}O_{40}$, respectively – have reported almost total fructose conversions, as well as yields in the range of 90–95% with DMSO, butanol or methyl isobutyl ketone (MIBK) as the solvents. The studies report the acid strength of the catalyst as the principal property that rules the yield and selectivity to HMF, which is linked to the proton exchange. The exchange by cesium, for example, enables to modify their acid-base properties and solubility in polar solvents, consequently changing the HMF yield [18,19]. HPW supported on MCM-41 has been tested for several reactions [16,17], but not for dehydration of fructose. As far as

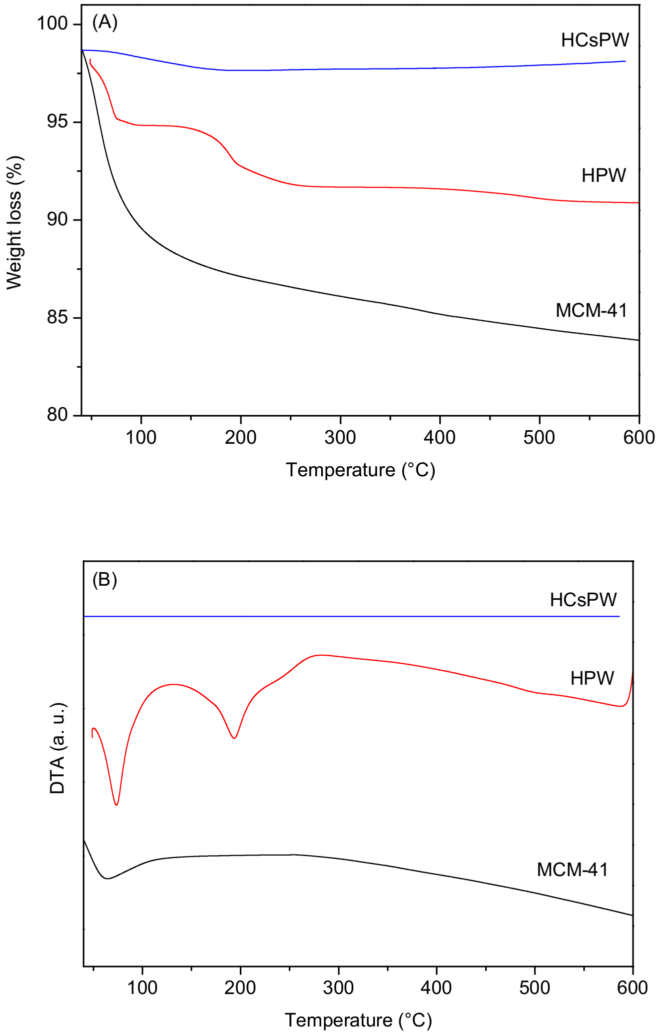

Fig. 2. TG/DTA profiles of the catalysts.

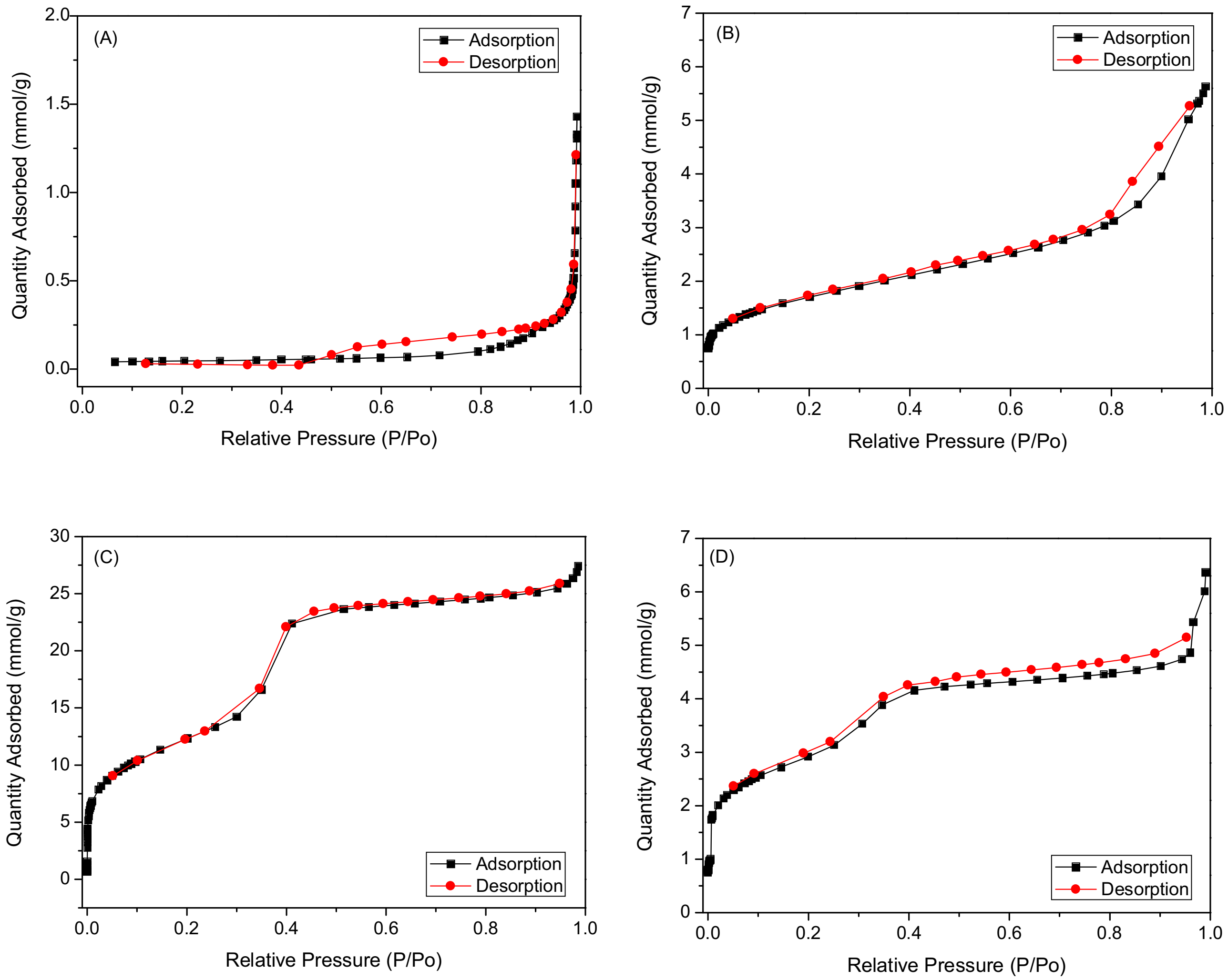

Fig. 3. N_2 adsorption–desorption isotherms of the catalysts: (A) HPW, (B) HCsPW, (C) MCM-41 and (D) HPW/MCM.

we know, the use of HPW supported on MCM-41 for dehydration of fructose is reported here for the first time.

All researches on hexose dehydration to HMF using HPAs found in the literature were carried out in organic medium or ionic liquids without evaluating the role of solvent, the need for proton exchange and the influence of the support [10,18–20]. Thus, this study aims to assess the catalytic activity of pure and cesium-exchanged phosphotungstic acids in HMF synthesis from fructose, with DMSO as solvent. The activity of the HPW supported on MCM-41 will also be investigated in fructose dehydration.

2. Experimental

2.1. Catalyst preparation

Fructose, Keggin-type 12-tungstophosphoric acid (HPW), cesium carbonate, methanol and dimethyl sulfoxide (DMSO) were obtained from Sigma-Aldrich Corporation. MCM-41 (mesoporous aluminosilicate) was purchased from Tianjin Chemist Scientific Ltd. (Chemist). All reagents were used as supplied without further purification.

12-tungstophosphoric acid and MCM-41 were firstly calcined in air for 3 h at 350 °C. MCM-41 supported 12-tungstophosphoric acid (HPW/MCM) was prepared by incipient wetness method [21]. Typically, 1.5 g of HPW was dissolved in 90 mL of methanol. Then 1.5 g of MCM-41 was added into the HPW solution, which corresponded to 50 wt.% of HPW in the catalyst. The mixture was stirred at room temperature for 12 h, and the methanol was evaporated under reduced pressure. The resulting solid was dried at 120 °C overnight and then calcined using the previous conditions.

Cesium-exchanged 12-tungstophosphoric acid ($H_{0.5}Cs_{2.5}PW_{12}O_{40}$) was synthesized by dropwise addition of an aqueous solution of cesium carbonate to an aqueous solution of 12-tungstophosphoric acid, in the desired stoichiometry, according to the literature [22]. In a typical preparation protocol of $H_{0.5}Cs_{2.5}PW_{12}O_{40}$ (HCsPW), 1 mmol of $H_3PW_{12}O_{40}$ was dissolved in 30 mL of distilled water. This solution was added dropwise into 1.25 mL, 1 mol L^{-1} of Cs_2CO_3 aqueous solution with vigorous stirring at room temperature. The mixture was continuously stirred for about 30 min, the water was evaporated at 80 °C under reduced pressure and then the precipitate was aged for 12 h at room temperature. The white solid was dried at 120 °C overnight and then calcined as described above.

2.2. Catalyst characterization

N_2 adsorption-desorption experiment was carried out at −196 °C using an ASAP 2020 equipment (Micromeritics). The samples were outgassed for 24 h at 300 °C. The specific surface area was obtained by using the Brauner-Emmett-Teller (BET) method, and pore volume and mean pore diameter by Barrett-Joyner-Halenda (BJH) method.

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Table 1
Physico-chemical properties of the catalysts determined by N_2 adsorption/desorption and NH_3-TPD measurements.

Catalyst	S_{BET} ($m^2\,g^{-1}$)	Pore volume ($cm^3\,g^{-1}$)	Mean pore diameter (Å)	Total acidity ($\mu molNH_3\,g_{cat}{}^{-1}$)
HPW	<5	0.00	0.00	466
HCsPW	135	0.17	79.4	52
MCM-41	≥800	≥0.70	30.0	403
HPW/MCM	114	0.08	87.8	816

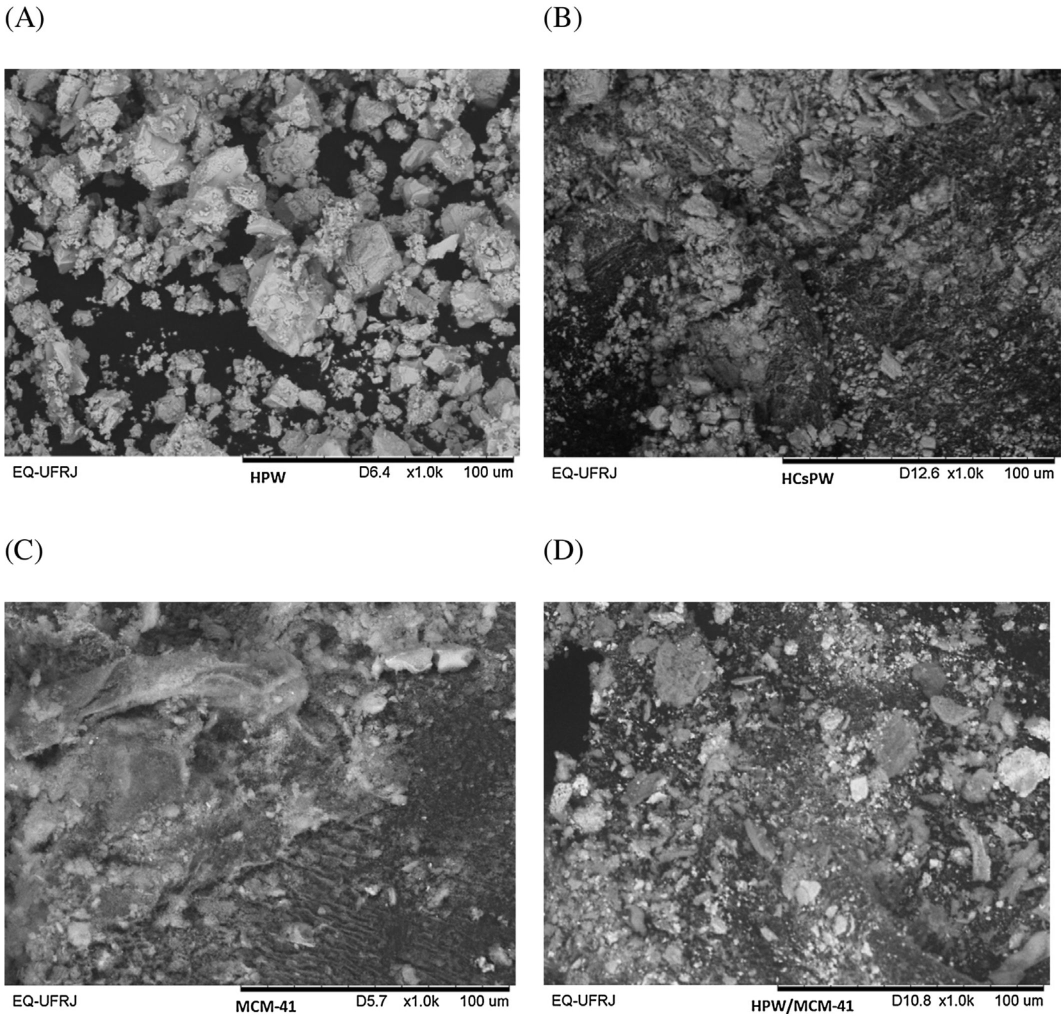

Fig. 4. SEM micrographs of the catalysts: (A) HPW, (B) HCsPW, (C) MCM-41 and (D) HPW/MCM.

Thermogravimetric (TG) and differential thermal (DTA) analyses were performed under a nitrogen flow at constant rate of 10 °C min^{-1} using a TA Instrument SDT-Q600.

Fourier transform infrared spectroscopy (FTIR) measurements were recorded in KBr discs on a Shimadzu PRESTIGE-21 spectrometer with the wavenumber range of 400–1500 cm^{-1}.

X-ray powder diffraction (XRD) patterns were determined with a Rigaku Miniflex II diffractometer equipped with a graphite monochromator and CuKα radiation (30 kV and 15 mA). The measurements were carried out with a speed of 0.05° s^{-1} and over the 2θ range of 2–90°. XRD in low angle was performed in Rigaku Dmax 2200 diffractometer, with a speed of 0.02° s^{-1} from 1 to 5°.

Morphology of the samples and the energy dispersive X-ray analysis (EDS) of W, P and Cs elements were investigated by means of Scanning Electron Microscope Hitachi TM-1000. Chemical composition of the HPW/MCM and MCM was determined by X-ray fluorescence (XRF) using a Rigaku PRIMINI spectrometer.

Acid properties of the support and catalysts were determined by temperature-programmed desorption (TPD) of NH_3. Ammonia adsorption was carried out at room temperature with 4% NH_3/He (30 mL min^{-1}) for 30 min, followed by purging with He for 1 h. The desorption of chemisorbed ammonia was realized by heating up to 1000 °C at 10 °C min^{-1} under He flow (30 mL min^{-1}). The desorbed NH_3 was detected using a mass spectrometer Pfeiffer Vacuum PRISMA PLUS.

2.3. Catalytic activity tests

All fructose dehydration reactions were carried out in 100 mL glass reactor equipped with a reflux condenser. This system was heated with a thermostatically controlled oil bath. In a typical procedure, fructose (500 mg—2.77 mmol) was dissolved in DMSO (20 mL) and then the catalyst (50 mg) was added into the fructose solution, which corresponded to 10 wt.% of active phase in the fructose solution. The resulting mixture was charged into a reactor and

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it was placed in the oil bath at 120 °C. The samples were collected from 0 to 120 min. Once defined the catalyst, other reaction conditions were tested, like temperature (100, 120 and 140 °C) and catalyst:substrate mass ratio (1:10, 1:30 and 1:50).

2.4. *Analysis*

After each fructose dehydration reaction, the catalyst was filtered and all products were analyzed by high-performance liquid chromatography (HPLC) in a Shimadzu Prominence system, equipped with diode-array (DAD) and refractive index (RID) detectors and an Aminex HPX-87H column (Biorad), using 0.01 mol L^{-1} H_2SO_4 as the mobile phase at a flow rate of 1.0 mL min^{-1}. The column temperature was maintained at 40 °C.

The fructose conversion (C_f) and the HMF yield (Y_{HMF}) are described in Eqs. (1) and (2), respectively.

$$C_t\,(\%) = \frac{\text{moles of fructose reacted}}{\text{moles of fructose initial}} \times 100 \qquad (1)$$

$$Y_{HMF}\,(\%) = \frac{\text{moles of HMF prodced}}{\text{moles of fructose initial}} \times 100 \qquad (2)$$

3. Results and discussion

3.1. *Catalyst characterization*

Chemical composition of the pure phosphotungstic acid, measured by energy dispersive X-ray (EDS), is consistent with the literature. The molar ratio between phosphorus and tungsten was 11 (the theoretical value is 12). Considering that this analysis is superficial, a small variation in the real value is acceptable. Chemical composition of the MCM-41 (89 wt.% SiO_2 and 5 wt.% Al_2O_3) and the mass percentage between HPW/MCM (45% HPW and 55% MCM-41), measured by X-ray fluorescence (XRF), are in agreement with the real value and indicate that impregnation of the active phase on the support by incipient wetness method is a simple method with good results.

The stability of HPW, HCsPW and MCM-41, before calcination, was examined by TG/DTA measurements, under N_2 atmosphere, as displayed in Fig. 2. The profile obtained for MCM-41 exhibits only a weight loss up to 150 °C, corresponding to the loss of water molecules adsorbed on the surface of material [23]. Typical TG/DTA patterns for the Keggin-type heteropolyacids were presented by pure phosphotungstic acid. For this catalyst, the major weight loss occurred before 100 °C, which is related to the elimination of water molecules. These molecules are responsible for the crystallization of heteropolyanions into a hydrate. The second weight loss for HPW occurred from 150 to 250 °C and corresponds to the loss of constitutional water. After, there was a plateau between 250 and 400 °C, which can be described as the formation of anhydrous acid. Finally, the third weight loss is reported as decomposition of heteropolyanion, with crystallization of oxides [24]. These three events are endothermic, as seen in DTA profile. As the protons of the Keggin structure are replaced by cesium atoms, the weight loss is decreased, as shown by HCsPW profile, indicating that the proton-exchange improves the thermal stability of phosphotungstic acid [14,24].

The textural properties of the catalysts were obtained by N_2 adsorption-desorption isotherms (Fig. 3). The BET specific surface area, pore volume and mean pore diameter of all catalysts are depicted in Table 1. MCM-41 presented a type IV isotherm, typical of mesoporous materials. The profile of adsorption-desorption isotherm is completely changed as cesium is inserted in the HPW structure. The pure acid presented a type II isotherm, characteristic of non-porous or macroporous solids [25]; however, the HCsPW presented a type IV isotherm. Moreover, the BET specific surface area of the HCsPW (135 $m^2\,g^{-1}$) was much higher than HPW (<5 $m^2\,g^{-1}$).

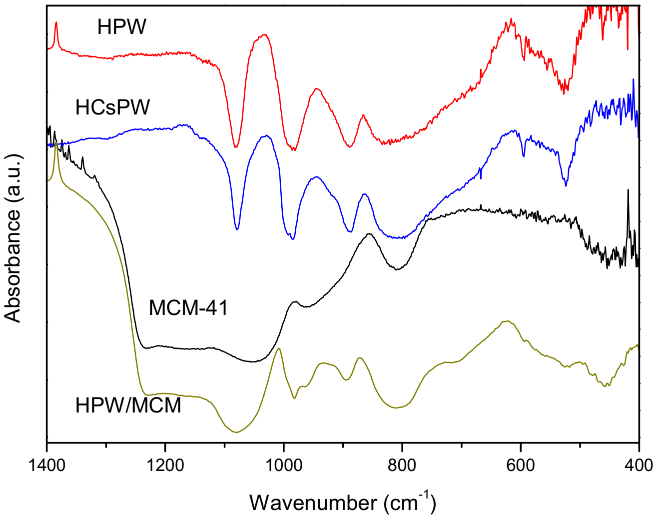

Fig. 5. FTIR spectra of the catalysts.

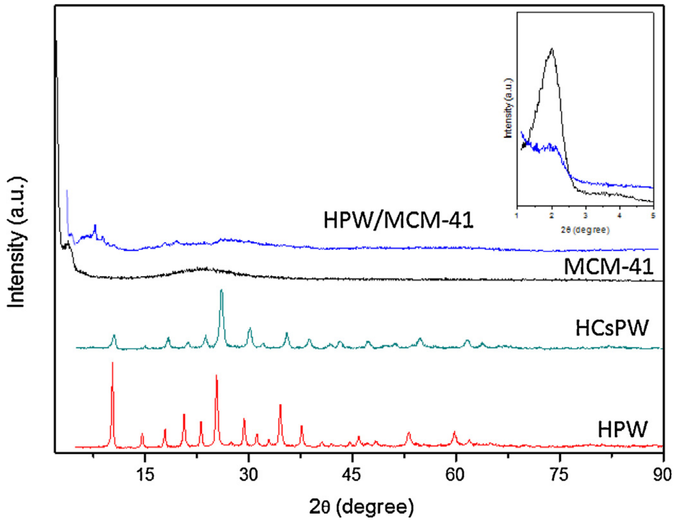

Fig. 6. XRD patterns of the catalysts.

The decrease in the BET specific surface area and pore volume of the supported catalyst (HPW/MCM) is significant, about 90% of reduction when compared to MCM-41, but it is still much higher than the unsupported compound (Table 1). This reduction is consistent with the literature and suggests that the HPW is deposited inside the mesochannels and well dispersed on the surface of MCM-41 [16].

SEM images of solids are illustrated in Fig. 4. The micrographs enabled to observe a decrease of the particle size with the insertion of Cs in the structure of phosphotungstic acid and indicate that HPW/MCM is well dispersed in homogeneous particles in comparison with pure MCM-41.

The HPAs of Keggin structure have four different types of oxygen, which are responsible for characteristic IR bands of heteropolyacids of this class: 1060–1080, 960–980, 880–860, 740–790 cm^{-1}, attributable to υ_{as} (P-O_a), υ_{as} (M = O_t), υ_{as} (M-O_b-M) and υ_{as} (M-O_c-M) vibrations, respectively, where M is the metal ion (W, Mo, etc.). The four distinct oxygen sites correspond to the following description: oxygen of the central tetrahedral PO_4 (O_a), terminal oxygen linked to metal atom alone (O_t), bridge oxygen between

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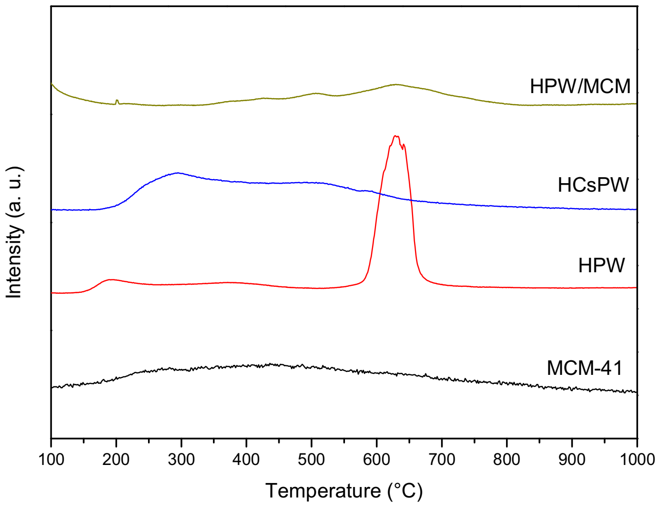

Fig. 7. NH_3-TPD profiles of the catalysts.

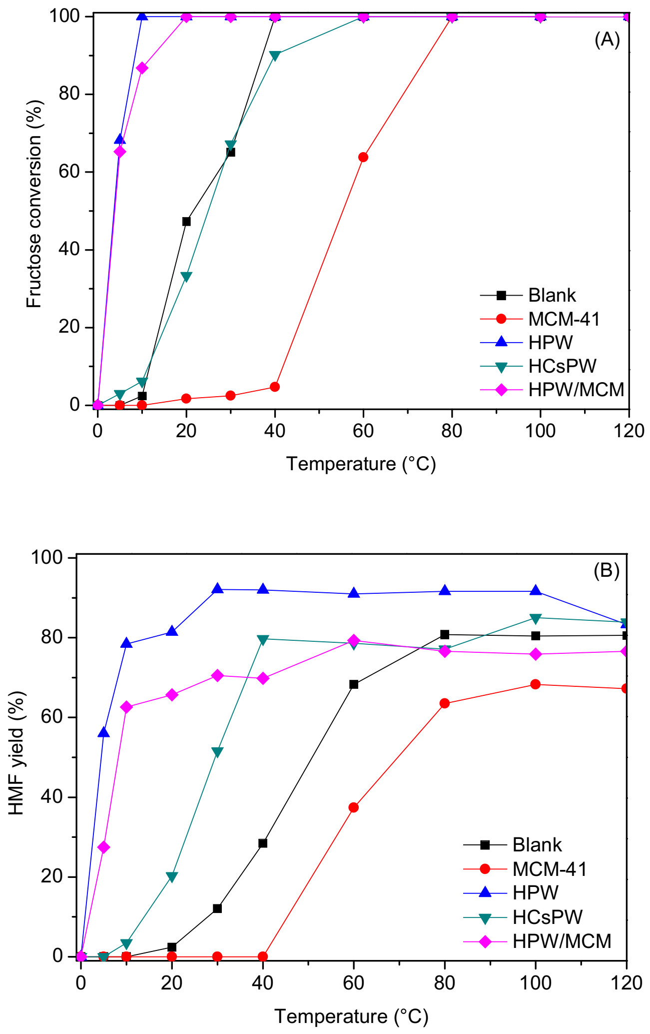

Fig. 8. Conversion (A) and HMF yield (B) for fructose dehydration reaction with different catalysts. Reaction conditions: 500 mg of fructose, 20 mL of DMSO, 50 mg of catalyst, 120 °C.

two different M_3O_{13} groups (O_b) and bridge oxygen in the same M_3O_{13} group (O_c) [19,22,26].

Fig. 5 shows the FTIR spectra of the catalysts. The FIIR bands characteristics of the Keggin structure can be clearly seen for HPW sample. A minor band at 993 cm^{-1} is observed for the HCsPW. This split in the υ_{as} ($M = O_t$) band can be attributed to interactions of Cs atoms in the HPW structure. Li et al. [22] reported that the band at 984 cm^{-1} is associated with hydrogen bonding between $W = O_a$ and residual protons (H^+), while the band at 993 cm^{-1} results from the interaction between $W = O_a$ and counter cations (Cs^{2+}). FTIR spectrum of 50 wt.% HPW/MCM indicates that the Keggin structure is preserved on MCM support. The characteristic peaks of the HPW and MCM-41 appear without any shift in the position for the supported catalyst (HPW/MCM-41), although there is an overlapping of the peaks characteristics of unsupported HPW and MCM-41.

X-ray diffraction patterns of the catalysts are displayed in Fig. 6. The structure of the calcined HPW is very close to the hydrated acid and is in agreement with the literature (JCPDS—#7521-25). For this catalyst, the main XRD lines are at $2\theta = 10.5°$, 18.3°, 23.7°, 26.1°, 30.2°, 35.6° and 38.8°, which are commonly assigned to cubic structure. The pattern for the acid modified with cesium (HCsPW) presented a significant reduction in its intensity, together with a broader and small shift toward higher angles. The literature reports these facts and associated with a decrease in the value of the cubic lattice parameters due to cesium insertion into the secondary structure [25,27].

The XRD pattern of MCM-41 shows a sharp peak at $2\Theta = 2.2°$ resulted from a strong reflection (see insert of Fig. 6), and two small peaks at $2\Theta = 4.0°$ and 4.4°, which are indexed to (1 0 0), (1 1 0) and (2 0 0) planes, respectively [15,17]. The XRD pattern of 50 wt.% HPW/MCM shows no reflections corresponding to HPW. Therefore, this is a clear evidence of the uniform distribution of HPW on MCM-41, as described in the literature [16,17]. This result shows that catalyst synthesis by incipient wetness method with methanol as solvent is more effective in the distribution of the heteropolyacid on the support as compared to the use of water as solvent. The aqueous impregnation method for higher loadings of HPW (>20 wt.%) on MCM-41 can cause support hydrolysis or a nonhomogeneous distribution of anionic species [15].

The acidity of the catalysts was investigated by NH_3-TPD, including the amount of acid sites and acid strength. Fig. 7 shows the NH_3-TPD profiles of HPW, HCsPW, MCM-41 and HPW/MCM. According to NH_3 desorption temperature, the acid sites can be classified as weak- (150–300 °C), medium- (300–500 °C), and strong- (500–650 °C) strength. For the heteropolyacids, this classification is associated with different sites of ammonia adsorption in bulk HPAs. The profile of HPW exhibits two small peaks at 180 and 400 °C ascribed to the desorption of hydrogen-bonded NH_3 molecules (weak-strength) and the decomposition of ionically bonded NH_4^+ ions with contact with oxygen atom of one Keggin unit (medium-strength), respectively. Furthermore, the HPW has an intense peak at 630 °C (strong-strength), which is ascribed to the decomposition of ionically bonded NH_4^+ ions in contact with oxygen atom between two neighboring Keggin units [28,29]. Table 1 presents the total acid density of HPW and the other catalysts, calculated from the amount of NH_3 desorbed from room temperature to 800 °C, which is provided in a weight-specific value ($\mu mol\,g^{-1}$).

The Cs substitution in the HPW modified the NH_3-TPD profile: there was a significant reduction of desorption peaks, in particular of the strong-strength acid site, due to partial replacement of the protons of phosphotungstic acid by Cs^+ ions. The total acid density was reduced from 466 to 52 $\mu mol\,g^{-1}$. The NH_3-TPD profile of the MCM-41 material displays a small and wide peak from 180 to 500 °C, which corresponds to weak and medium-strength acid sites (403 $\mu mol\,g^{-1}$). This acid strength is associated with the presence of only hydrogen bonding due to connection of silanol groups in the hexagonal structure. The same observation was made by pyridine gaseous adsorption [15]. After impregnation of HPW in MCM-41 it is observed an increase in the total amount of acid sites of this new

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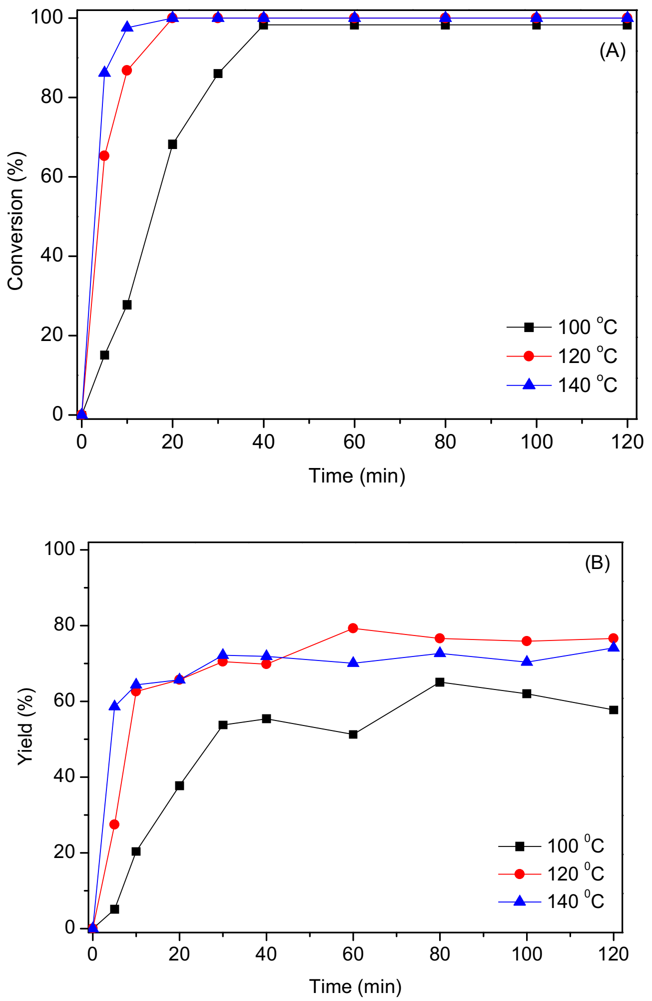

Fig. 9. Effect of temperature on conversion (A) and HMF yield (B) for the fructose dehydration using HPW/MCM catalyst. Reaction conditions: 500 mg of fructose, 20 mL of DMSO, 50 mg of catalyst.

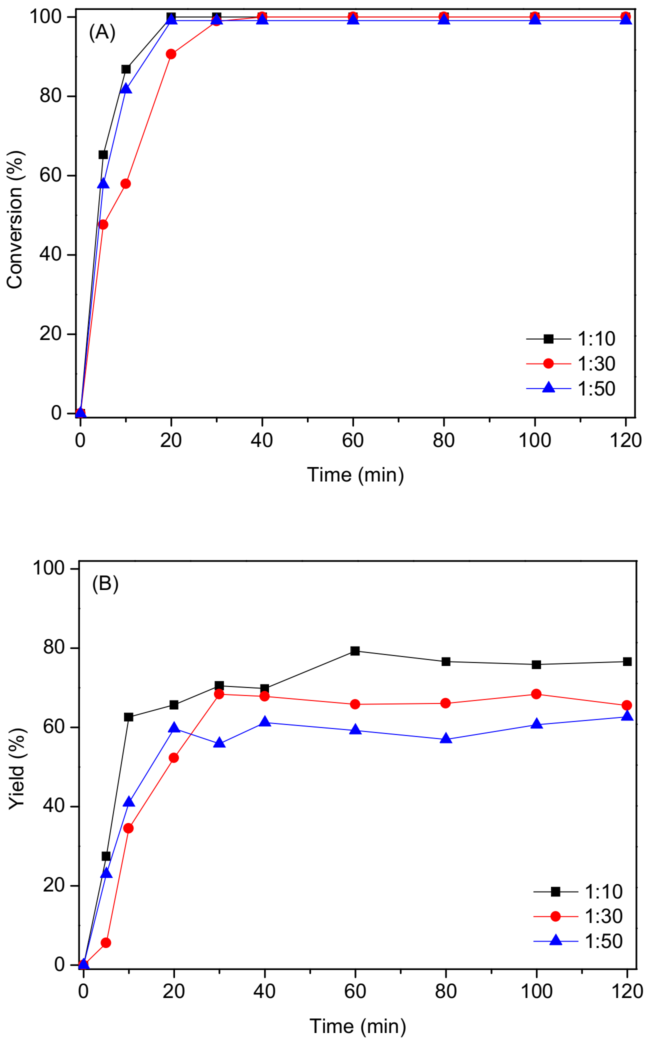

Fig. 10. Effect of catalyst: fructose mass ratio on conversion (A) and HMF yield (B) for the fructose dehydration using HPW/MCM catalyst. Reaction conditions: 500 mg of fructose, 20 mL of DMSO, 120 °C.

catalyst (816 μmol g^{-1}), which is ascribed to the higher amount of available protons that were not bonded directly to the MCM-41 framework, for large amounts of HPW supported in MCM-41 [15,25].

3.2. Catalytic tests of fructose dehydration

The dehydration of fructose to HMF by heteropolyacid catalysts was evaluated in dimethyl sulfoxide (DMSO) as aprotic solvent. According to the literature [10,11], DMSO is a good solvent that could suppress unwanted side reactions in hexose dehydration. In addition to the formation of HMF, by elimination of three water molecules from fructose, the main byproducts reported in hexose dehydration are humins, soluble polymers, furfural, levulinic and formic acids. These compounds are products of cross-polymerization, condensation and rehydration reactions.

In DMSO, the furanose conformation of fructose is prevalent, which favors the formation of HMF because this form is more reactive than other structures of fructose. In addition, DMSO also acts as catalyst in fructose dehydration. A NMR study on fructose dehydration in DMSO by Amareseka et al. [30] showed that the mechanism is very similar to cyclic pathway in aqueous medium.

The results of the blank test (without any catalyst) and catalytic evaluation of fructose dehydration in DMSO at 120 °C are displayed in Fig. 8. It is noteworthy that DMSO alone has a high catalytic activity for the conversion of fructose to HMF: the fructose is totally converted in 40 min of reaction and the maximum HMF yield is 80% in 80 min. These results can be due to solvating ability of DMSO towards cations, that is, the solvent may stabilize the positively charged intermediates of fructose conversion and thus inhibit their side reaction to byproducts, such as cited by Dias et al. [25] in the dehydration of xylose to furfural. This observation can be extended to explain the slow HMF formation. Some works reported good HMF yield from fructose in absence of catalyst in different systems, but with much longer reaction times (at least several hours) than in this work [10,11].

The use of 10% of HPW resulted in an increased fructose conversion and HMF yield with much shorter time when compared with the blank test: 100% of fructose conversion in only 10 min and maximum yield of 92% in 30 min. Qu et al. [20] reported 98% of fructose conversion and 97% of HMF yield in 120 min with the same catalyst, temperature and solvent. However, these authors used a very diluted fructose solution (0.5%), higher ratio of catalyst:fructose (1:2) and they did not report the results of blank test.

The exchange of protons by Cs in HPW resulted in a great decrease of catalytic activity, which may be related to its lower acidity (Table 1). It should be noticed that HPW forms a homogeneous system, while HCsPW is heterogeneous. Qu et al. [20] also observed a decrease in catalytic activity of $Cs_3PW_{12}O_{40}$ in relation

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to HPW for fructose dehydration in DMSO. For the same catalysts and solvent used in this work, Shimizu et al. [3] did not report a decrease in catalytic activity of HCsPW in relation to HPW, but the reaction was carried out under evacuation. Evaluating the catalytic activity of $FePW_{12}O_{40,}$ these authors concluded that the removal of water by a mild evacuation suppresses two side reactions: the hydrolysis of HMF to levulinic acid and the reaction of partially dehydrated intermediates to condensation products.

It is surprising that the conversion and yield of MCM-41 are lower than those obtained in the blank test, despite the presence of acid sites. This can be related to the strong adsorption of fructose on the high surface area of MCM-41 [31], making its conversion to HMF slower. When HPW is supported on MCM-41, the HMF yield is lower than that of pure HPW, but considering the advantages of a heterogeneous catalyst, this system seems to be a good option for fructose dehydration.

Initial reaction rates were calculated based on HMF concentration *vs.* time curves. The obtained values were 0.34, 0.08 and 0.22 mol h^{-1} g^{-1} for HPW, HCsPW and HPW/MCM, respectively. These values clearly show that HCsPW is less active for fructose dehydration to HMF, and HPW/MCM is a good choice due to its relatively large reaction rate and heterogeneity on reaction media. Shimizu et al. [3] reported a reaction rate of approximately 0.9 mol h^{-1} g^{-1} for HPW using DMSO as solvent, at 120 °C, but under evacuation conditions. Other catalysts, such as Amberlyst-15, WO_3/ZrO_2 and H-BEA showed reaction rates much lower, in the order of 0.05–0.2 mol h^{-1} g^{-1} [3]. Moreau et al. [32] reported reaction rates of approximately 0.03 mol h^{-1} g^{-1} for fructose dehydration using H-MOR as catalyst, in MIBK/water solvent, at 165 °C.

The effect of the temperature on dehydration of fructose catalyzed by HPW/MCM was also evaluated, as shown in Fig. 9. According to the experimental data, it is possible to observe that the reaction temperature influences both fructose conversion and HMF yield. At 140 °C, 98% of fructose conversion was obtained in 10 min of reaction, while at lower temperatures, 120 and 100 °C, in the same time, the fructose conversion reached about 86 and 27%, respectively. This result confirms that an increase of the temperature favors the fructose conversion, as reported in the literature [7,18–21].

Regarding the HMF yield, the temperature increase presents an ambiguous effect. When the reaction temperature is 100 °C, the HFM yield is 65% in 80 min, and when the temperature increases to 120 or 140 °C, the same yield is reached in 10 min. According to the literature, the formation rate of HMF is increased by a higher enolization rate, as well as by a higher proportion of the acyclic and furanose forms of fructose at higher temperature [33]. This effect is further increased in the presence of DMSO, since the furanose proportion is quite high (70% at 20 °C) and increases with temperature [31]. Thus, it can be said that the temperature increase plays a positive role on the HMF yield; however, this observation is only valid for times lower than 10 min. After 20 min, there is almost no difference in HMF yield with increasing temperature from 120 to 140 °C, which suggests a change of reaction pathway. The elevated temperature together with long reaction times cause a decrease in HMF yield because of side reactions that lead fructose and HMF to byproducts. The activation energy for HMF degradation, as rehydration reactions, is favored by increasing the temperature [7,8,18]. The maximum yield of 80% was obtained at 120 °C after a reaction time of 60 min.

The rate constants at different temperatures for fructose conversion to HMF using HPW/MCM were obtained by plotting $\ln(1-X)$ *vs.* time, where X is the fractional conversion. The first-order kinetic model was assumed based on previous reports [34,35]. The activation energy calculated from the slope of Arrhenius plot was 58.7 kJ mol^{-1}, with a correlation coefficient of 0.997. This value is much lower than those reported by Moreau et al. [32] (141 kJ mol^{-1}) using zeolites or Bicker et al. [34] (99 kJ mol^{-1}), using sulfuric acid as catalyst. On the other hand, it is higher than that calculated by Xiao et al. [35] (31.88 kJ mol^{-1}) using HPW in ionic liquid.

The effect of catalyst:fructose mass ratio was evaluated in the range of 1:10–50, for HPW/MCM, and the results are shown in Fig. 10. The amount of catalyst practically has no influence on the fructose conversion. The highest HMF yield (80%) was obtained using 1:10 ratio in 60 min, achieved in a shorter time than in blank test (80 min). However, a further increase in the mass ratio to 1:30 or 50 decreased the HMF yield to 65 and 60%, respectively. This result can be associated with the absence of enough amount of catalytic sites necessary for converting the intermediate compounds to HMF, since there was no formation of byproducts, such as levulinic and formic acids. Therefore, the optimal catalyst:fructose mass ratio was 1:10 under the reaction conditions used.

4. Conclusions

Aiming to transform the biomass rich in carbohydrates into chemicals that can be used as direct substitutes of non-renewable source compounds, this study evaluated the synthesis of HMF (5-hydroxymethylfurfural) from fructose in the presence of DMSO as solvent. The use of HPW (phosphotungstic acid) in the synthesis of HMF has shown to be promising (92% of HMF yield at 120 °C), but this acid is soluble in aprotic solvent. Thus, it was also evaluated the Cs-exchanged phosphotungstic acid (HCsPW) as catalyst, since this heteropolyacid is turned into insoluble compound by substituting a fraction of their protons, and the HPW supported on mesoporous MCM-41. Both catalysts showed similar results at 120 °C in 1 h of reaction (80% of HMF yield). Thus, it was demonstrated that the HPW/MCM-41 shows high catalytic activity for the conversion of fructose to HMF, with advantage that its synthesis is much easier than the HCsPW.

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