One-Pot Conversion of Glucose into 5-Hydroxymethylfurfural using MOFs and Brønsted-Acid Tandem Catalysts

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The direct conversion reaction of glucose to 5-hydroxymethylfurfural (HMF) is studied using metal organic framework (MOF) as Lewis-acid catalysts and a polyoxometalate (POM), silicotungstic acid, as a Brønsted-type acid with a mixture of 1% glucose solution in γ-valerolactone (GVL)-10% H₂O at 140 °C. The study is carried out with two routes: one using MOF and POM tandem catalysts added independently and the other through the synthesis of a composite material denoted POM@MOF. The activity tests show that the profiles of the conversion and yield of HMF achieved in both routes are similar, with the reactions with MIL-53(Al) and MIL-101(Cr) catalysts producing the highest yield of HMF (40% after 8 h of reaction). Stability tests are performed on the POM@MOF catalysts based on MIL-53(Al) and MIL-101(Cr). MIL-53(Al) and HSiW@MIL-101(Cr) can be reused, showing a progressive loss in HMF yield due to the leaching of POM.

1. Introduction

Lignocellulosic biomass is a good choice of renewable energy source and can be the precursor of numerous compounds. 5-Hydroxymethylfurfural (HMF) is a furan of great importance because it is a well-known platform molecule that can be converted into a range of industrially significant fine chemicals [1,2] such as biofuels, platform chemicals, solvents, bulk chemicals, and different monomers for polymer production, as shown in Figure 1.

The synthesis of HMF is carried out by dehydration of fructose by the action of a Brønsted-acid catalyst. [3,4] Fructose can be generated on a large scale during the production of corn syrup using enzymatic catalysts [5,6,7]; however, fructose is not as abundant a product as glucose, the most abundant sugar in lignocellulosic biomass, and it is easy to obtain. To carry out this reaction starting from glucose (Figure 2), isomerization of glucose to fructose must be achieved using basic [8–12] or acid [13–17] catalysts, with a special interest in recent years being the use of Lewis-acid catalysts [15,16,17].

With the use of glucose as the starting material for HMF production, a tandem reaction is required. Tandem reactions, which enable two-step reactions in one pot [18] could be a very interesting route to produce HMF [19] which is why it is important to find a bi-functional catalyst for the isomerization reaction and, then, for the dehydration reaction of fructose. The isomerization reaction is catalyzed by Lewis acid-type centers, and metal–organic frameworks (MOFs) can act as Lewis acids [17,20]. Then, the second reaction (dehydration of fructose to HMF) requires Brønsted-acid catalysts [3,19] and in this case, a polyoxometalate (POM) was selected.

One of the most promising applications of MOFs is the valorization of biomass as acid catalysts. Especially in the industrial processes of fine chemicals, where many reactions come from acid catalysis. In addition, MOFs have a series of remarkable characteristics for these processes since they allow in their synthesis to obtain bifunctional systems and have great stability in water. They are very attractive since most of the reactions catalyzed by acid to obtain compounds of added value are reactions in the liquid phase that contains water [21].

MOFs are an advanced porous material used for the preparation of solid catalysts. MOFs have shown a large specific surface area and crystalline open structure and allow adjustable functionalities [21–25]. As catalysts, hybrid organic–inorganic materials have the possibility of combining the different characteristics of the components to obtain unusual structures, properties, or applications [26,27]. In addition, Keggin-type POM acids have potential properties and applications in catalysis [27]. The encapsulation of POMs in the porous cavities of MOFs could produce...
an interesting catalyst for the HMF production process in one step.

Several studies have been carried out using different solvents to obtain HMF from glucose or fructose with MOF-based catalysts. HMF is very unstable in the aqueous phase, easily decomposing to levulinic acid and acetic acid,[28] therefore it is necessary to study this process in aprotic reaction media. Some of the solvents and solvent mixtures that work best in this process are dimethylsulfoxide (DMSO)[29] or the mixtures of H₂O/(DMSO),[30,31] H₂O/2-propanol,[32] H₂O/tetrahydrofuran (THF),[13] H₂O/methyl isobutyl ketone (MIBK).[4,34] Another solvent with good characteristics for this process is γ-valerolactone (GVL). The solvent used is a mixture of water and GVL, which is a nontoxic, safe, and eco-friendly green sustainable solvent that can be obtained from lignocellulosic biomass.[35–37] It has been shown that the addition of a percentage of water offers an efficient and selective reaction medium for the conversion of carbohydrates into furan compounds.[22,38] In particular, a mixture of GVL and water (GVL-10%H₂O) will be used because, in previous works, it has favored glucose conversion and fructose formation using different MOFs.[37]

This work aims to study five different MOF catalysts with different structures and ions (MIL-53(Cr), MIL-53(Al), CuBTC, MIL-100(Fe), and MIL-101(Cr)) combined with tungstosilicic acid (H₄SiW₁₂O₄₀) (POM@MOF) to obtain HMF from glucose in one step. The reactions were carried out in two ways: adding the MOF catalyst and POM catalyst in an independent way and using a synthesized POM@MOF catalyst (HSiW@MIL-53(Cr), HSiW@MIL-53(Al), HSiW@CuBTC, HSiW@MIL-100(Fe), and HSiW@MIL-101(Cr)), where the metal–organic skeletons incorporate POM.

2. Experimental Section

2.1. Materials: Reagents and Solvents

The reagents used in the preparation of the composite materials were chromium(III) nitrate monohydrate (Sigma–Aldrich, 99%),
benzene-1,4-dicarboxylic acid (Sigma–Aldrich, 98%), hydrofluoric acid (Sigma–Aldrich 40–45%), copper nitrate (Cu(NO₃)₂·3H₂O (AR, Damao), 1,3,5-benzene tricarboxylic acid (H₃BTC, 99%, J&K), N,N-dimethylformamide (DMF, AR, Fuyu), ethanol (EtOH, AR, Damao), and acetonitrile (Sigma–Aldrich). All of the reagents were used without further purification. Glucose, Basolite A100 (MIL-53(Al)), γ-valerolactone (GVL, ≥99%), and tungstosilicic acid hydrate (H₄SiW₁₂O₄₀) were acquired from Sigma–Aldrich. Finally, KRICT F100 (MIL-100(Fe)) was acquired from Stream Chemicals, Inc.

2.2. Catalyst Preparation

2.2.1. Composite Material H₄SiW₁₂O₄₀@MOF

The immobilization of H₄SiW₁₂O₄₀ in porous solid support was carried out using a previously described method. A solution of H₄SiW₁₂O₄₀ in acetonitrile (10⁻³ M, 11.25 mL) was added to 0.5 g of the corresponding MOF (MIL-53(Cr), MIL-53(Al), CuBTC, MIL-100(Fe) or MIL-101(Cr)) and stirred at room temperature for 24 h. Finally, to obtain the corresponding composite material, the solution was centrifuged, and the solid was washed three times with EtOH.

2.3. Physicochemical Characterization

2.3.1. Attenuated Total Reflection Infrared Spectroscopy

The attenuated total reflection of the solids was recorded with a Jasco FT/IR-6300 spectrophotometer equipped with a PIKE MIRacle universal ATR sampling accessory with a diamond/ZnSe crystal plate. A total of 180 cumulative scans were performed with a resolution of 4 cm⁻¹ in the frequency range of 4000–450 cm⁻¹ in transmittance mode.

2.3.2. Powder X-Ray Diffraction

Powder X-ray diffraction (XRD) analyses were performed at the Instituto de Física dos Materiais da Universidade do Porto, IFIMUP (Porto, Portugal), using an X'Pert Pro PANalytical diffractometer equipped with a λ = 0.1518 nm CuKα radiation source and X'Celerator detector based on real-time multiple-strip (RTMS) detection. The samples were ground and placed on a stainless steel plate and recorded in steps over a range of Bragg angles (2θ) between 4° and 90° at a scanning rate of 0.02° per step and an accumulation time of 50 s. Diffractograms were analyzed with X'Pert HighScore Plus software.

2.3.3. Inductively Coupled Optical Emission Spectrometry

The composition of the original and recovered catalysts was determined using an Analytik Jena ICP–OES PlamaQuant PQ9000 spectrometer.

2.4. Catalytic Activity

2.4.1. One-Pot Conversion to Glucose into HMF

The use of different MOF catalysts combined with tungstosilicic acid to form POM@MOF catalysts and the use of the MOF and POM added separately (MOF+POM) were tested. The one-pot conversion of glucose into HMF was carried out in a pressurized glass stirred tank (Mettler-Toledo EasyMax 102®) reactor with 5 mL of a solution of 1 wt.% glucose (50 mg) in GVL-10%H₂O with the appropriate amount of catalyst (MOF and POM amounts of 80 and 16.5 mg, respectively; 80 mg of POM@MOF) under stirring. After 15 min of temperature stabilization, the reaction begins. All catalysts were tested at 15, 30, 60, 120, 240, 360, and 480 at 140 °C.

The liquid was analyzed by HPLC using an HPLC 1200 series chromatograph (Agilent Technologies) equipped with a HiPLEX H column heated at 60 °C, using 0.6 mL min⁻¹ aqueous sulfuric acid solution (0.01 m) as the mobile phase and two detectors in series, a refractive index detector (RID) and a variable-wavelength detector (VWD). This method analyzed sugars (glucose and fructose) and products (HMF and furfural). Identification and quantification of all components were carried out by comparison of retention times and using calibration curves from dissolution for compounds with known concentrations.

2.4.2. Recycling Tests

For a typical catalytic reuse experiment, after a reaction cycle, the solid catalyst was collected from the reaction mixture via centrifugation and washed three times in GVL-10% H₂O, three times with acetonitrile, and, finally, three times with ethanol. Then, the solid was dried in an oven at 50 °C overnight. Finally, this solid was used as a catalyst in the same reaction, as described in the preceding paragraphs.

3. Results and Discussion

3.1. Structural Characterization

3.1.1. Catalyst Preparation and Characterization

The three synthesized MOFs (MIL-53(Cr), CuBTC, and MIL-101(Cr)) and commercial MOF samples were characterized by...
XRD and FTIR (see Figures S1 and S2, Supporting Information, respectively); in all cases, the structure was similar to previously published structures.[17],[42–46]

The tungsten content of the prepared POM@MOF determined by chemical analysis is recompiled in Table 1. The content of W in POM@MOFs is directly related to the content of the POM, because the W can only come from the addition of the POM to the MOF, thus an increase in the W concentration implies a higher POM incorporation. These analyses indicate similar incorporation of the POM in all samples, ≈15 wt%, except in the case of HSiW@MIL-53(Al) and HSiW@CuBTC, whose POM contents are higher than 20 wt%.

The composites of different MOFs and tungstosilicic acid, called HSiW@MOF, were characterized by XRD and FTIR. XRD patterns of HSiW@MOFs are displayed in Figure 3. None of the XRD patterns of HSiW@MOF samples showed clear diffraction peaks of H$_4$SiW$_{12}$O$_{40}$ (see Figure S3a, Supporting Information, for the H$_4$SiW$_{12}$O$_{40}$ pattern), in contrast, all HSiW@MOFs showed only the diffraction peaks of the respective MOFs (see Figure S1, Supporting Information, for MOFs patterns). However, some differences in the XRD patterns concerning the starting MOF were detected after POM incorporation. HSiW@MIL-53(Cr) and HSiW@MIL-53(Al) present a similar pattern as the starting MOF (Figure 3; Figure S1, Supporting Information), which implies poor incorporation of the POM into the pore structure of the MOF. HSiW@MIL-100(Fe) and HSiW@CuBTC diffraction patterns showed some changes in the intensity and peak position, which indicates partial incorporation of the POM into the MOF pore structure, causing the structure to distort due to the flexibility of the MOF structures. The changes in the structure are more evident in HSiW@MIL-101(Cr), with significant changes between 2$\Theta$ = 4° and 2$\Theta$ = 12°. This higher distortion of the crystalline structure of MIL-101(Cr) (Figure S1, Supporting Information) is clear evidence of the introduction of POM because of the good swelling behavior of MOFs when substances are adsorbed in the pore framework.[47]

FTIR spectra of HSiW@MOFs are shown in Figure 4. The vibrational spectra of the composite exhibit the characteristic bands of both materials, the MOF and POM (H$_4$SiW$_{12}$O$_{40}$) (see Figure S2, Supporting Information). The spectra contain the main bands in the region of 850–950 cm$^{-1}$, confirming a redshift in the absorption peaks of the Keggin structure of H$_4$SiW$_{12}$O$_{40}$ (see Figure S3b, Supporting Information), except in the case of HSiW@MIL-53(Cr), where no peaks attributed to the Keggin structure of the POM were detected. These observations indicate that the POM has been incorporated into the MOFs in almost all cases.

### Table 1. Tungsten (POM) contents determined by chemical analysis of the prepared POM@MOF.

| POM@MOF          | W [wt%] |
|------------------|---------|
| HSiW@MIL-53(Al)  | 20.5    |
| HSiW@MIL-101(Cr) | 13.3    |
| HSiW@MIL-53(Cr)  | 15.6    |
| HSiW@CuBTC       | 22.4    |
| HSiW@MIL-100(Fe) | 14.7    |

3.2. Catalytic Activity for One-Pot Conversion to Glucose in the HMF Reaction

The one-pot conversion of glucose to HMF has two steps, first an isomerization of glucose to fructose and then the dehydration of fructose to HMF. Each step is catalyzed by different catalysts, the isomerization is catalyzed by Lewis acid sites[17] (we selected MOF as Lewis acid) and the dehydration is catalyzed by Bronsted acid catalysts[4] (we selected silicotungstic acid as Bronsted acid). The addition of both types of catalysts to the reaction mixture was separate, the addition of MOF and POM, (POM+MOF), or by the addition of the prepared composite (POM@MOF) that contained both kinds of catalysts. The HMF yields for the POM+MOF and POM@MOF catalysts are depicted in Figures 5 and 6, respectively. In both cases, the catalysts helped form HMF, while in a blank experiment without any catalyst, the formation of HMF was not observed. Note that in addition to the formation of HMF in the reaction, other reaction products, such as levulinic acid, fructose, furfural, and humic compounds, formed.
3.2.1. Addition of the MOF and POM Separately (POM + MOF)

The use of the MOF and POM separately showed differences for each type of MOF catalyst. Figure 5a showed glucose conversion versus time for each type of catalyst used. An increase in conversion is observed over time in all cases above 50% except for the MIL-100(Fe) + HSiW catalyst, which needs 2 h of reaction to reach 50% conversion. All catalysts showed an increase in HMF conversion over time, but there were clear differences among the catalytic systems (Figure 5b). Mainly, two different catalyst behaviors can be distinguished, after only 8 h: systems with HMF yields lower than 15% (MIL-100(Fe) + HSiW, CuBTC + HSiW, and MIL-53(Cr) + HSiW) and conversions around 60%, 80%, and 95% respectively, and on the other hand catalytic systems with HMF yields higher than 35% (MIL-101(Cr) + HSiW and MIL-53(Al) + HSiW) and conversions around of 95% in both cases after only 8 h.

3.2.2. Addition of POM@MOF Catalysts

Figure 6 shows the profiles of the glucose conversion and yield of HMF versus reaction time obtained using POM@MOF catalysts, in which POM is incorporated into the MOF. All prepared POM@MOF catalysts are active, yielding high conversion (Figure 6a), and the conversion of glucose increases with reaction time. The conversion of glucose is smaller at short reaction times than in using MOF+POM (Figure 5a vs Figure 6a). This effect can be related to the incorporation of POM into the pore structure of the MOF. The presence of the POM in the MOF pore network indicates that the reagents and products have more difficulties reaching the active centers, reducing the catalytic activity. Despite these differences, the conversion level obtained with the different POM@MOF catalysts follows the same trend observed for MOF+POM.

The yield of HMF depends on the nature of the MOF employed (Figure 6b). The observed behavior showed similarities with the results obtained with the separate addition of the MOF catalysts and POM. Two kinds of behaviors can be detected: catalysts with high yields of HMF (HSiW@MIL-53(Al) and HSiW@MIL-101(Cr)) and catalysts with moderate yields of HMF (HSiW@MIL-100(Fe), HSiW@CuBTC, and HSiW@MIL-53(Cr)). The second group of catalysts showed an HMF yield that starts with a low yield but increases at long reaction times, reaching 20% at the end of the experiment. HSiW@MIL-100(Fe) increases the HMF yield in the first 2 h of reaction and then stabilizes with longer reaction times.

The most interesting catalysts are the first group to reach a 40% HMF yield at the end of the reaction. These results are comparable to those obtained with a MIL-101(Cr)-SO3H bifunctional catalyst;[24] however, the required temperatures are greater than 150 °C, and the reaction times are shorter. The behaviors of the two catalysts are slightly different. The HSiW@MIL-53(Al) catalyst presents an HMF yield profile that increases quickly at short reaction times, showing a small increase with increasing reaction times. In contrast, the HMF yield profile of the HSiW@MIL-101(Cr) catalyst showed a lower initial slope at short times, but the increase in the HMF yield was maintained during the whole experiment, reaching similar performance at the end of the experiment.

As in previous work,[17] we showed that the combination of a MOF and GVL(10%H2O) solvent, as a nonprotic solvent, favors the isomerization reaction of glucose to fructose. In this work, we showed that the combination of an MOF and a POM can yield the formation of HMF, especially in cases where MIL-53(Al) and MIL-101(Cr) MOFs were used. The higher activity and HMF yield of HSiW@MIL-101(Cr) are related to the high isomerization activity of MIL-101(Cr) described in other works,[21,48] where the isomerization mechanisms catalyzed by Cr(III) are reported in different solvents. The Cr(III) sites of MIL-101(Cr) may octahedrally coordinate with the -OH of glucose and three water molecules, thus forming the active catalytic site CrOH2+, which plays a fundamental role in the isomerization reaction of glucose to fructose, a mechanism proposed and described by Mushrif et al.[49] The higher activity of HSiW@MIL-53(Al) has two causes: on the one hand, the higher contents of the POM (Table 1) and, on the other hand, the isomerization activity described for MIL-53(Al) in previous works,[15] which was the next best after those of MOFs with Cr in the first hours of reaction.

3.3. Catalyst Recycling Capacity

The most promising catalysts based on MOFs, MIL-101(Cr) and MIL-53(Al), at 8 h of reaction and 140 °C were tested for...
reusability during the one-pot conversion of glucose into HMF. The use of catalysts in the two options (use of a MOF and a POM added independently or POM@MOF catalysts) were employed and reused (MIL-53(Al)+HSiW, MIL-101(Cr)+HSiW, HSiW@MIL-53(Al), and HSiW@MIL-101(Cr)). The used catalysts were recovered by centrifugation after washing three times with GVL-10%H2O, three times with acetonitrile, and three times with ethanol. Then, it was dried in an oven at 50 °C overnight.

3.3.1. MIL-53(Al)-Based Catalysts

The activity results obtained for the recovered solids based on aluminum catalysts are shown in Figure 7. The reuse of the system HSiW+MIL-53(Al) showed that the conversion of the used catalyst is lower than that of the original (Figure 7a). In addition, the HMF yield is suppressed when the catalytic system is reused, while the presence of fructose is observed.

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**Figure 5.** a) Conversion of glucose and b) yield of HMF for catalysts (MOF+POM) that were added separately. Reaction conditions: 5 mL of a solution of 1% glucose in GVL-10%H2O at 140 °C, Catalyst: MOF+POM (80 mg + 16.5 mg) or POM@MOF (80 mg).

**Figure 6.** Conversion of glucose a) and yield of HMF b) for synthesized POM@MOF catalysts. Reaction conditions: 5 mL of a solution of 1% glucose in GVL-10%H2O at 140 °C, Catalyst: MOF+POM (80 mg + 16.5 mg) or POM@MOF (80 mg).
These results point to the absence of a POM catalyst in the reused system. The MOF catalyst is capable of generating fructose by glucose isomerization, but the absence of the POM indicates the absence of the Bronsted-acid function responsible for fructose dehydration to HMF. The reaction results obtained with the reuse of HSiW@MIL-53(Al) are very similar to the results obtained with HSiW+MIL-53(Al). The conversion decreased faster than it did in the HSiW+MIL-53(Al) system. These results indicate a strong lixiviation of POM, remaining only a small amount in the recovered HSiW@MIL-53(Al) after its first use in the reaction.

Chemical analysis of the used catalysts based on MIL-53(Al) showed a clear decrease in the concentration of tungsten relative to the starting material (Tables 1 and 2), in consequence, the amount of POM is lower than the starting material. The POM was not incorporated during the first use of MIL-53(Al)+HSiW; the main part of the POM was lixiviated in the first reaction cycle, but a small amount of the POM was still present. The infrared spectra of the reused samples (Figure 8) show the vibration peaks of the MOF but no signal at approximately 850–950 cm$^{-1}$ due to the absence of silicotungstic acid with a Keggin structure. These characterization results indicate that the reused samples have no POM, and this absence is responsible for the loss in HMF yield.

### 3.3.2. MIL-101(Cr)-Based Catalysts

The activity results of the reused MIL-101(Cr)-based catalysts are recompiled in Figure 9. The conversion results, fructose yield,
and HMF yield of MIL-101(Cr)+HSiW (Figure 9) show a slight decrease in the conversion for reuse of the catalyst, but there are changes in the yield to HMF and fructose. In reuse, we detect a clear decrease in the HMF yield with a parallel increase in the fructose yield (Figure 9). The decreases in the HMF yield are less marked than those in MIL-53(Al)+HSiW. The HMF yield observed in the reuse of the catalyst indicated that the catalyst remained at some Brønsted-acid sites. The decrease in the HMF yield and increase in fructose can be attributed to the loss of the Brønsted-acid site in each cycle.

The behavior of the reused HSiW@MIL-101(Cr) changes. Glucose conversion remains more or less stable in each cycle carried out (Figure 9). However, the HMF yield and fructose yield changed with reuse. After the first reuse, the HMF yield decreases, while the fructose yield increases, but in the following reuse, very slow changes are observed. This observation indicates that after the first use of the lost part of the Brønsted acid site due to the presence of POM, the presence of these acid sites is more stable.

In all cases, recovery of the catalysts showed that the catalytic activity for the isomerization of glucose to fructose (Figures 7 and 9) does not decrease from the first recovery and is maintained with the cycles, especially for HSiW@MIL-101(Cr). The recovery of the catalysts maintains the catalytic activity of the MOFs.

Chemical analysis of the used samples of HSiW@MIL-101(Cr) and MIL-101(Cr)+HSiW (Table 2) showed similar W contents (similar amount of POM), but this value is lower than that of the original HSiW@MIL-101(Cr) catalyst (Table 1). This observation is surprising and is a clear indication of the encapsulation of silicotungstic acid within MIL-101(Cr) during the initial reaction. The concentration of the POM is lower in MIL-101(Cr)+HSiW than in HSiW@MIL-101(Cr), which can explain the lower HMF yield observed in the first reuse in MIL-101(Cr)+HSiW versus HSiW@MIL-101(Cr). The FTIR spectra of the recovered catalysts and the original catalyst are shown in Figure 10. All spectra show the vibration peaks of the MOF and some peaks characteristic of the Keggin structure of silicotungstic acid at ≈850–950 cm⁻¹. These results clearly point to the presence of POM in both used samples. The intensity of the

Figure 9. Results of the reuse tests performed on the recovered solids a) MIL-101(Cr)+HSiW and b) HSiW@MIL-101(Cr). Reaction conditions: 5 mL of a solution of 1% glucose in GVL-10%H₂O at 140 °C, Catalyst: MOF+POM (80 mg + 16.5 mg) or POM@MOF (80 mg).

Figure 10. Comparison of the infrared spectra of solids recovered after the first reaction of HSiW+MIL-101(Cr) and HSiW@MIL-101(Cr).
peaks characteristic of the POM is correlated with the results of chemical analysis, where the intensity of the peaks is higher for the samples with a higher concentration of the POM in the sample. These observations confirm the presence of the POM in reused HSiW@MIL-101(Cr) and MIL-101(Cr)+HSiW.

After six cycles were carried out with the HSiW@MIL-101(Cr) catalyst, the solid was characterized by FTIR (Figure 11a) and XRD (Figure 11b). The characteristic features found in diffraction patterns and the vibratory bands are largely those of MIL-101(Cr) (Figure S1, Supporting Information). In addition, in the IR spectrum, some possible peak characteristics of POM vibrations remain.

The differences in the reuse of HSiW@MIL-53(Al) and HSiW@MIL-101(Cr) can be related to the different pore sizes of their structures. MIL-101(Cr) has a larger pore size than MIL-53(Al) due to its different structure. Then, the POM can be incorporated easily in the MIL-101(Cr) pore structure, while the incorporation of the POM will be done mainly on the external surface of MIL-53(Al). Consequently, lixiviation from the external surface of the MOF is easier than that from the pore structure. However, lixiviation still occurs in HSiW@MIL-101(Cr), and the use of a MOF system with a large pore size (such as MIL-101(Cr)) and a way of fixing the POM can be very interesting options for designing a very efficient catalyst.

4. Conclusion

Two ways to obtain HMF from glucose in one step have been tested by tandem catalysts, one by adding MOF and POM independently and the other by adding a synthesized catalyst, POM@MOF. In both cases, HMF was obtained with a similar profile, however, a lower conversion was obtained when POM@MOF was used due to the presence of the POM at the MOF structure that makes the diffusion of the reagents difficult.

The best result in HMF one-step production from glucose was obtained with MIL-53(Al)+HSiW, HSiW@MIL-53(Al), MIL-101(Cr)+HSiW, and HSiW@MIL-101(Cr), which achieved HMF yields up to 40% yield with long reaction times. The recycling study showed that the best catalyst was HSiW@MIL-101(Cr), which was reused up to six times. However, a loss of POM was noted from the first use, which decreased the HMF uptake and increased the fructose yield because POM is necessary for the dehydration of fructose to HMF. These results indicate that HSiW@MIL-101(Cr) is a very interesting catalytic system, but the anchor of the POM in the MOF structure must be improved.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.
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