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Catalytic dehydration of fructose to HMF over sulfonic acid functionalized periodic mesoporous organosilicas: role of the acid density†

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Here, we reported the catalytic efficiency of sulfonic acid functionalized periodic mesoporous organosilica (PMO) materials with crystal-like pore walls in the dehydration of fructose to HMF in water. We found that the proton loading, the localization of acid sites and the surface hydrophobicity played a crucial role in the PMO activity.

Introduction

During the last two decades, much effort has been given to the catalytic conversion of biomass to chemical platforms, bioproducts and transportation fuels. Within this context, carbohydrates have attracted considerable attention mainly because they represent a huge reservoir of renewable carbon with a production estimated to about 140 billion tons per year.

Among all possible transformations, the acid-catalyzed dehydration of hexoses to 5-hydroxymethylfurfural (HMF) is of prime importance since HMF is now considered as a chemical platform with strong market potential especially for the fabrication of safer and renewably sourced polymers.[1–3] In this reaction, the choice of the solvent is crucial and governs the selectivity of the process. In the current literature, ionic liquids (ILs) are often preferred for the dehydration of hexoses since ILs are capable of dissolving large amounts of hexoses while allowing convenient isolation of HMF by liquid–liquid phase extraction.[4] However, the best ILs are also prohibitively expensive for use on a large scale. In addition, utilization of ILs as a reaction medium is mostly restricted to the use of Lewis acids since cation metathesis readily occurs in the presence of a Brønsted acid, thus limiting the development of such processes. Clearly, innovative strategies need to be investigated to decrease the cost and ecological footprint of these processes. In this context, the rational design of solid acid catalysts capable of promoting the dehydration of hexoses to HMF directly in water remains a challenging issue.

Although a large amount of hexoses can be dissolved in water, its use as a solvent for the production of HMF requires two scientific issues to be tackled: (1) the possible acid-catalyzed rehydration of HMF yielding formic and levulinic acids as two side products and (2) the deactivation of catalytic acid sites either by solvation with water or leaching. To date, heterogeneously-catalyzed dehydration of hexose to HMF has been successfully performed in water in the presence of metal phosphates (mainly based on Nb, Fe, V, Zr or Ti),[5–7] metal oxides (ZrO_2 or TiO_2) and zeolites.[8,9] In most of the reported processes, HMF was extracted (sometimes in a continuous mode) from the aqueous phase by liquid–liquid phase extraction thus limiting the side rehydration of HMF to levulinic and formic acids and affording HMF with 20–60% yield. Recently, SBA-type mesoporous silica-supported sulfonic sites (SBA-SO_3H) have been found to be capable of catalyzing the dehydration of fructose in a water–methylisobutylketone-2-butanol biphasic system affording HMF with a yield of 60%.[10] In 2013, Karimi hypothesized that the surface hydrophilicity of sulfonated SBA materials facilitated the desorption of HMF from the catalytic surface, thus contributing to limit the side rehydration of HMF.[11] Although high yield of HMF was obtained in aqueous solution in the presence of a sulfonated SBA material, one should mention that such a catalyst is unfortunately deactivated in water due to a strong solvation and leaching of the active sites.[12,13]

In 2002, Inagaki and co-workers reported the synthesis of mesoporous benzene–silica with crystal-like pore walls (Ph-PMO).[14] We[12,13,15] and others[16] have shown that their functionalization with propylsulfonic acid sites yields solid acid catalysts (Ph-PMO-PrSO_3H) that are much more active

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and stable in water than the traditionally used sulfonated periodic mesoporous silicas such as SBA-SO_3H, MCM-SO_3H or HMS-SO_3H. Although sulfonated PMO cannot be considered as a hydrophobic material, the high activity of Ph-PMO-PrSO_3H was attributed to the presence of phenyl rings in the pore wall that creates a hydrophobic environment capable of partly preventing the solvation of sulfonic sites by water.[13,15] Owing to its high stability in water, Ph-PMO-PrSO_3H is now receiving more and more attention, especially in the field of water-generating reactions. Recently, Dumesic and co-workers[17] have reported the use of ethane-bridged PMO materials for the continuous production (in tubular reactors) of HMF in a single phase solution of THF and H_2O (4 : 1 w/w). Although this PMO is amorphous, authors have clearly demonstrated the superior stability of ethane-bridged PMO materials as compared to that of SBA-SO_3H further confirming the contribution of such materials for biomass processing.

Here, we report that the chemical nature of organic bridges within the pore wall, the location of the sulfonic sites, as well as the proton density, play a key role in the activity of sulfonated PMO in the aqueous catalytic synthesis of HMF from fructose. In particular, we show that sulfonated mesoporous benzene and biphenylene bridged PMOs with crystal-like pore walls are capable of promoting the dehydration of fructose in neat water with high turn-over frequencies (TOF). In an attempt to understand the difference of catalytic behavior observed between all tested sulfonated PMO, ^{31}P magic-angle spinning (MAS) NMR spectroscopy of chemisorbed triethylphosphine oxide (TEPO) was employed as a local phosphorous-based probe molecule is highly sensitive to the nature and strength of acid sites.[18–23] To the best of our knowledge this is the first time that the acid sites contained in a sulfonic acid functionalized PMO material are characterized at a molecular level by ^{31}P MAS NMR using adsorbed TEPO probe molecules.

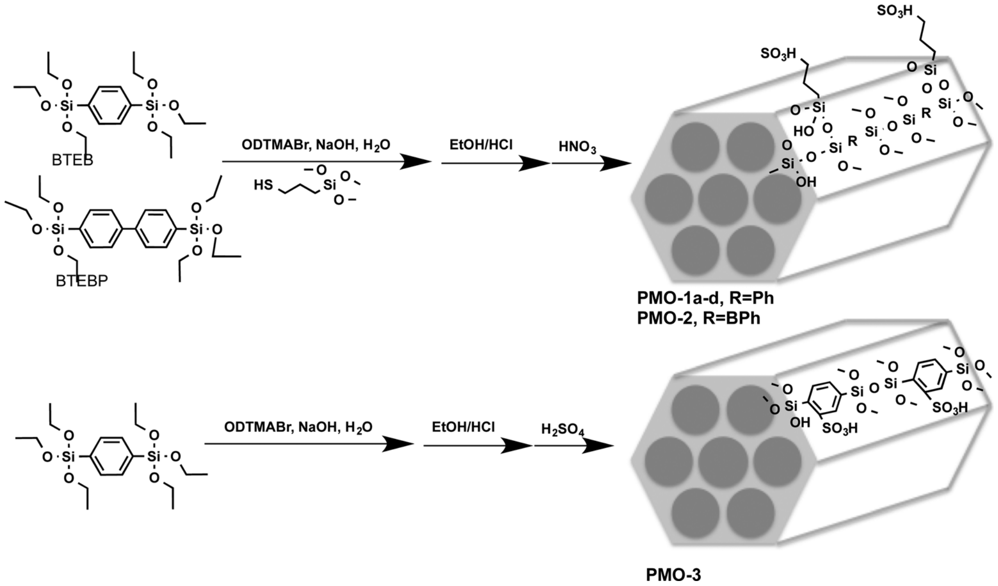
Results and discussion

Synthesis and characterization of acid-functionalized PMOs

Different kinds of sulfonated PMO with varying sulfonic acid loadings and molecular structures were synthesized using literature procedures or modification of existing ones (Scheme 1).[24,25] PMO-**1a–d** were prepared by co-condensation of different molar ratios of 1,4-bis(triethoxysilyl)benzene (BTEB) and 3-mercaptopropyltrimethoxysilane (MPTMS) in the presence of a surfactant, followed by oxidation of the thiol to sulfonic acid groups. The acid loadings in the PMO-**1** from **a** to **d** were, respectively, 1.11, 0.56, 0.36 and 0.25 mmol g^{-1}. A propylsulfonic acid biphenyl PMO material named PMO-**2** was obtained using a similar methodology but substituting the BTEB for 4,4′-bis-(triethoxysilyl)biphenyl (BTEBP). The acid concentration in the final material was 0.56 mmol g^{-1}. A phenyl-bridged PMO sulfonated in the aromatic ring, called PMO-**3**, was prepared by sulfonation of the phenyl PMO (Ph-PMO) obtained by polycondensation of BTEB.[26] The description of the protocol adopted to prepare the studied materials is given in the ESI.† The acid content in PMO-**3** was 0.64 mmol g^{-1}. All materials were characterized by the usual solid state analytical techniques (see the ESI†).

Acid-catalyzed dehydration of fructose to HMF

In our experiments, fructose was chosen as a model feed for HMF production from sugars. Note that glucose is a far more relevant feed but, to date, Bronsted acids are not capable of converting glucose to HMF. Therefore, the activity of different PMOs was evaluated in neat water in the acid-catalyzed dehydration of fructose to HMF. Typically, 0.23 g of fructose was dissolved in 0.52 g of water (*i.e.* 44 wt% of fructose) and heated to 160 °C in the presence of 16 wt% (related to the amount of fructose, *i.e.* 37 mg) of solid acid catalyst. To limit



Scheme 1 Schematic representation of sulfonic acid functionalized PMO materials prepared in this work.

the side rehydration of HMF to levulinic and formic acids, the reaction was conducted in a biphasic system composed of H_2O as the catalytic phase and a mixture MIBK (methylisobutylketone)–2-butanol (70/30) as an extraction phase. Such a biphasic system aimed at separating HMF from the water phase to limit its rehydration to levulinic and formic acids. The reaction progress (fructose conversion and yield of HMF) was monitored by HPLC. Prior to evaluating the performance of sulfonated PMO, the reaction was first performed in the presence of SBA-SO_3H which was used here as the reference catalyst. Results are compiled in Table 1. Please note that in all cases, the yield of HMF reached a maximum and then drops for a longer reaction time due to the acid catalyzed degradation of HMF. Hence, otherwise noted, in Table 1, only the maximum yield of HMF is provided.

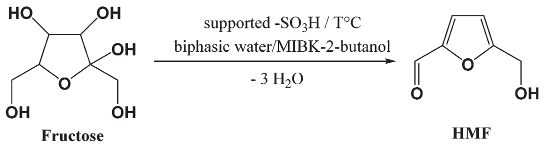
From the results presented in Table 1, it appeared that the reference SBA-SO_3H was highly active (TOF = 860 h^{-1}) affording a maximum yield of HMF of 55% after 70 min of reaction. Under similar conditions, **PMO-1a** also exhibited a high TOF (520 h^{-1}) but lower than that of SBA-SO_3H. The maximum yield of HMF remained, however, in a similar range (58%). The lower activity of **PMO-1a** compared to that of SBA-SO_3H might be attributed, in the first approximation, to hydrophobic interactions. Fructose is indeed a highly polar molecule and one may suspect that adsorption of fructose on the organosiliceous **PMO-1a** may be less favourable than over a material containing a highly hydrophilic surface like SBA-SO_3H. Note that other parameters (acid strength, acid site location, hydrophobicity, silanol concentration) may also impact the activity of **PMO-1a**. This aspect will be discussed later in the manuscript.

The influence of temperature and fructose content on the HMF yield, collected with **PMO-1a**, was also investigated. A decrease of the fructose content from 44 wt% to 10 wt% did not result in a significant change of the HMF yield (58% at 44 wt% *vs.* 53% at 10 wt%) (Table 1). A decrease of the reaction temperature from 160 °C to 130 °C, however, dropped the reaction rate and the yield of HMF at an unacceptable level. At this temperature, only 24% yield of HMF was obtained after 180 min of reaction. In this case, the thermal degradation of HMF was faster than its formation explaining the low selectivity observed at 130 °C. Reversely, an increase of the reaction temperature from 160 °C to 180 °C had obviously a positive effect on the reaction rate but with no significant improvement in the selectivity to HMF. Under these conditions, a maximum yield of HMF of 59% was obtained after 45 min of reaction (*vs.* 58% at 160 °C). Altogether, these results showed that, over **PMO-1a**, 160 °C is an acceptable compromise between reaction rate and HMF selectivity.

In an attempt to identify more active catalysts, different sulfonated PMO materials were tested in the dehydration of fructose to HMF in water (Table 2). We applied the optimized conditions described in Table 1 to all PMOs.

We observed that the catalyst activity of propylsulfonic benzene-bridged PMO was related to the proton loading. As a general trend, decreasing the proton loading from 1.11 mmol g^{-1} (**PMO-1a**) to 0.56 mmol g^{-1} (**PMO-1b**) and then to 0.36 mmol g^{-1} (**PMO-1c**), gradually increased the TOF from 520 h^{-1} to 660 h^{-1} and finally to 945 h^{-1}, respectively. On the other hand, a decrease of the proton loading from 0.36 to 0.25 mmol g^{-1} has nearly no effect on the TOF. These results highlighted that isolation/dispersion of sulfonic acid sites on the PMO surface plays a key role in its activity. In addition, we checked the influence of remaining surface silanol groups on the PMO activity. To this end, silanol groups of **PMO-1c** were silylated according to a conventional method involving reaction with trimethylchlorosilane yielding **Si-PMO-1c** (see the ESI†). When comparing **PMO-1c** and **Si-PMO-1c** (with similar proton loading, entries 3 and 5, Table 2), it clearly showed that the silylation of the silanol groups caused a dramatic decrease in the PMO activity (TOF = 945 h^{-1} and 380 h^{-1} for **PMO-1c** and **Si-PMO-1c**, respectively). A similar trend was observed when phenyl bridges were replaced by a more hydrophobic moiety such as biphenyl (**PMO-2**, TOF = 350 h^{-1}). It should be noted that, for the most active PMO (1a–d), the maximum yield of HMF remained in a similar range (50–58%). Selected kinetic profiles are provided in the ESI† (Fig. S9 and S10).

Table 1 Acid-catalyzed dehydration of fructose over A15, SBA-SO_3H and PMO-**1a**



Catalyst	H^+ loading[a] (mmol g^{-1})	Time (min)	Conv. (%)	Yield[b] (%)	TOF[c] (h^{-1})
SBA-SO_3H[d]	0.89	70	96	55	860
PMO-1a[d]	1.11	75	95	58	520
PMO-1a[e]	1.11	90	96	53	244
PMO-1a[f]	1.11	180	82	24	nd
PMO-1a[g]	1.11	45	96	59	nd

[a] Determined by titration (see Experimental section for more details). [b] Determined by HPLC. [c] The TOF was measured at a conversion <20%. [d] 44 wt% of fructose in water (0.5 mL), 1.5 mL of MIBK/2-butanol (70/30), 160 °C. [e] From an aqueous solution of 10 wt% of fructose. [f] Reaction performed at 130 °C, 10 wt% of fructose. [g] Reaction performed at 180 °C, 10 wt% of fructose.

Table 2 Acid-catalyzed dehydration of fructose over different PMO[a]

Entry	Catalyst	H^+ loading[b] (mmol g^{-1})	TOF[c] (h^{-1})
1	PMO-**1a**	1.11	520
2	PMO-**1b**	0.56	660
3	PMO-**1c**	0.36	945
4	PMO-**1d**	0.25	910
5	Si-PMO-**1c**	0.34	380
6	PMO-2	0.56	350
7	PMO-3	0.64	450

[a] 44 wt% of fructose in water (0.5 mL), 1.5 mL of MIBK/2-butanol (70/30), 160 °C. [b] Determined by titration (see Experimental section for more details). [c] The TOF was measured at conversion <20%.

Altogether, these results tend to support that the reinforcement of the hydrophobicity of PMO has also a detrimental effect on its activity. In particular, we suspect that an optimal hydrophilic/lipophilic balance is required to assure an efficient dispersion of sulfonated PMO in the aqueous phase while favouring an optimal adsorption of fructose on the PMO surface.

In the last set of experiments, we investigated the effect of the localization of sulfonic sites on the PMO activity. The PMO activity was lowered from 660 to 450 h^{-1} when the propyl sulfonic acid sites (in PMO-**1b**) were replaced by the direct anchoring of sulfonic acid groups on the phenyl ring (PMO-3). This result suggests that the interaction of fructose with the active sites is more favourable when the sulfonic acid groups are attached to the surface through a propyl chain which is more flexible and away from the PMO surface.

In order to assess the stability of the materials in water, the PMO-**1a** and SBA-15-SO_3H have been recycled (see Experimental section for more details on the procedure). The results are presented in Table 3. In agreement with previous reports from us[12,13,15] and others,[16,17] PMO-**1a** was found to be more robust in water than SBA-SO_3H. In particular, while the PMO-**1a** maintained its activity during the second run, the TOF of SBA-SO_3H was decreased by a factor of 2 (450 h^{-1}) during the second cycle further confirming the higher tolerance of propylsulfonic acid functionalized PMO to water than SBA-SO_3H. However, it is worth mentioning that at 160 °C the activity of PMO-**1a** started to irreversibly drop after the second catalytic cycle.

Characterization of PMO-1a–d using ^{31}P solid-state NMR

To obtain a deeper structural insight on PMO materials, ^{31}P MAS NMR experiments using TEPO as a Brønsted acidity probe molecule were carried out. This technique has been previously applied to characterize the acidity of solid acids such as zeolites,[19,21] 12-tunstophosphoric acid materials,[19] Al-MCM-41 with different aluminum contents,[21] sulfonic resin (Amberlyst 15),[21] functionalized SBA-15 with different acid loadings,[17,20,21] and arenesulfonic acid functionalized SBA-15.[22] TEPO acts as a base that binds to the acid sites located on the material surface. Depending on the strength and nature of the TEPO-surface binding, the phosphorous nucleus (of TEPO) will sense differences in its chemical environment due to changes of the local ^{31}P electron density, thus resulting in distinct ^{31}P chemical shifts. Overall, monitoring ^{31}P chemical shifts of TEPO will give us a scale for acidity strength. ^{31}P resonances located at high frequencies (left-shifted) reflect the presence of strong acid sites, such as the TEPO···HO_3S hydrogen bond interactions. In opposite, interactions involving TEPO···HOSi groups yield, in general, the most right-shifted resonances as they are the less acidic functional groups in the studied PMOs.

Fig. 1 shows the ^{31}P MAS NMR spectra of chemisorbed TEPO on propylsulfonic acid PMO materials containing different acid loadings (PMO-**1a**–**c**). The ^{31}P spectra of the silylated PMO-**1c** sample (Si-PMO-**1c**) and sulfonic acid free Ph-PMO are also shown in Fig. 1 for comparison. The latter is used as a reference and is characterized by a single ^{31}P resonance at *ca.* 58.5 ppm typical of TEPO adsorbed at silanol groups.[20,27]

For propylsulfonic acid PMOs functionalized with distinct acid loadings (PMO-**1a**–**c**), a large distribution of ^{31}P chemical

Table 3 Recycling experiments[a]

Catalyst	Catalytic cycle	TOF[b] (h^{-1})
PMO-1a	1	520
PMO-1a	2	650[c]
SBA-SO_3H	1	860
SBA-SO_3H	2	410

[a] 44 wt% of fructose in water (0.5 mL), 1.5 mL of MIBK/2-butanol (70/30), 160 °C. [b] The TOF was measured at conversion <20%. [c] The increase of TOF between the first and second cycles was due to the presence of remaining HMF in the PMO material after the first cycle.

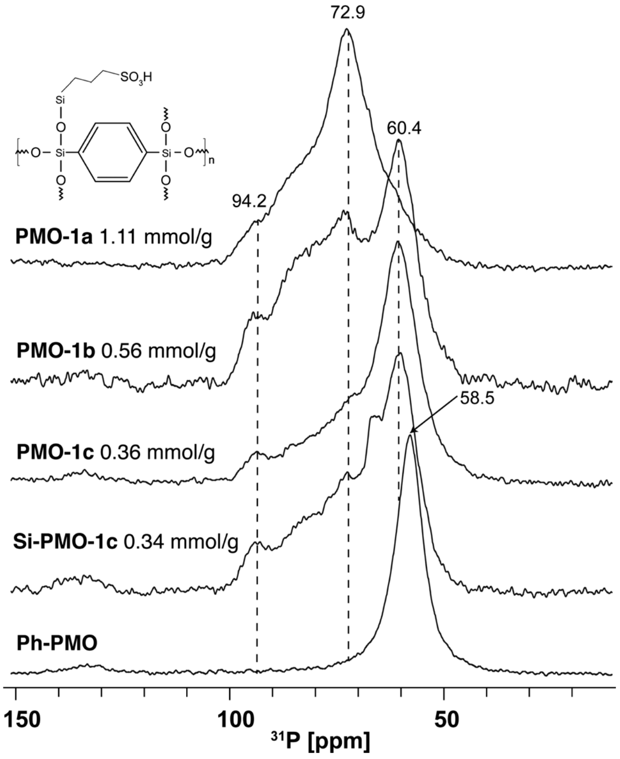


Fig. 1 ^{31}P MAS NMR spectra of TEPO probe molecules adsorbed on PMO-**1a**, PMO-**1b**, PMO-**1c**, Si-PMO-**1c** and Ph-PMO.

shifts covering the 35 ppm region (from 60 to 95 ppm) was observed. This indicates a broad distribution of Brønsted acid sites associated with the co-existence of various sulfonic sites in distinct local environments. Based on the literature, the ^{31}P peak observed at 94.2 ppm for PMO-**1a**–**c** was attributed to very strong Brønsted acid sites while the peak at *ca.* 60.4 ppm is the signature of weaker acid sites.[21] Compared to the Ph-PMO, the ^{31}P resonances associated with the silanol acid sites in PMO-**1a**–**c** are now slightly left-shifted by ~ +2 ppm. This small discrepancy is likely to be associated with the introduction of the SO_3H groups during the preparation of PMO-**1a**–**c**, which influences the local chemical environment of the neighbour –SiOH groups at the surface.[21,22,27] In order to unambiguously assign the silanol sites of the resonance at 60.4 ppm, we have silylated the sample PMO-**1c** resulting in the spectrum labeled as Si-PMO-**1c** (Fig. 1). As expected, the resonance at 60.4 ppm decreases with respect to the resonances at the left side of the spectrum (the intensity of the Si-PMO-1c spectrum was vertically expanded intentionally, with respect to the others, to emphasize this aspect). Similar effects were reported in the literature.[27]

Regardless of the acid loading, all functionalized propylsulfonic acid PMO materials show the ^{31}P resonance corresponding to the strong Brønsted acid sites (*ca.* 94 ppm), which seems to maintain its relative peak intensity, compared to other acid sites. Interestingly, increasing the proton loading of PMOs (from 0.36 to 1.11 mmol g^{-1}) mainly increases the intensity of the resonance at 72.9 ppm, which is associated to –SO_3H sites having an intermediate Brønsted acidity strength. The material containing the highest acid loading (PMO-**1a**) shows clearly a distribution of Brønsted acid sites, with the maximum intensity centered at *ca.* 72.9 ppm that corresponds to the main –SO_3H acid population. PMO-**1a** exhibits the lowest TOF on the dehydration of fructose supporting that the local environment of the –SO_3H groups plays a pivotal role in the PMO activity. In particular, one may suspect that Bronsted acid sites located at 72.9 ppm are less effective in the acid-catalyzed dehydration of fructose to HMF presumably due to lower acid strength. It should be however noted that at a loading ≥0.56 mmol, other parameters may also influence the PMO activity. In particular, solvation of –SO_3H in a larger extent (phenyl ring being incapable to protect all sulfonic sites from solvation at such a high loading)[13] or the problem of acid sites accessibility cannot be ruled out. In addition, change of the sulfonic loading may also affect the catalyst surface hydrophilicity and thus the selectivity of the reaction.[15] At this stage, extra analysis is definitely required to ascertain the role of the proton loading on the PMO activity.

Conclusion

We report here that sulfonated phenylene- and biphenylene-bridged PMOs with crystal-like pore walls are promising acid solid catalysts for the dehydration of fructose to HMF in water. ^{31}P MAS NMR clearly proves the existence of sulfonic sites with different local environments at the PMO-**1a**–**c** surfaces and thus with different acid strengths.

Generally, the catalytic activity of the PMOs closely relies on: 1) the sulfonic site density; 2) the localization of sulfonic sites and 3) the surface hydrophobicity. Ideally, a PMO exhibiting: 1) phenylene in the pore wall; 2) an anchorage of sulfonic sites on a propyl chain and 3) a sulfonic site loading of 0.36 mmol g^{-1} is the most active one. Although, at 160 °C, the long term stability of these PMOs is far from satisfying, we nevertheless confirmed here that these materials are more stable in water than Amberlyst 15 or purely siliceous acid-functionalized materials such as SBA-SO_3H opening an interesting route for biomass processing in water.

Experimental section

Typical procedure for the acid-catalyzed dehydration of fructose to HMF

To a series of thick-walled glass reactors, an aqueous layer consisting of 44 wt% fructose in deionized water (0.5 g) and 1.5 g of an organic layer consisting of 7 : 3 (w : w) MIBK : 2-butanol were added with 16 wt% (related to fructose) of solid catalyst and a triangular magnetic stirring bar. The temperature was maintained at 160 °C. At the end of the reaction, the MIBK : 2-butanol organic phase was decanted and the aqueous phase was further extracted with MIBK (3 × 10 mL) and analyzed by HPLC. Please note that fresh sulfonated PMO and SBA were used. It is worth mentioning that we observed a decrease of sulfonated PMO and SBA activities after aging these solid catalysts under air for a few weeks.

Recycling experiments

At the end of each reaction, the organic phase containing the HMF was separated by decantation. The aqueous phase was washed again with MIBK and then analyzed by HPLC. The PMO was removed from the aqueous phase by centrifugation and then reused as collected without any intermediate purification.

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