Green Chemistry

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/greenchem

Dynamic Article Links ►

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Conversion of Fructose into 5-Hydroxymethylfurfural Catalyzed by Recyclable Sulfonic Acid–Functionalized Metal–Organic Frameworks

Jinzhu Chen,*[a] Kegui Li,[a,c] Limin Chen,[b] Ruliang Liu,[a,c] Xing Huang[a,b] and Daiqi Ye[b]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

A series of sulfonic acid–functionalized Metal–Organic Frameworks (MOF-SO_3H) were prepared by postsynthetic modification (PSM) of the organic linkers within the MOF with chlorosulfonic acid. The obtained MOF-SO_3H, including sulfonic acid–functionalized MIL-101(Cr) [MIL-101(Cr)-SO_3H], UIO-66(Zr) [UIO-66(Zr)-SO_3H], and MIL-53(Al) [MIL-53(Al)-SO_3H], have been systematically studied as solid acids in fructose transformation to 5-hydroxymethylfurfural (HMF). With MIL-101(Cr)-SO_3H as catalyst, an HMF yield of 90% with a full fructose conversion was obtained at 120 °C for 60 min in DMSO. The concentration of $-SO_3H$ in MOF-SO_3H as well as the contribution of Brønsted acidity of MOF-SO_3H parallels its $-SO_3H$ grafting rate. Under a lower $-SO_3H$ grafting lever, a good linear correspondence between catalytic activity, in terms of turnover frequency, and sulfonic acid-site density of MOF-SO_3H was found. Moreover, the sulfonic acid groups, function as the catalytic sites, are equivalent in all MOF-SO_3H for fructose-to-HMF transformation, regardless of precursor MOFs. Both conversions of fructose and selectivities towards HMF increase with the sulfonic acid-site density of MOF-SO_3H at an initial stage of fructose-to-HMF transformation. Kinetics studies reveal that the MIL-101(Cr)-SO_3H promoted fructose-to-HMF transformation may follow pseudo-first-order kinetics with observed activation energy of 55 kJ mol^{-1} under the investigated conditions. Moreover, MIL-101(Cr)-SO_3H, behaves as heterogeneous catalyst, can be easily recovered and reused. The research highlights a good prospect for catalytic application of MOF-derived solid acid catalyst for biomass carbohydrate valorization.

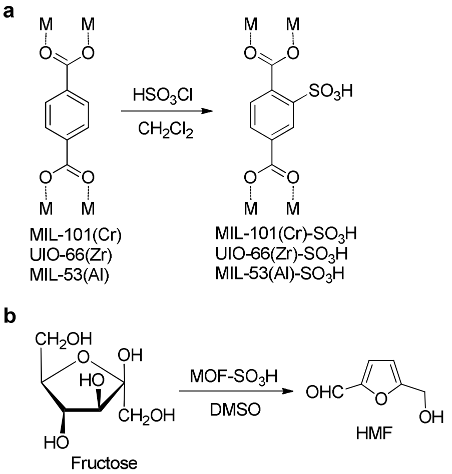
Introduction

The production of fuels and chemicals from abundant and renewable biomass resource has recently attracted much attention, owning to growing concerns of the exhaustion of fossil fuel resources and degradation of the environment.[1] Ongoing research on this topic is being mainly focused on both chemical and biological transformations of biomass into bio-based platform chemicals as an alternative to petroleum-based building blocks. Among the biomass-derived platform chemicals, 5-hydroxymethylfurfural (HMF) is regarded as a versatile and key building block for biorefinery.[2] HMF can be converted into a number of valuable chemicals, including 2,5-dimethylfuran, 2,5-diformylfuran, 2,5-furandicarboxylic acid, levulinic acid, 1,6-hexanediol, adipic acid, caprolactam, and caprolactone, with a high potential in fuel, polymer, and solvent applications.[3]

HMF is mainly prepared from bio-based hexose sugars through acid promoted dehydration. To date, many acid catalysts have been investigated for this important transformation, including mineral or organic acid, zeolites, metal ions, acidic ionic liquids, and acidic resins.[2] Homogenous acids show inherent drawbacks on product separation and equipment corrosion. Solid acids suffer from low catalytic performance as well as long reaction times. In the case of acidic resins, reaction temperature is strictly limited due to their thermal stability. Therefore, the development of a green and efficient acid catalyst is a promising research direction.[4,5a] Moreover, a comprehensive study of a correlation between structure and performance to this catalyst as well as a kinetic research for fructose-to-HMF transformation is highly important to this crucial progress.[4k,5]

Recently, a series of novel solid acids such as acidic ionic liquids,[4a-b,5a] Sn-Beta zeolite,[4c] lignosulfonic acid,[4d] biomass-derived sulfonated carbonaceous materials,[4e] nafion-resin-modified mesocellular silica foam,[4f] polymer bound sulfonic acids,[4g] layered niobic acid,[4h] PVP/propylsulfonic acid-modified ordered mesoporous silica[4i] and Fe_3O_4-SBA-SO_3H[4j] were developed for the purpose of fructose-to-HMF transformation. Moreover, we recently reported a systematic study on the conversion of fructose into HMF and alkyl levulinates using sulfonic acid-functionalized carbon materials.[4k]

One of the core principles of green chemistry is the application of heterogeneous and recyclable catalysis with renewable feedstock for chemical productions. Metal–organic frameworks (MOFs), a new class of porous crystalline materials, are very promising candidates for application to catalyst based on their high surface area, tunable pore sizes, and controllable structures. Therefore, MOF-derived solid acid is targeted herein as heterogeneous catalyst for transformation of renewable biomass carbohydrate into HMF. In contrast to carbon materials and inorganic solids, MOFs contain an organic ligand component which provides a potential approach for introducing functional groups into MOFs through postsynthetic modification (PSM).[6] PSM methods are, in fact, particularly attractive for the fabrication of acid-functionalized MOFs as solid acid catalysts. First, the presence of organic ligand component in MOFs provides a convenient employment of varieties of organic transformations. Second, the acid strength of as-prepared acid-functionalized MOFs basically can be precisely tuned by PSM through grafting rate of the reaction. Moreover, the highly porous and order nature of MOFs can presumably promote substrate transfer within the MOF catalyst, which may facilitate the catalytic reaction.



Scheme 1. (a) Synthetic routes to MOF-SO_3H, (b) Conversion of fructose into HMF.

In a limited report on an application of MOFs as catalyst for biomass valorization, Li and Hensen reported a selective dehydration of fructose to HMF with phosphotungstic acid (PTA)-encapsulated MIL-101(Cr), [PTA/MIL-101(Cr)], as solid acid catalyst.[7a] Matsuda and Kitagawa developed sulfonic acid-functionalized MIL-101(Cr) [MIL-101(Cr)-SO_3H] for cellulose hydrolysis.[7b] Very recently, bifunctional acid-metal catalysts [Ru-PTA/MIL-100(Cr)] containing ruthenium and PTA as active species with a MIL-100(Cr) as support and encapsulation matrix, respectively, were synthesized by us to achieve an one-pot conversion of cellobiose and cellulose into sorbitol.[7c]

In the present work, to further extend a catalytic application of MOFs for biomass conversion, the sulfonic acid-functionalized MOFs (MOF-SO_3H) are evaluated as potential solid acid catalysts (Scheme 1a) for the selective fructose-to-HMF transformation (Scheme 1b). MOFs such as MIL-101(Cr),[8] UIO-66(Zr),[9] and MIL-53(Al)[10] were chosen as substrate materials for covalent ligand PSM due to their excellent chemical stability. The as-prepared MOF-SO_3H with different -SO_3H grafting rates was denoted as MOF-SO_3H (grafting rate) in this research. The grafting rate was calculated based on the literature method,[9b,11b] and donated as the molar ratio of sulfonic acid group (-SO_3H) to aromatic terephthalate units in MOF-SO_3H [based on organic linker of 1,4-benzenedicarboxylic acid (BDC)]. Under the optimal conditions, a high HMF yield of 90% with a full fructose conversion was achieved with MIL-101(Cr)-SO_3H (15.0%) as catalyst. Moreover, we present the results of a comprehensive study of a correlation of structure-to-performance, kinetics, as well as MIL-101(Cr)-SO_3H recycling in fructose-to-HMF transformation.

Experimental

Materials

Unless otherwise stated, all chemicals in this work were commercial available and used without further purification. $Cr(NO_3)_3{\cdot}9H_2O$ (98%), $Al(NO_3)_3{\cdot}9H_2O$ (98%), $ZrCl_4$ (98%), 5-hydroxymethylfurfural (HMF, 98%), D-fructose (99%), D-glucose (99%), inulin (BC), sucrose (AR), cellobiose (98%), 1,4-benzendicarboxylic acid (H_2BDC, 99%), and hydrofluoric acid (38-40% solution in water) were obtained from Aladdin Industrial Inc. (Shanghai, PR China). Chlorosulfonic acid (97%) and phosphotungstic acid ($H_3PW_{12}O_{40}$) was obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, PR China). H-Beta (Si/Al = 12.5), HY-zeolite (Si/Al $\geq$ 5.2) and HZSM-5 (Si/Al = 25) were commercially purchased from Nankai University Co. Ltd. (Tianjin, PR China).

Characterization techniques

FT-IR spectra of KBr pellets were recorded at room temperature in the 400–4000 cm^{-1} region with a Bruker Tensor 27 spectrotometer, equipped with a Data Station, at a spectral resolution of 1 cm^{-1} and accumulations of 128 scans. XRD patterns were obtained using a PANalytical X'pert Pro multipurpose diffractometer operated at 40 KV and 40 mA, using Ni-filtered CuK_a radiation. Potentiometric acid–base titration was performed by using a Metrohm 877 Titrino plus instrument. Elemental analysis of MOFs-SO_3H was obtained from an Elementar Vario EL III. Scanning electron microscopy (SEM) images were recorded by Hitachi S-4800 instrument operated at 10 KV. The Brunauer-Emmett-Teller (BET) surface area measurements were performed with N_2 adsorption-desorption isotherms at 77 K (SI-MP-10/PoreMaster 33, Quantachrome). After degassed under vacuum at 423 K for 24 h and then measured over the range of $10^{-6} < P/P_0 < 0.1$. The specific BET surface areas were evaluated using the method in the p/p_0 range 0.05 to 0.3.

Preparation of MOFs

MIL-101(Cr),[8] UIO-66(Zr),[9] MIL-53(Al),[10] and PTA/MIL-101(Cr) (PTA 33.8 wt%)[7a] were prepared according to literature method (see the Supporting Information for details).

Sulfonation of MOFs

Before sulfonation, MIL-101(Cr) was degassed at 150 °C under vacuum for 24 h. The activated MIL-101(Cr) (1 g) was stirred in 30 mL CH_2Cl_2 at 0 °C for 20 min, $ClSO_3H$ (0.5 g) in 10 mL CH_2Cl_2 was dropwisely added to the mixture under vigorous magnetic stirring.[11c] After 30 min, the solid product was filtered off, rinsed with ultrapure water and acetone, soaked in ethanol for 24 h at 70 °C and dried to give MIL-101(Cr)-SO_3H with -SO_3H grafting rate of 15.0%. UIO-66(Zr)-SO_3H (9.5%) and MIL-53(Al)-SO_3H (8.2%) were prepared following same synthetic procedure as for MIL-101(Cr)-SO_3H used except that MIL-101(Cr) was replaced by UIO-66(Zr) and MIL-53(Al), respectively.

Fructose conversion into HMF

Fructose dehydration was performed in a thermostatted Ace Pressure Tube. Each time, MOF-SO_3H was pre-dried at 150 °C under vacuum overnight before the reaction. The reactants were always loaded into the reactor at ambient temperature. The reactor was then purged with nitrogen to expel air before heating up. In a typical run, fructose (500 mg), MIL-101(Cr)-SO_3H (15.0%) (300 mg) and DMSO (5 mL) were added to the reactor. After the vial was closed, the reactor was placed in a preheated oil bath at 120 °C with vigorous stirring for 60 min. After the reaction, it was quenched by placing the vial in an ice bath at 0 °C. The mixture was filtered and then decanted into a volumetric flask using water as diluents, and analyzed by high-performance liquid chromatography (HPLC). For the recycling experiment, typically, fructose (500 mg), MIL-101(Cr)-SO_3H (15.0%) (300 mg) and DMSO (5 mL) were added to a reactor. The mixture was heated in a batch reactor at 120 °C for 60 min. The solid was separated by filtration, washed with DMSO, dried at 150 °C under vacuum overnight and then reused directly for the next run by adding a fresh fructose (500 mg) and DMSO (5 mL).

Analysis of product

The HPLC analysis was performed on Shimadzu LC-20AT equipped with a UV-Vis/refractive index detector and a Shodex Sugar SH-1011 column (ø8×300 mm). H_2SO_4 (0.005 M) solution was used as the mobile phase at a flow rate of 0.5 mL min^{-1}, and the column temperature was maintained at 50 °C. The amounts of fructose and HMF were calculated based on external standard curves constructed with authentic standards.

Results and Discussion

Sulfonic acid-functionalized MOFs

Previously, MIL-101(Cr)-SO_3H was synthesized by a one-pot self-assembly of chromium trioxide and 2-sulfoterephthalic acid under hydrothermal conditions.[7b] A PSM method for MIL-101(Cr)-SO_3H preparation involves sulfation of MIL-101(Cr) with concentrated sulfuric acid (H_2SO_4, 98%) in the presence of trifluoromethanesulfonic anhydride (Tf_2O) in nitromethane (CH_3NO_2).[11a-b] In this study, MIL-101(Cr)-SO_3H was prepared by PSM of MIL-101(Cr) at the backbone phenylene units with chlorosulfonic acid as sulfonation reagent in dichloromethane.[11c] MIL-101(Cr)-SO_3H with different -SO_3H grafting rates was achieved by variable amount of chlorosulfonic acid added. UIO-66(Zr)-SO_3H and MIL-53(Al)-SO_3H were prepared following the same synthetic procedure as for MIL-101(Cr)-SO_3H except that MIL-101(Cr) was replaced by UIO-66(Zr) and MIL-53(Al), respectively. Figure 1 shows the proposed structures of MIL-101(Cr)-SO_3H, UIO-66(Zr)-SO_3H, and MIL-53(Al)-SO_3H.

A FT-IR study on the sulfonated structures confirms the successful functionalization of MOFs with -SO_3H (Figure S1). For MOF-SO_3H, new bands, appear at 1137 and 1294 cm^{-1} along with a shoulder at 1427 cm^{-1}, can be attributed to the O=S=O symmetric and asymmetric stretching modes (Figure S1b, d and f), which is in accordance with the literature.[11c] The XRD patterns of bare MOF and its corresponding MOF-SO_3H are shown in Figure S2. For MIL-101(Cr)-SO_3H (Figure S2b) and UIO-66(Zr)-SO_3H (Figure S2d), their patterns are almost the same as that of their corresponding precursors MIL-101(Cr) (Figure S2a) and UIO-66(Zr) (Figure S2c), respectively, only with some slight variations in the Bragg intensities. These results indicate that the structures are reserved after sulfonic acid groups inserted onto the framework of MIL-101(Cr)[11b] and UIO-66(Zr). In the case of MIL-53(Al)-SO_3H (Figure S2f), despite some changes compared with MIL-53(Al), framework still retains its intrinsic porosity as illustrated by Gascon and co-worker.[11b]

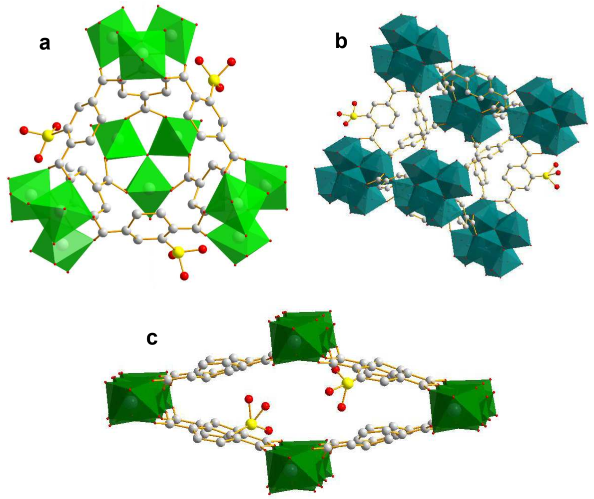


Fig. 1 The proposed structures of (a) MIL-101(Cr)-SO_3H, (b) UIO-66(Zr)-SO_3H, and (c) MIL-53(Al)-SO_3H. Gray, yellow and red balls represent carbon, sulphur and oxygen atoms, respectively. Chromium octahedral in (a), zirconium octahedral in (b), and aluminum octahedral in (c) are in green, dark blue, and dark green, respectively. Hydrogen atoms are omitted for clarity.

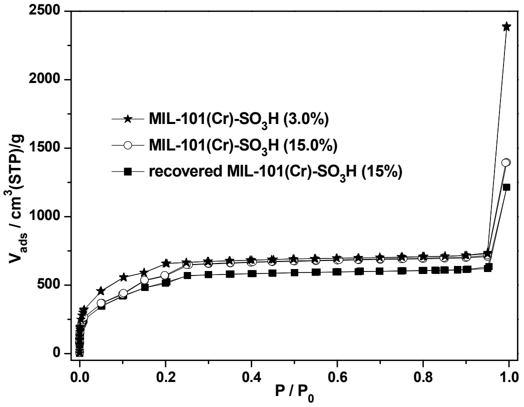


Fig. 2 N_2 adsorption/desorption isotherms of MIL-101(Cr)-SO_3H (3.0%), MIL-101(Cr)-SO_3H (15.0%) and recovered MIL-101(Cr)-SO_3H (15.0%) with the reaction conditions described in Figure 9.

Compared with the bare MOFs, the resulting pore modification is also visible on the N_2 adsorption isotherms of the MOF-SO_3H. MIL-101(Cr)-SO_3H exhibits a significant decrease of porous surface area from 2693 m^2g^{-1} for MIL-101(Cr)[8c,b] to 2023 m^2g^{-1} for MIL-101(Cr)-SO_3H (3.0%) and to 1757 m^2g^{-1} for

Table 1. Characterization of MOF-SO_3H [a]

Run	Catalyst	S content [a] [mmol g^{-1}]	grafting rate [a] -SO_3H [%]	acid density [b] H^+ [mmol g^{-1}]	Adsorption [mmol g^{-1}] [c]		fructose Conv. [%]	HMF	
					fructose	HMF		Selec. [%]	Yield [%]
1	MIL-101(Cr)-SO_3H	0.54	15.0	0.60	0.0060	0.088	>99	91	90
2	MIL-101(Cr)-SO_3H	0.22	6.1	0.29	0.0045	0.048	91	78	71
3	MIL-101(Cr)-SO_3H	0.11	3.0	0.25	0.0039	0.035	83	76	63
4	UIO-66(Zr)-SO_3H	0.32	9.5	0.41	0.0052	0.061	>99	86	85
5	MIL-53(Al)-SO_3H	0.29	8.2	0.34	0.0023	0.094	>99	80	79
6	MIL-101(Cr)	/	/		0.0031	0.028	45	53	24

[a] Based on elemental analysis. [b] Acid-density values were determined through potentiometric acid–base titration and calculated using the amount of NaOH added to the corresponding MOF material. [c] Determined by HPLC based on corresponding concentration change of fructose and HMF in DMSO. Reaction conditions: fructose (500 mg), MOF-SO_3H (300 mg), DMSO (5 mL), time (1 h), 120 °C.

MIL-101(Cr)-SO_3H (15.0%) due to pore blocking (Figure 2).

Table 1 shows a comparison of the as-prepared MOF-SO_3H. The grafting rate of -SO_3H in the MOF-SO_3H were calculated by elemental analysis based on the sulfur component, the sulfonic acid-site density was estimated by the potentiometric acid–base titration method, whereas the amount of adsorbed HMF and fructose over MOF-SO_3H was chromatographically determined by corresponding concentration change of fructose and HMF. Both elemental analysis and acid–base titration experiment further confirmed the successful grafting of –SO_3H in MOF-SO_3H. The results given in Table 1 suggest that the loading level of -SO_3H in MOF-SO_3H as well as the contribution of Brønsted acidity in MOF-SO_3H decreases in the order of MIL-101(Cr)-SO_3H (15.0%) > UIO-66(Zr)-SO_3H (9.5%) > MIL-53(Al)-SO_3H (8.2%) > MIL-101(Cr)-SO_3H (6.1%) > MIL-101(Cr)-SO_3H (3.0%), demonstrating that the acid strength of MOF-SO_3H parallels its -SO_3H grafting level. Moreover, all of the MOF-SO_3H shows significant adsorption of HMF than in the case of fructose, presumably owning to an interaction between an aromatic ring on HMF and a connecting organic linker of BDC in MOF-SO_3H.[5b]

Conversion of fructose into HMF

Table 1 shows the dehydration of fructose to HMF in DMSO at 120 °C for 1 h with MOF-SO_3H as solid acid catalysts (Scheme 1). An initial experiment was carried out to investigate the effect of the -SO_3H grafting rate in MIL-101(Cr)-SO_3H on the fructose-to-HMF transformation. For MIL-101(Cr)-SO_3H with a -SO_3H grafting rate of 15.0%, an HMF yield of 90% was obtained with a full fructose conversion (Table 1, Run 1). With a decrease of the -SO_3H grafting rate to 6.1%, the HMF yield was 71% (Table 1, Run 2). A further decrease of the -SO_3H grafting rate to 3.0% resulted in an HMF yield of only 63% (Table 1, Run 3), suggesting the catalytic performance of MIL-101(Cr)-SO_3H as a function of the -SO_3H loading level as well as the sulfonic acid-site density. Polymeric humins were found as the main by-products in the reaction. Moreover, the MIL-101(Cr)-SO_3H was substantially more active than bare MIL-101(Cr). MIL-101(Cr) produced an HMF yield of 24% with a fructose conversion of 45% under the investigated conditions (Table 1, Run 6).

Apart from MIL-101(Cr)-SO_3H (15.0%), UIO-66(Zr)-SO_3H (9.5%) and MIL-53(Al)-SO_3H (8.2%) were also evaluated as solid acid for fructose dehydration, producing HMF yields of 85% (Table 1, run 4) and 79% (Table 1, run 5), respectively. Figure 3 further shows that the catalytic performance of MOF-SO_3H in fructose-to-HMF transformation decreases with the following order of MIL-101(Cr)-SO_3H (15.0%) > UIO-66(Zr)-SO_3H (9.5%) > MIL-53(Al)-SO_3H (8.2%). Notably, this result is in line with the sequence of their corresponding sulfonic acid-site density as described in Table 1, suggesting that MOF-SO_3H with the highest concentration of sulfonic acid-group proved to be most active catalyst for fructose-to-HMF transformation.

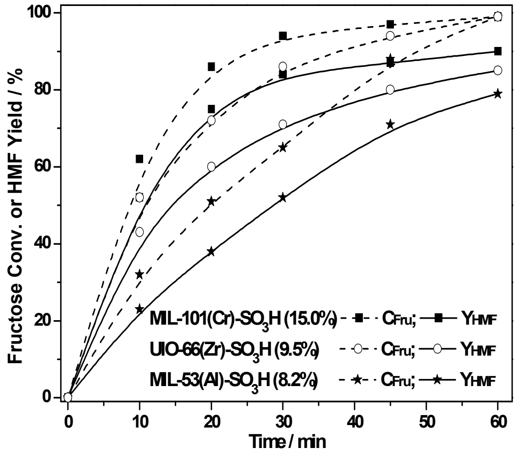


Fig. 3 The comparison of catalytic performance of MOF-SO_3H on fructose-to-HMF transformation. Conditions: fructose (500 mg), MOF-SO_3H (300 mg), DMSO (5 mL), 120 °C.

Figure 4 shows the influence of reaction temperature and time on the conversion of the fructose into HMF with MIL-101(Cr)-SO_3H (15%) as solid acid. Generally, the yield of HMF increased with time. The HMF yield increased slowly to 63% after 60 min at 100 °C, while it increased quickly to 78% after 20 min at 140 °C, confirming that raising the reaction temperature promotes the fructose-to-HMF transformation. The slight decrease of the HMF yields with prolonged reaction time after 24 min at 140 °C may be attributed to a further polymerization of HMF to form oligomers under the relatively high temperature.

We further compared our results with another type of MOF-derived solid acid PTA/MIL-101(Cr). According to the literature, an HMF yield of 63% with fructose conversion of 82% was obtained in 30 min with PTA/MIL-101(Cr) (PTA 33.8 wt%) as catalyst in DMSO at 130 °C.[7a] In our case, under similar conditions, an HMF yield of 84% with fructose conversion of 94% was obtained with MIL-101(Cr)-SO_3H (15%) at 120 °C. Moreover, the maximum HMF yield of 90% with a full fructose conversion was achieved at 120 °C after a reaction time of 60 min, further demonstrating a comparable catalytic performance of MIL-101(Cr)-SO_3H (15.0%).

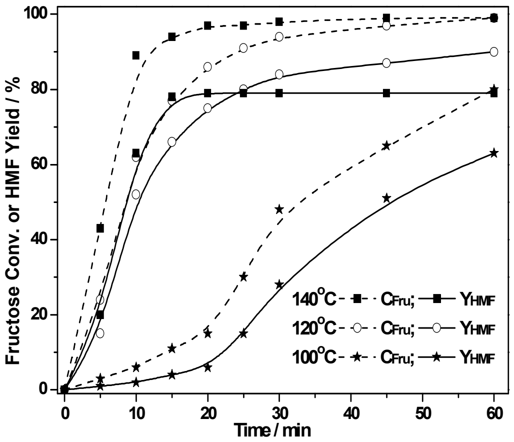


Fig. 4 Effect of temperature and reaction time on fructose-to-HMF transformation. Conditions: fructose (500 mg), MIL-101(Cr)-SO_3H (15%) (300 mg), DMSO (5 mL).

Kinetics studies

Kinetics studies of fructose-to-HMF transformation were investigated with MIL-101(Cr)-SO_3H (15%) as catalyst. According to ongoing research, transformation of fructose into HMF may obey pseudo-first order process.[5a] This assumption is supposed under the conditions that 1) HMF is sole product of fructose dehydration, and 2) HMF is stable enough under the investigated conditions without further degradation. Under the above conditions, the rate of fructose transformation (r[fructose]) can be expressed as the following equation as a first order reaction:

$$-\mathrm{r}[\mathrm{fructose}] = -\frac{d[\mathrm{fructose}]}{dt} = k[\mathrm{fructose}] = \frac{d[\mathrm{HMF}]}{dt}$$

[fructose] and [HMF] indicate molar concentrations of fructose and HMF, respectively; whereas, *k* is the rate constant of fructose dehydration at a certain temperature.

$$\ln k = -\frac{\mathrm{Ea}}{\mathrm{RT}} + \ln \mathrm{A}$$

According to the above Arrhenius equation, the original equation is transformed into the following equation with the [fructose] in terms of conversion X. Herein, t and C are the reaction time and an arbitrary constant, respectively.

$$-\ln(1-\mathrm{X}) = kt + \mathrm{C}$$

After a data fitting as shown in Figure 4, the linear relationship between Ln(1-X) and reaction time (t) (Figure 5a) thus supported the hypothesis as pseudo-first order for fructose-to-HMF transformation. Figure 5a further shows that the observed rate constant (*k*) of fructose-to-HMF transformation increases from 2.01 to 11.3 h^{-1} as the increased reaction temperature from 100 to 140 °C, which quantitatively confirms that raising the reaction temperature promotes fructose transformation. Figure 5b plots the (Ln*k*) versus ($1/T \times 10^3$) based on the Arrhenius equation, demonstrating that the observed activation energy (Ea) and pre-exponential factor (A) for the fructose transformation were 55 kJ mol^{-1} and 8.95×10^7 h^{-1}, respectively. In contrast, an observed activation energy of 70 kJ/mol was obtained with molecular sieve HZSM-5 (Si/Al = 25) as catalyst under the investigated conditions, further suggesting a high efficiency of MIL-101(Cr)-SO_3H (15%) over HZSM-5 (Si/Al = 25). Moreover, a bifunctional catalyst designed by sulfonic acid- and ionic liquid-functionalization over mesoporous silica nanoparticles (MSN) was recently prepared for fructose dehydration to HMF in DMSO.[5a] Activation energies of 67.5 and 80.05 kJ mol^{-1} were obtained with and without the bifunctional catalyst, respectively. In our case, the observed activation energy of 55 kJ mol^{-1} for MIL-101(Cr)-SO_3H (15%) further indicates MOF-SO_3H catalyst can efficiently lower the activation energy and lead to a relatively higher reaction rate.

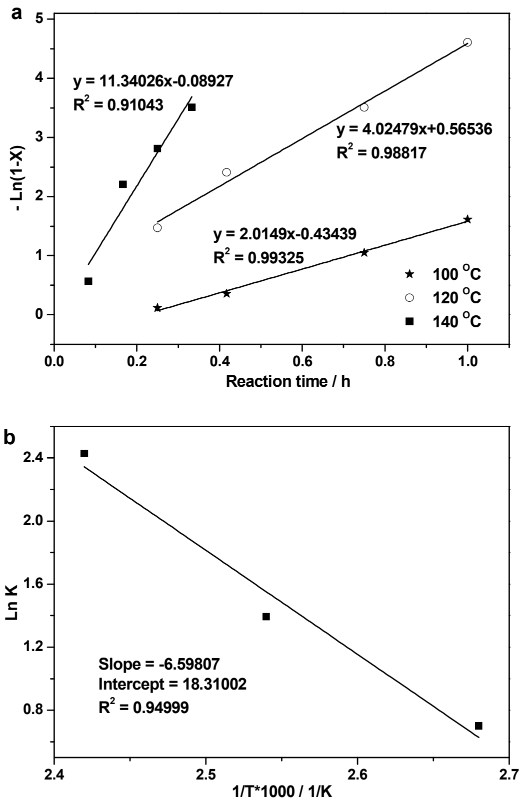


Fig. 5 (a) The kinetics profiles of fructose dehydration to HMF (fitted by first order assumption) with MIL-101(Cr)-SO_3H (15%) as catalyst. (b) Arrhenius plots for fructose dehydration to HMF. Conditions: fructose (500 mg), MIL-101(Cr)-SO_3H (15%) (300 mg), DMSO (5 mL).

Correlation between structure and performance of MOF-SO_3H

Figure 6a shows a strong correlation between fructose conversion/HMF selectivity and the sulfonic acid-site density of MOF-SO$_3$H. Whereas, Figure 6b plots fructose conversion/HMF selectivity versus S content of MOF-SO$_3$H. Under a fixed reaction of 10 min, HMF selectivity (about 84%) and fructose conversion (about 62%) is highest for catalyst MIL-101(Cr)-SO$_3$H (15.0%) with the highest Brønsted sulfonic acid-site density (Figure 6a). Figures 6a and 6b further indicate an increase in selectivity towards HMF as well as conversion of fructose with an increase in Brønsted acidity contribution from MOF-SO$_3$H.

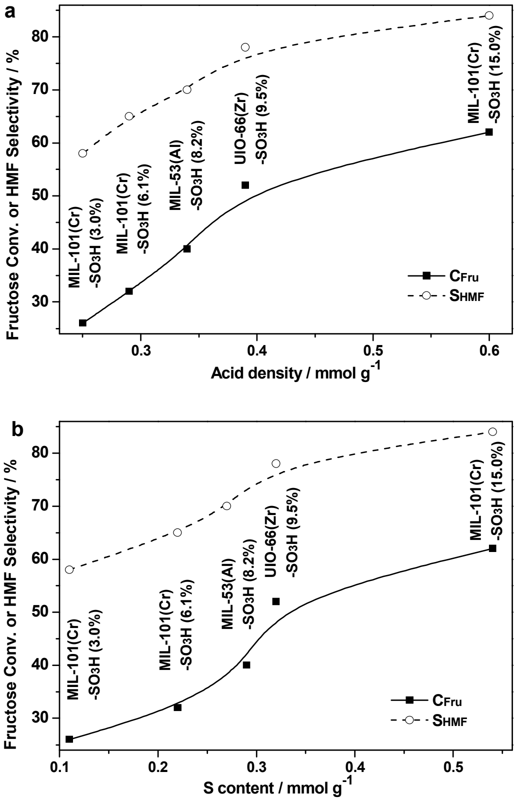


Fig. 6 The conversion of fructose and selectivity towards HMF at reaction time of 10 min versus acid density of MOF-SO$_3$ (a) and S content of MOF-SO$_3$H (b). Conditions: fructose (500 mg), MOF-SO$_3$H (300 mg), DMSO (5 mL), 120 °C, 10 min.

Recently, we revealed a linear correspondence between the catalytic activity and acid density for sulfonic acid-functionalized carbon materials in fructose dehydration to HMF.[4k] Herein, a similar structure of precursor MOFs with the same sulfonation method makes MOF-SO$_3$H an ideal model to quantitatively investigate the relationship between structure and performance in fructose-to-HMF transformation. Figure 7a shows a comparison of sulfonic acid-site density and turnover frequencies (TOFs) of MOF-SO$_3$H for fructose-to-HMF transformation. Notably, both sulfonic acid-site density and TOFs of MOF-SO$_3$H increase as grafting rate of -SO$_3$H in MOF-SO$_3$H. Moreover, Figure 7b plots fructose transformation rates in terms of TOF against the sulfonic acid-site densities of MOF-SO$_3$H. Interestingly, the sulfonic acid-site density of MOF-SO$_3$H shows a good linear correspondence to fructose transformation rate under a grafting rate of -SO$_3$H lower than 9.5% in MOF-SO$_3$H. This result reveals that the catalytic performance of MOF-SO$_3$H mainly comes from sulfonic acid groups of MOF-SO$_3$H for fructose-to-HMF transformation. Moreover, the sulfonic acid groups, function as the catalytic sites, are equivalent in all MOF-SO$_3$H for fructose dehydration, regardless of precursor MOFs. An arbitrary extrapolation of the plot in Figure 7b further suggests that MIL-101(Cr)-SO$_3$H with a higher -SO$_3$H grafting rate of 15.0%, corresponding to a higher sulfonic acid-site density of 0.60 mmol g^{-1}, should have a TOF of about 8.3 h^{-1} which is, however, in sharp contrast with an observed value of 6.2 h^{-1}. This behavior may be explained as a result of the increase in the sulfonic acid-group density of MOF-SO$_3$H on the one hand and the decrease in the micropore volume as well as porous surface area of MOF-SO$_3$H on the other hand as -SO$_3$H grafting rates increase.[7c,5c]

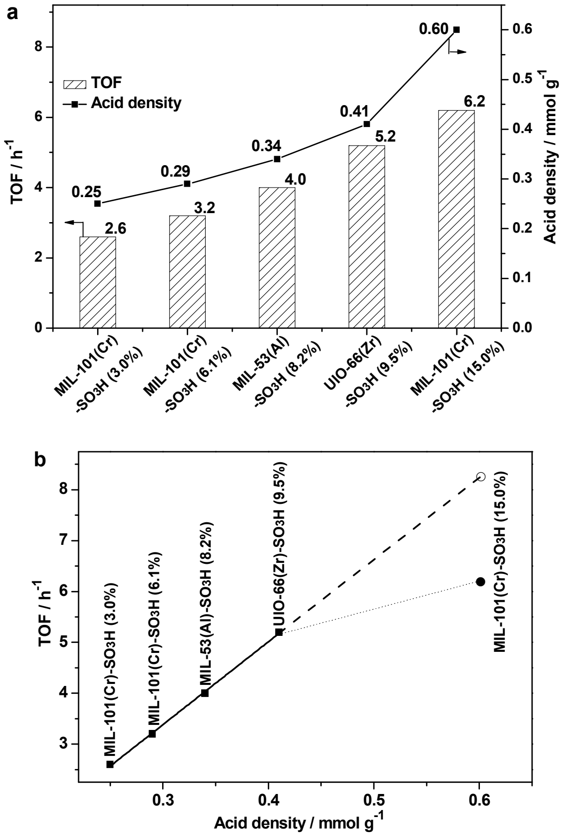


Fig. 7 (a) The comparison of sulfonic acid-site density and turnover frequencies (TOFs) of MOF-SO$_3$H for fructose-to-HMF transformation. (b) TOFs of MOF-SO$_3$H versus sulfonic acid-site density of MOF-SO$_3$H. (TOFs for the fructose-to-HMF transformation were measured at t = 10 min, given as amounts of consumed fructose per amounts of MOF-SO$_3$H per hour. Conditions: fructose (500 mg), MOF-SO$_3$H (300 mg), DMSO (5 mL), 120 °C, 10 min.)

Comparison MOF-SO$_3$H and other solid acids in fructose conversion

In addition to MOF-SO$_3$H, solid acids such as PTA/MIL-101(Cr) (PTA 33.8 wt%),[7a] H-Beta (Si/Al = 12.5), HY-zeolite (Si/Al ≥ 5.2) and HZSM-5 (Si/Al = 25) were subjected to fructose dehydration for comparison purpose. Figure 8a shows the catalytic activity for fructose dehydration at 120 °C decreases with the order of MIL-101(Cr)-SO$_3$H (15.0%) > PTA/MIL-101

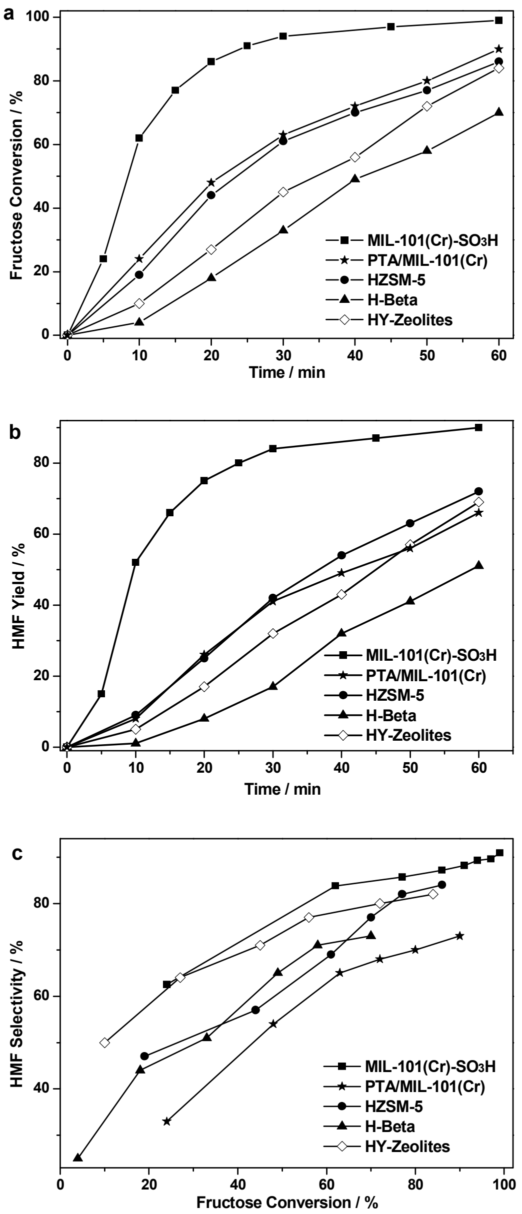


Fig. 8 (a) Fructose conversion versus time; (b) HMF yield versus time; (c) selectivity to HMF versus fructose conversion over solid acid catalysts. Reaction conditions: fructose (500 mg), catalyst [MIL-101(Cr)-SO_3H (15.0%), PTA/MIL-101(Cr) (PTA 33.8 wt%), H-Beta (Si/Al = 12.5), HY-zeolite (Si/Al ≥ 5.2) and HZSM-5 (Si/Al = 25), 300 mg], DMSO (5 mL), 120 °C.

(PTA 33.8 wt%) > HZSM-5 (Si/Al = 25) > HY-zeolite (Si/Al ≥ 5.2) > H-Beta (Si/Al = 12.5). In case of HMF formation (Figure 8b), the highest HMF yield was observed over MIL-101(Cr)-SO_3H (15.0%) among the solid acid catalysts under the investigated conditions. Whereas, the catalytic performance of PTA/MIL-101 (PTA 33.8 wt%) for HMF production was comparable to HZSM-5 (Si/Al = 25) and HY-zeolite (Si/Al ≥ 5.2). This result suggested that the higher acid strength, the cubic crystal, three-dimensional and highly porous system of MIL-101(Cr)-SO_3H could presumably promote the dehydration of fructose to HMF. Figure 8c shows the selectivity to HMF versus conversion of the fructose in fructose dehydration over different solid acids. In these reactions, the selectivity to HMF generally increased with an increase of fructose conversion. Notably, the highest selectivities to HMF were observed over MIL-101(Cr)-SO_3H (15.0%) with a constant fructose conversion; whereas, the lowest selectivities to HMF were found over PTA/MIL-101 (PTA 33.8 wt%). According to the literature, PTA/MIL-101(Cr) (PTA 33.8 wt%) corresponds to a loading level of approximately three PTA clusters per cage of the MIL-101(Cr) MOF.[7a] A relatively high loading level of PTA clusters in PTA/MIL-101(Cr) could, on the one hand, increase acidity as well as catalytic acitivity of PTA/MIL-101(Cr) towards fructose dehydration. On the other hand, bulky and abundant PTA clusters in the cage of the MIL-101(Cr) might lead to serious diffusion limitations. It has been established that mass transfer limitations often lead to a reduced selectivity for exothermic reactions.[5c] In this case, the observed low selectivities towards HMF over PTA/MIL-101(Cr) can presumably be related to diffusion limitations of fructose within PTA/MIL-101(Cr).

Catalyst recycling

In order to demonstrate the reusability of MIL-101(Cr)-SO_3H (15.0%), a five-cycle experiment was performed, and the results are shown in Figure 9. Notably, the measured yields of the HMF only slightly reduced from 90 to 85%. The decrease in catalytic activity could be presumably attributed to minor leaching of acidic proton from MOF-SO_3H or the adsorption and accumulation of oligomeric products on the acid site of highly microporous catalyst.[4k,7c] Notably, the observed reusability of MIL-101(Cr)-SO_3H is still far higher than that achieved with regards to recently reported PTA/MIL-101(Cr) (PTA 33.8 wt%). For PTA/MIL-101(Cr)-catalyzed fructose dehydration, a fast deactivation process with time was observed due to the leaching of active species from PTA/MIL-101(Cr) into solvent.[7a]

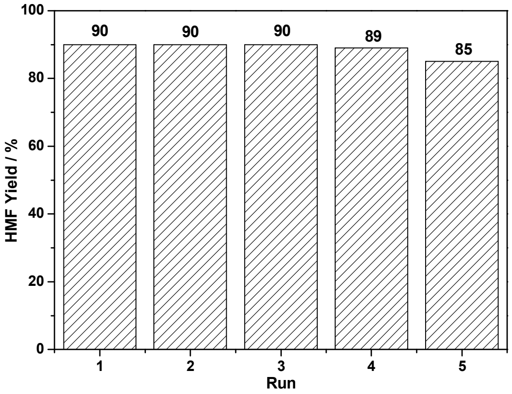


Fig. 9 Catalyst recycling. Conditions: fructose (500 mg), MIL-101(Cr)-SO_3H (15%) (300 mg), DMSO (5 mL), 120 °C, 60 min.

To check the contribution of released acidic proton from MIL-101(Cr)-SO_3H (15.0%) to homogeneous reactions, MIL-101(Cr)-SO_3H was removed from the reaction medium by filtration after 5 min of reaction (at an HMF yield of 12%) and the experiment proceeded with the filtrate under the same conditions as described in Figure 10. As expected, the reaction slowly proceeded after the removal of MIL-101(Cr)-SO_3H, producing an HMF yield of only 35%. Notably, without using

MIL-101(Cr)-SO_3H, the contribution of the blank experiment gave an HMF yield of 24% (Figure 10). Moreover, the blank experiment showed a similar trend to the catalyst filtration reaction upon the removal of MIL-101(Cr)-SO_3H. The above results thus indicate that a slight increase in HMF yield from 12% to 35% in catalyst filtration reaction may be attributed to the contribution of the blank experiment, rather than released acidic proton from MIL-101(Cr)-SO_3H. Moreover, the recovered MIL-101(Cr)-SO_3H after a five-cycle experiment showed almost identical sulfonic acid-site density to the fresh one, further suggesting the stability of MIL-101(Cr)-SO_3H and verifying the heterogeneous catalysis of MIL-101(Cr)-SO_3H. ICP–OES analysis showed that only 0.01% of the total amount of Cr had leached from MIL-101(Cr)-SO_3H after the first run. BET analysis indicates that the specific surface area decreases from 1757 m^2g^{-1} for the fresh MIL-101(Cr)-SO_3H (15.0%) to 1146 m^2g^{-1} for the recovered one (Figure 2), suggesting the adsorption of humins on the surface of the catalyst. Therefore, the slightly reduced activity of MIL-101(Cr)-SO_3H in catalyst recycling can reasonably be related to the adsorption and accumulation of oligomeric products on the catalyst surface.

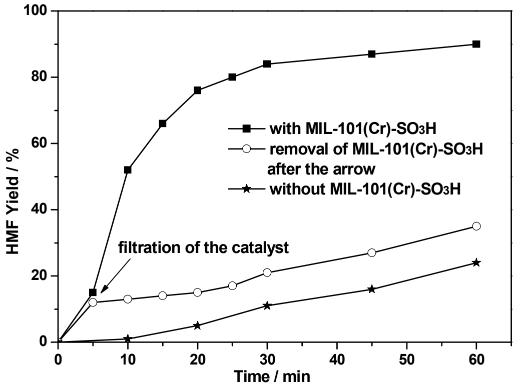


Fig. 10 Effects of the removal of MIL-101(Cr)-SO_3H on the fructose dehydration. Conditions: fructose (500 mg), MIL-101(Cr)-SO_3H (15.0%) (300 mg), DMSO (5 mL), 120 °C.

Conversion of other feedstocks to HMF

Table 2. Conversion of other feedstocks to HMF [a]

Run	Substrate	Solvent	*T* [°C]	Yield [%]
1	Inulin	DMSO	120	46
2	Sucrose	DMSO	120	44
3	Glucose	DMSO	120	7
4	Cellobiose	DMSO	150	24
5	Cellulose	DMSO	150	trace
6	Inulin	[Bmim]Cl	120	57
7	Sucrose	[Bmim]Cl	120	49
8	Glucose	[Bmim]Cl	120	8
9	Cellobiose	[Bmim]Cl	150	27
10	Cellulose	[Bmim]Cl	150	trace

[a] Reaction conditions: substrate (100 mg), MIL-101(Cr)-SO_3H (15.0%) (60 mg), solvent (DMSO 2 mL or [Bmim]Cl 2 mL), time (2 h).

Besides fructose, the MIL-101(Cr)-SO_3H was further extended to inulin, sucrose, glucose, cellobiose, and cellulose, and the results are presented in Table 2. When inulin was used, the HMF yield reached 46%, which is slightly higher than the HMF yield of 44% obtained from sucrose (Table 2, Runs 1–2). These results indicate that MIL-101(Cr)-SO_3H catalyzes the hydrolysis of sucrose and inulin without the need for higher temperature or longer reaction times. When glucose, cellobiose, and cellulose were subjected to our reaction conditions, the HMF yield was remarkably inferior (Table 2, Run 3–5). This result clearly indicates that only fructose in sucrose and inulin was converted to HMF and MIL-101(Cr)-SO_3H does not catalyze the isomerization of glucose to fructose. In addition to DMSO, when ionic liquid 1-butyl-3-methylimidazolium chloride [BMIM]Cl was used as solvent, similar results for HMF formation were observed (Table 2, Runs 6–10).

Conclusion

In summary, MOF-SO_3H, prepared by covalent PSM of the backbone phenylene units within the MOFs with chlorosulfonic acid resulted in active solid acid catalysts. The MOF-SO_3H was effective for catalytic fructose-to-HMF transformation. A high HMF yield of up to 90% with a full fructose conversion was obtained with MIL-101(Cr)-SO_3H as catalyst. Both the concentration of –SO_3H in MOF-SO_3H and the contribution of Brønsted acidity of MOF-SO_3H can be precisely tuned by –SO_3H grafting rate of MOF-SO_3H. Under lower –SO_3H grafting levers, the relationship between the catalytic activity in terms of TOF and sulfonic acid-site density of MOF-SO_3H shows a good linear correspondence. Moreover, the sulfonic acid groups are equivalent in all MOF-SO_3H for fructose-to-HMF transformation, regardless of precursor MOFs. Our studies also reveal that the MIL-101(Cr)-SO_3H promoted fructose-to-HMF transformation may obey pseudo-first-order kinetics with observed activation energy of 55 kJ mol^{-1}. Moreover, MIL-101(Cr)-SO_3H, behaves as heterogeneous catalyst, can be recovered and reused.

Acknowledgements

This work was financially supported by National Natural Science Foundation of China (21172219, 21207039 and 21101053), National Basic Research Program of China (973 Program, 2012CB215304), 100 Talents Program of the Chinese Academy of Sciences, and Guangdong Provincial Key Laboratory of Atmospheric Environment and Pollution Control.

Notes and references

[a] *CAS Key Laboratory of Renewable Energy, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences. Guangzhou 510640 (PR China). E-mail: chenjz@ms.giec.ac.cn. Tel./Fax: +86-20-3722-3380.*
[b] *Guangdong Provincial Key Laboratory of Atmospheric Environment and Pollution Control, College of Environment and Energy, South China University of Technology, Guangzhou 510006 (PR China)*
[c] *University of Chinese Academy of Sciences. Beijing 100049 (PR China).*

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

1 a) P. Gallezot, *Chem. Soc. Rev.* 2012, **41**, 1538–1558; b) A. Corma, S. Iborra, A. Velty, *Chem. Rev.* 2007, **107**, 2411–2502; c) G. W. Huber, S. Iborra, A. Corma, *Chem. Rev.* 2006, **106**, 4044–4098; d) J. N. Chheda, G. W. Huber, J. A. Dumesic, *Angew. Chem. Int. Ed.*

2007, **46**, 7164–7183; e) G. W. Huber, A. Corma, *Angew. Chem. Int. Ed.* 2007, **46**, 7184–7201.

2 a) R. J. van Putten, J. C. van der Waal, E. de Jong, C. B. Rasrendra, H. J. Heeres, J. G. de Vries, *Chem. Rev*. 2013, **113**, 1499−1597; b) A. A. Rosatella, S. P. Simeonov, R. F. M. Frade, C. A. M. Afonso, *Green Chem.* 2011, **13**, 754–793.

3 a) L. Hu, G. Zhao, W. W. Hao, X. Tang, Y. Sun, L. Lin, S. J. Liu, *RSC Adv.* 2012, **2**, 11184–11206; b) G. Y. Li, N. Li, Z. Q. Wang, C. Z. Li, A. Q. Wang, X. D. Wang, Y. Cong, T. Zhang, *ChemSusChem* 2012, **5**, 1958–1966; c) S. Dutta, S. De, B. Saha, *ChemPlusChem* 2012, **77**, 259–272.

4 a) X. L. Tong, Y. D. Li, *ChemSusChem* 2010, **3**, 350–355; b) D. A. Kotadia, S. S. Soni, *Catal. Sci. Technol.* 2013, **3**, 469–474; c) E. Nikolla, Y. Román-Leshkov, M. Moliner, M. E. Davis, *ACS Catal.* 2011, **1**, 408–410; d) H. B. Xie, Z. K. Zhao, Q. Wang, *ChemSusChem* 2012, **5**, 901–905; e) X. H. Qi, H. X. Guo, L. Y. Li, R. L. Smith, *ChemSusChem* 2012, **5**, 2215–2220; f) Z. Huang, W. Y. Pan, H. B. Zhou, F. Qin, H. L. Xu, W. Shen, *ChemSusChem* 2013, **6**, 1063–1069; g) Z. Zhang, B. Du, L. J. Zhang, Y. X. Da, Z. J. Quan, L. J. Yang, X. C. Wang, *RSC Adv*. 2013, **3**, 9201–9205; h) Q. B. Wu, Y. N. Yan, Q. Zhang, J. H. Lu, Z. J. Yang, Y. H. Zhang, Y. Tang, *ChemSusChem* 2013, **6**, 820–825; i) R. Alamillo, A. J. Crisci, J. M. Gallo, S. L. Scott, J. A. Dumesic, *Angew. Chem.* 2013, **125**, 10539–10541; j) Z.-Z. Yang, J. Deng, T. Pan, Q.-X. Guo, Y. Fu, *Green Chem.* 2012, **14**, 2986–2989; k) R. L. Liu, J. Z. Chen, X. Huang, L. M. Chen, L. L. Ma, X. J. Li, *Green Chem.* 2013, **15**, 2895–2903.

5 a) Y. Y. Lee, K. C. W. Wu, *Phys. Chem. Chem. Phys.* 2012, **14**, 13914–13917; b) V. V. Ordomsky, J. van der Schaaf, J. C. Schouten, T. A. Nijhuis, *ChemSusChem* 2012, **5**, 1812–1819; c) C. Aellig, I. Hermans, *ChemSusChem* 2012, **5**, 1737–1742; d) H. Kimura, M. Nakahara, N. Matubayasi, *J. Phys. Chem. A* 2013, **117**, 2102−2113; e) B. Cinlar, T. F. Wang, B. H. Shanks, *Appl. Catal. A* 2013, **450**, 237–242; f) G. Yang, E. A. Pidko, E. J. M. Hensen, *J. Catal.* 2012, **295**, 122–132; g) R. S. Assary, P. C. Redfern, J. Greeley, L. A. Curtiss, *J. Phys. Chem. B* 2011, **115**, 4341–4349; h) Y. S. Qu, C. P Huang, Y. L. Song, J. Zhang, B. H. Chen, *Bioresour. Technol.* 2012, **121**, 462–466.

6 a) S. M. Cohen, *Chem. Rev*. 2012, **112**, 970–1000; b) J. M. Taylor, K. W. Dawson, G. K. H. Shimizu, *J. Am. Chem. Soc*. 2013, **135**, 1193−1196; c) K. K. Tanabe, S. M. Cohen, *Chem. Soc. Rev.* 2011, **40**, 498–519; d) D. Zhao, D. J. Timmons, D. Q. Yuan, H. C. Zhou, *Acc. Chem. Res.* 2011, **44**, 123–133; e) A. Corma, H. García, F. X. Llabrés i Xamena, *Chem. Rev.* 2010, **110**, 4606–4655; f) A. Dhakshinamoorthy, M. Opanasenko, J. Čejka, H. Garcia, *Adv. Synth. Catal.* 2013, **355**, 247–268.

7 a) Y. M. Zhang, V. Degirmenci, C. Li, E. J. M. Hensen, *ChemSusChem* 2011, **4**, 59–64; b) G. Akiyama, R. Matsuda, H. Sato, M. Takata, S. Kitagawa, *Adv. Mater*. 2011, **23**, 3294–3297; c) J. Z. Chen, S. P. Wang, J. Huang, L. M. Chen, L. L. Ma, X. Huang. *ChemSusChem*, 2013, **6**, 1545–1555.

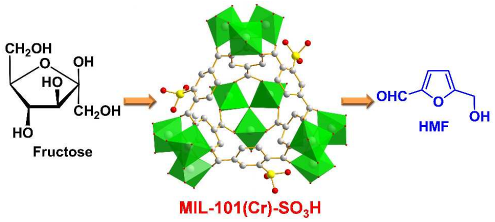
8 a) Y. K. Hwang, D. Y. Hong, J. S. Chang, S. H. Jhung, Y. K. Seo, J. Kim, A. Vimont, M. Daturi, C. Serre, G. Férey, *Angew. Chem. Int. Ed.* 2008, **47**, 4144–4148; b) D. Y. Hong, Y. K. Hwang, C. Serre, G. Férey, J. S. Chang, *Adv. Funct. Mater.* 2009, **19**, 1537–1552; c) I. Senkovska, S. Kaskel, *Microporous Mesoporous Mater.* 2008, **112**, 108–115.

9 a) V. Guillerm, F. Ragon, M. Dan-Hardi, T. Devic, M. Vishnuvarthan, B. Campo, A. Vimont, G. Clet, Q. Yang, G. Maurin, G. Férey, A. Vittadini, S. Gross, C. Serre, *Angew. Chem. Int. Ed.* 2012, **51**, 9267–9271; b) M. L. Foo, S. Horike, T. Fukushima, Y. Hijikata, Y. Kubota, M. Takata, S. Kitagawa, *Dalton Trans*. 2012, **41**, 13791–13794.

10 a) T. Loiseau, C. Serre, C. Huguenard, G. Fink, F. Taulelle, M. Henry, T. Bataille, G. Férey, *Chem. Eur. J*. 2004, **10**, 1373–1382.

11 a) Y. D. Zang, J. Shi, F. M. Zhang, Y. J. Zhong, W. D. Zhu, *Catal. Sci. Technol.* 2013*,* **3***,* 2044–2049; b) M. G. Goesten, J. Juan-Alcaňiz, E. V. Ramos-Fernandez, K. B. Sai Sankar Gupta, E. Stavitski, H. van Bekkum, J. Gascon, F. Kapteijn, *J. Catal.* 2011, **281**, 177–187; c) B. Li, Y. Zhang, D. Ma, L. Li, G. Li, G. Li, Z. Shi, *Chem. Commun.* 2012, **48**, 6151–6153.

Sulfonic acid-functionalized Metal-Organic Frameworks are efficiently used as recyclable solid acid catalysts for the fructose-to-HMF transformation.



TOC