Title

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Cooperative Brønsted-Lewis acid sites created by phosphotungstic acid encapsulated metal-organic frameworks for selective glucose conversion to 5-hydroxymethylfurfural

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Abstract

Production of 5-hydroxymethylfurfural (HMF) from biomass-derived glucose has great potential for synthesis of renewable fuels and chemicals. Selective glucose conversion to 5-hydroxymethylfurfural requires a balance between Lewis and Brønsted acids for the cascade of glucose isomerization followed by fructose dehydration. A dual Brønsted-Lewis acid, phosphotungstic acid encapsulated MIL-101(Al)-NH_2 metal-organic frameworks (MOFs) was developed to catalyze the glucose dehydration reaction. The encapsulated catalysts had a high HMF selectivity of 58% at 44% glucose conversion at 120°C in $[C_4C_1im]Cl$. Phosphotungstic acid was uniformly dispersed in the MOF pores, which provided both Brønsted and Lewis acid sites for this cascade reaction. The Brønsted acidic phosphotungstic acid-encapsulated MOF catalyst was stable and recyclable at least four times. These findings explain the effect of phosphotungstic acid location for maximizing the HMF selectivity and suggest a new approach for the design of bifunctional solid acid catalysts for selective HMF production from glucose. Moreover, the tunability of the acid properties of the encapsulated MOF catalysts provides opportunities for other biomass transformations.

Keywords. Metal-organic frameworks; phosphotungstic acid; encapsulation; glucose dehydration; hydroxymethylfurfural, cooperative

1. Introduction

Negative consequences of fuel and chemical production from petroleum, especially sizeable greenhouse gas emissions, price volatility [1], and non-renewability [2], have propelled the production of commodity chemicals from renewable plant biomass. Hydroxymethylfurfural (HMF) is a versatile platform chemical

47 derived from biomass with potential applications for fuels, chemicals, plastics, and pharmaceuticals [3-
48 5]. The challenge of glucose dehydration to HMF is to obtain high HMF selectivity. Although the glucose
49 dehydration reaction has been studied extensively, its mechanism is still being debated [6, 7].

50 In general, glucose dehydration to HMF can occur by two chemical pathways (**Scheme 1**), direct
51 dehydration (path 1) and tandem isomerization-dehydration reactions (path 2). The direct dehydration
52 of glucose to HMF by Brønsted acid catalysts is slow, and HMF selectivity is low because of side
53 reactions such as cross-condensation with formation of undesired humins [8-11]. Tandem isomerization-
54 dehydration reactions in one-pot afford opportunities to transform glucose to HMF selectively [12].
55 Selective production of HMF from glucose requires cooperation between Lewis and Brønsted acid
56 catalysts for glucose isomerization to fructose and subsequent fructose dehydration to HMF [8, 13-15].
57 Lewis acid promotes the isomerization of glucose to fructose and then dehydration of fructose to HMF
58 by Brønsted acid [16-18].

59 Swift et al. demonstrated this concept of tandem isomerization-dehydration reactions by
60 incorporating a Lewis acid ($CrCl_3$) with a Brønsted acid (HCl) catalyst, an approach that enhanced both
61 catalytic activity for glucose dehydration and HMF selectivity [19]. Vieira et al. used the combination of
62 Lewis acid Nb_2O_5 and Bronsted acid HCl in a water/tetrahydrofuran (THF) biphasic system. They found
63 that the Brønsted acid HCl was necessary to improve HMF selectivity from 7.6% to 51% and glucose
64 conversion from 49% to 93%, compared with Nb_2O_5 alone [18]. Nikolla et al. used the combination of Sn-
65 containing β-zeolite and HCl in H_2O/THF biphasic system to reach 72% HMF selectivity at 79% glucose
66 conversion [20]. However, all these studies were conducted with homogeneous Brønsted acid catalysts
67 that complicate product purification [21] and catalyst recycling. Therefore, it would be most useful to
68 have solid catalysts that possess both Brønsted and Lewis acid active sites for selective glucose

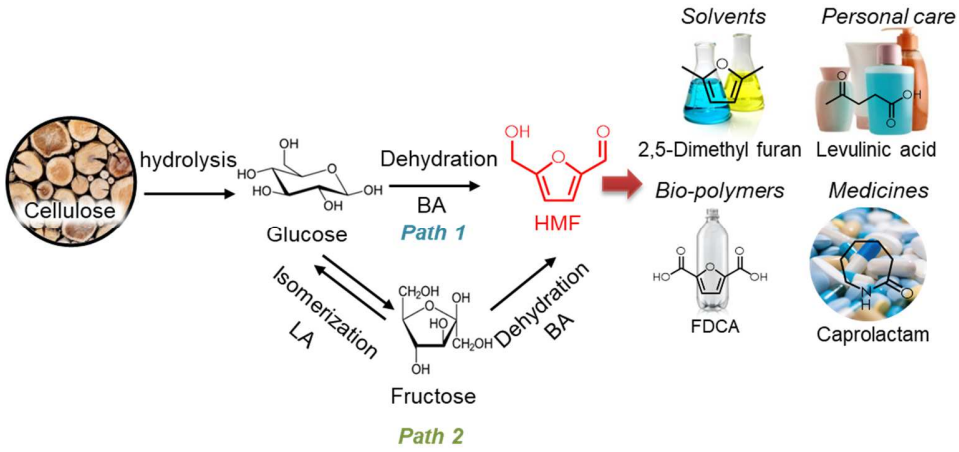
conversion to HMF. In answer to this need, this report describes metal-organic frameworks that have both Brønsted and Lewis acid sites for selective glucose conversion to HMF.

Metal-organic frameworks (MOFs) are porous crystalline materials that consist of metal ions or clusters coordinated with organic linkers to form highly uniform solid networks [22-27]. The coordinated unsaturated metal sites (cus) endow MOFs with Lewis acidity [28, 29]. Lewis acid sites of MOFs have been used to catalyze various reactions, such as aldol condensation [30], deacetalization-Knoevenagel condensation [31, 32], Meinwald rearrangement [33], and CO oxidation [34]. The porosity of MOFs enables incorporation of large Brønsted acidic molecules to create bifunctional acid catalysts for various acid-catalyzed organic reactions [22, 23, 35-38].

Polyoxometalates (POMs) are versatile catalysts because of their many active sites [39, 40]. The Keggin family of POMs ($[XM_{12}O_{40}]^{n-}$ anions (X = Si and P, M = Mo and W) with protons as the only countercations are heteropolyacids; examples include phosphotungstic acid, silicotungstic acid, silicomolybdic acid, and phosphomolybdic acid. These heteropolyacids have high acid strength and they are less corrosive compared with ordinary mineral acids (HBr, H_2SO_4, HNO_3, and HCl) [41, 42]. Although these properties make heteropolyacids attractive in acid-catalyzed reactions [43-47], they are soluble in water and many organic solvents. Thus, they are difficult to recycle, and their presence complicates purification of soluble products.

Trapping heteropolyacids in MOF pores generates bifunctional catalysts with both Lewis and Brønsted acids, which are important for selective glucose conversion to HMF [15, 48]. Indeed, as reported in **Table S2,** the Keggin-type heteropolyacids have been encapsulated successfully in the pores of MOFs[49-52]. For example, phosphotungstic acid (PTA)-encapsulated MIL-101(Cr) was used for various catalytic reactions such as the esterification of *n*-butanol with acetic acid [53], dehydration of

methanol [53], oxidative desulfurization of dibenzothiophene[54], carbohydrate dehydration to 5-hydroxymethylfurfural [52], and oxidation of the alkenes [55]. Zhang et al. synthesized PTA⊂MIL-101(Cr) by encapsulating PTA in MIL-101(Cr) for sugar dehydration [52]. Fructose dehydration by PTA⊂MIL-101(Cr) was selective for HMF (77% HMF selectivity at 82% fructose conversion). However, PTA⊂MIL-101(Cr) was not selective for HMF in glucose dehydration (10% HMF selectivity at 21% glucose conversion). Moreover, the use of fructose as a feedstock is not cost-effective because glucose is less expensive than fructose [56]. In addition, the chromium in PTA⊂MIL-101(Cr) catalysts is harmful to humans, animals, and the environment [57]. Therefore, there is a need to develop heterogeneous chromium-free acid catalytic systems that possess both Brønsted and Lewis acid sites to regulate the HMF selectivity in glucose dehydration.



Scheme 1. Reaction network of HMF production (BA = Brønsted acid, LA = Lewis acid)

Here, this work describes encapsulation of phosphotungstic acid in the pores of MIL-101(Al)-NH_2 to form PTA⊂MIL-101(Al)-NH_2. The effect of PTA encapsulation on catalytic performance in glucose dehydration with $[C_4C_1im]Cl$ as solvent was evaluated. The $[C_4C_1im]Cl$ was selected as the reaction solvent because our previous studies established that the alkyl imidazolium chloride ionic liquids, such as $[C_2C_1im]Cl$ and $[C_4C_1im]Cl$, can dissolve cellulose and enable hydrolysis of cellulose to sugars [58-60].

The MIL-101(Al)-NH_2 was selected because it is chemically and thermally stable [32]. Moreover, Brønsted acidic PTA was used as the heteropolyacid because it has a high acid strength compared with other heteropolyacids[61]. The encapsulated PTA in MIL-101(Al)-NH_2 was uniformly dispersed and stable in NH_2-MIL-101(Al) pores, and it provided Brønsted acid sites that rendered the catalyst selective for HMF production. These results reveal the unrecognized catalytic performance of the PTA⊂MIL-101(Al)-NH_2 catalysts for selective glucose dehydration.

2. Materials and Methods

2.1 Materials

The following chemicals were purchased and used as received: D-glucose, 1-butyl-3-methylimidazolium chloride ([C_4C_1im]Cl), 2-aminoterephthalic acid (2-ATA), aluminum chloride hexahydrate, phosphotungstic acid (PTA), and *N,N*-dimethylformamide (DMF), methanol, ethanol, n-propanol, 2-propanol, n-butanol, 2-butanol, *p*-dioxane, ethyl acetate (EA), *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMA), dimethyl sulfoxide (DMSO), and tetrahydrofuran (THF). **Table S1** summarizes the list of chemicals/reagents, their supplier, purity, and CAS number. All other chemicals, solvents, and gases were of the highest purity available from commercial sources.

2.2 Synthesis of metal-organic frameworks

2.2.1 Synthesis of MIL-101(Al)-NH_2

MIL-101(Al)-NH_2 was synthesized by the solvothermal method with a slight modification [62]. Typically, a mixture of aluminum chloride hexahydrate (0.51 g, 2 mmol) and 2-aminoterephthalic acid (0.56 g, 3 mmol) in DMF (30 mL) was kept in a Teflon-lined autoclave reactor without stirring at 130 °C for 72 h. Then the reactor was cooled to ambient temperature, and the solids were separated from the solution by centrifugation (6000 RPM, 5 min). The solids were washed with DMF under sonication for 10 min. Finally, the solid catalysts were washed three times with methanol at room temperature followed by washing with hot (70 °C) methanol for 5 h and dried overnight under vacuum at 80 °C.

2.2.2 Synthesis of encapsulated PTA in MIL-101(Al)-NH_2 (PTA⊂MIL-101(Al)-NH_2)

PTA⊂MIL-101(Al)-NH_2 was synthesized by incorporating phosphotungstic acid (PTA) hydrated during the synthesis of MIL-101(Al)-NH_2. In short, aluminum chloride hexahydrate (0.51 g, 2.1 mmol), 2-amino terephthalic acid (0.56 g, 3.1 mmol), and different amounts of PTA hydrate (0.1-2.0 g) in DMF (30 mL, ρ = ~0.9 g/mL) were kept in a Teflon-lined autoclave reactor without stirring, and the mixture was heated at 130 °C for 72 h. After cooling to ambient temperature, the resulting solids were separated by centrifugation (6000 RPM, 5 min), washed with DMF, then washed with hot methanol (70°C), and finally washed with acetone, and dried under vacuum at 80 °C overnight.

2.3 Catalyst characterization

2.3.1 Transmission electron microscopy and energy-dispersive X-ray spectroscopy analysis

The microstructure and elemental distribution of the metal-organic frameworks (MOFs) were analyzed using transmission electron microscopy (TEM) in a Tecnai F20 (FEI company, OR, USA) microscope operating at 200 kV. TEM specimens were prepared by dispersing small amounts of catalysts onto Cu

grid-supported holey carbon films. For the analysis of the microstructure, scanning transmission electron microscopy (STEM) images were acquired with a high annular angle dark field (HAADF) detector (E.A. Fischione Instruments, Inc., PA, USA) and an electron probe of a 1 nm diameter. For the elemental distribution analysis, energy-dispersive X-ray spectroscopy (EDS) maps were collected using a TEAM EDS (EDAX, Inc., NJ, USA) spectrometer.

2.3.2 N_2 adsorption-desorption

The N_2 adsorption-desorption assay was conducted with a Micromeritics Tristar (Norcross, GA, USA) instrument. The function of TriStar was verified with reference materials (Micromeritics). Prior to the measurement, the samples were pretreated with a Micromeritics FlowPrep with sample degasser (Norcross, GA, USA) at 160 °C for 2 h. The surface area, S_{BET}, was determined from N_2 isotherms using the Brunauer–Emmett–Teller equation (BET) at -196.15 °C (77 K) [63, 64]. The BET model assumes multilayer gas adsorption on the adsorbent's surface and obtains the sample surface area value by determining the monolayer volume of adsorbed gas from the isotherm data [65, 66]. BET surface area was calculated at relative pressures between 0.05 and 0.3. The pore volume and size were calculated from the N_2 desorption values based on the Barrett–Joyner–Halenda (BJH) model [67-69]. The BJH model determines the mesopore volume distribution, which accounts for the change in adsorbate layer thickness and the liquid condensed in the pores [70]. The pore volume was calculated as the uptake (cm^3/g) at a relative pressure of 0.95.

2.3.3 Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed on an SDT Q600 TA instrument (New Castle, DE, USA). The TGA profiles were used to characterize the thermal stability of MOFs. About 20 mg of sample was placed in a cylindrical alumina crucible and heated in static air from ambient temperature to 700 °C with

a nominal heating rate of 10 °C/min. The change in weight of MOF samples was used to determine the moisture content, decomposition of the linkers, and formation of metal oxides.

2.3.4 Fourier transform infrared spectroscopy

Infrared spectra of the synthesized catalysts were recorded on a JASCO Fourier transform infrared (FTIR) spectrometer (Easton, MD, USA), equipped with an attenuated total reflection stage (ATR). Samples of about 5 mg were used in each analysis. The sample was scanned in the spectral range between 400 and 4000 cm^{-1} at a 4 cm^{-1} resolution. Spectra were collected using a deuterated triglycine sulfate (DTGS) detector averaging 256 scans.

2.3.5 Diffuse reflectance infrared Fourier transform spectroscopy

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) with adsorbed pyridine was performed to characterize acid sites; measurements were made with a JASCO FTIR-4700 equipped with high temperature DiffuseIR™ cell (PIKE Technology, WI, USA). The protocol for the DRIFTS experiments with temperature programmed desorption is described elsewhere and used with a slight modification [71, 72]. In short, MOF samples (~5 mg) were placed in a cylindrical alumina crucible and treated in nitrogen gas (50 mL/min) at 150°C for 30 min unless otherwise noted. After the treatment, the DRIFT spectra of MOF catalysts were recorded as the background spectra. The MOF catalysts were then saturated with pyridine vapor in the low of N_2 gas (50 mL/min). The adsorbed pyridine was removed by flushing with N_2 gas (50 mL/min) at 50, 100, or 150°C for 30 min before recording the DRIFT spectra. All spectra were recorded with 256 scans between 4000−400 cm^{-1} at a 4 cm^{-1} resolution using a mercury cadmium telluride (MCT) detector cooled with liquid nitrogen. The ratio of Brønsted acid to Lewis acid sites (B/L) was calculated from the integrated area of the bands (after background subtraction) of adsorbed pyridine at 1067 and 1030 cm^{-1} [73].

199 **2.3.6 X-ray diffraction**

200 X-ray diffraction of MOFs was conducted with a Bruker AXS Model D8 Advance A28 diffractometer
201 (Germany) using CuK_{α} radiation in the 2θ range from 5° to 40° with 0.02 degree/step. Samples of about
202 200 mg were used in each analysis.

203

204 **2.3.7 Inductively coupled plasma-optical emission spectroscopy**

205 Inductively coupled plasma-optical emission spectroscopy (ICP-OES) measurements were performed
206 using a 100 mg sample dissolved in 10 mL of nitric acid. Heating was used to ensure that the sample was
207 completely dissolved. Once cooled, the sample was further diluted to 25 mL with double distilled water.
208 Measurements were acquired on a Varian 720-ES spectrometer equipped with a seaspray nebulizer and
209 cyclonic class spray chamber. Parameters included a sample intake of 1 mL/min, argon plasma flow rate
210 of 15 L/min, and an auxiliary gas (Ar) flow rate of 1.5 L/min. The instrument was calibrated using a CRMS
211 manufactured by VHG.

212

213 **2.4 Dehydration of glucose**

214 A 50 mg sample of glucose and 1 g $[C_4C_1im]Cl$ were added to a 25 mL pressure tube. The catalyst was
215 loaded with respect to the glucose at a glucose:Al molar ratio of 25:1 unless otherwise noted. The
216 pressure tube was sealed, stirred at 700 RPM (to minimize mass transfer limitations) and kept in an oil
217 bath at 120^{o}C unless otherwise noted. The reaction was stopped by quenching in a cold-water bath,
218 followed by adding water (~5 mL) to dissolve the remaining glucose and prevent the solidification of
219 ionic liquid. The solution was centrifuged and the residual solids were removed. The liquid sample was
220 withdrawn and analyzed for changes in glucose and the occurrence of dehydration products.

2.5 Product analysis and quantification

The reactants and products were analyzed by a High-Pressure Liquid Chromatography (HPLC, Agilent Technology, Santa Clara, CA, USA) equipped with a refractive index detector (RID) and diode array detector (DAD). An Aminex HPX-87H column (300 x 7.8 mm, Bio-Rad®, Hercules, CA, USA) was used for reactant and product separation at 60°C with 0.6 mL/min of 4 mM H_2SO_4 as the mobile phase. The concentrations of sugars and other products were determined by the peak areas from the RID signals. The main HMF product was determined by the peak area from the DAD signals at 280 nm. Sugar and reaction products were calibrated against certified standards (Absolute Standards, Inc., Hamden, CT, USA). The glucose conversion, product yield, and product selectivity were calculated as follows:

$$\text{Glucose conversion (\%)} = \frac{\text{mole of glucose reacted}}{\text{initial mole of glucose}} \times 100$$

$$\text{Product yield (\%)} = \frac{\text{mole of product generated}}{\text{initial mole of glucose}} \times 100$$

$$\text{Product selectivity (\%)} = \frac{\text{Product yield}}{\text{Glucose conversion}} \times 100$$

To ensure that the determination of glucose conversion and HMF selectivity were accurate, control experiments using PTA⊂MIL-101(Al)-NH_2, ionic liquid, and water were conducted at ambient temperature for 2h. The change in glucose and HMF concentrations in the presence of MOFs was negligible (*see Supporting Information and Fig. S1 for detail*). Moreover, to confirm the formation of HMF, solvent extraction by ethyl acetate was used with the reaction solution. The extracted solution was analyzed by Agilent gas chromatography-mass spectrometry (GC-MS, model 7890A and 5977A, Agilent Technologies, Santa Clara, CA, USA) equipped with a DB-1701 column (Agilent Technologies, 30 m × 0.25 mm id, 0.25 μm) (*see Supporting Information and Fig. S2 for detail*).

3. Results

Encapsulating phosphotungstic acid (PTA) in MIL-101(Al)-NH_2 (Al-MOF) formed encapsulated PTA⊂MIL-101(Al)-NH_2 (PTA⊂Al-MOF) catalysts. The effect of PTA loading on MOF physicochemical and acid properties was investigated. Subsequently, the efficiency of PTA⊂Al-MOF catalysis of glucose dehydration was measured by comparing the performance of encapsulated PTA catalysts with different PTA loading.

3.1 Physicochemical properties of the PTA⊂MIL-101(Al)-NH_2 catalyst

To evaluate the physicochemical properties of the encapsulated PTA⊂Al-MOF catalysts, first, an N_2 adsorption-desorption was performed to measure the surface area and pore volume (**Fig. S3A**). The bare Al-MOF exhibited a Type IV isotherm, which suggested that the MIL-101(Al)-NH_2 catalyst was mesoporous. On the basis of the isotherms, the MOF total surface area and pore volume were calculated and shown in **Table 1**. As a control, the surface area and pore volume of Al-MOF were 1487 m^2/g and 0.92 cc/g, similar to reported values [74, 75]. As expected, an increase in PTA loading decreased both total surface area and pore volume, which indicated that the encapsulated PTA occupied the pores of the Al-MOF. The average pore diameter of the synthesized catalysts was ~2.4-2.7 nm, in agreement with reported values of 1.6-2.9 nm [32, 76]. The critical diameter for D-glucose was ~0.84-0.85 nm [77], which is sufficiently small to enable access to the active sites within the MOF structure.

Next, X-ray diffraction (XRD) was conducted to determine the crystallinity of the encapsulated PTA⊂Al-MOF catalysts **(Fig. S3B)**. As a control, the X-ray diffractogram of the PTA exhibited unique peaks at 7.2° and 9.0°, similar to reported values.[78] The consistency between the diffractograms of

265 the encapsulated PTA⊂Al-MOF catalysts and bare Al-MOF suggested that, during synthesis, the PTA⊂Al-
266 MOF catalysts retained the structural integrity of the MIL-101 framework. These PTA peaks were not
267 observed in the encapsulated PTA⊂Al-MOF catalysts, which suggested that PTA was well dispersed in
268 the pores of Al-MOF [78] and/or the PTA clusters in the pentagonal and hexagonal windows of Al-MOF
269 were indeed smaller than 1.6-1.2 nm [78-80]. Interestingly, the PTA⊂Al-MOF catalysts showed slightly
270 broader XRD peaks and a shoulder (~11°). The peak broadening and occurrence of the shoulder was
271 hypothesized to be due to the interaction of the encapsulated PTA clusters with the MIL-101 framework,
272 which resulted in changes in the symmetry of the clusters in the MOF cages. Previous studies using
273 POM-encapsulated MIL-101 MOFs showed similar XRD peak broadening [29, 30, 52, 55, 81, 82]. To
274 measure PTA dispersion in the Al-MOF catalyst's pore structure, the encapsulated 14%PTA⊂Al-MOF
275 catalyst was imaged by STEM-HAADF. As a control, the STEM-HAADF image and elemental mapping of
276 the bare Al-MOF showed that it was highly porous with dispersed Al (**Figs. 1A and B**). The STEM-HAADF
277 image and elemental composition mapping of aluminum (Al) and tungsten (W) of the 14%PTA⊂Al-MOF
278 showed a highly porous and uniform distribution of W and Al clusters within the Al-MOF catalyst (**Figs.**
279 **1C-F**), which confirmed our XRD data which indicated that PTA was highly dispersed in the pores of the
280 Al-MOF catalyst.

281 To determine the surface functionality of the synthesized catalysts, FTIR was performed on
282 catalysts (**Fig. S4**). The bare Al-MOF showed -NH_2 bands. The FTIR spectra of encapsulated PTA⊂Al-MOF
283 catalysts contained bands from -NH_2 and W=O/W-O-W functionalities, which confirmed the
284 encapsulation of PTA (*see Supplementary Materials, Fig. S4*).

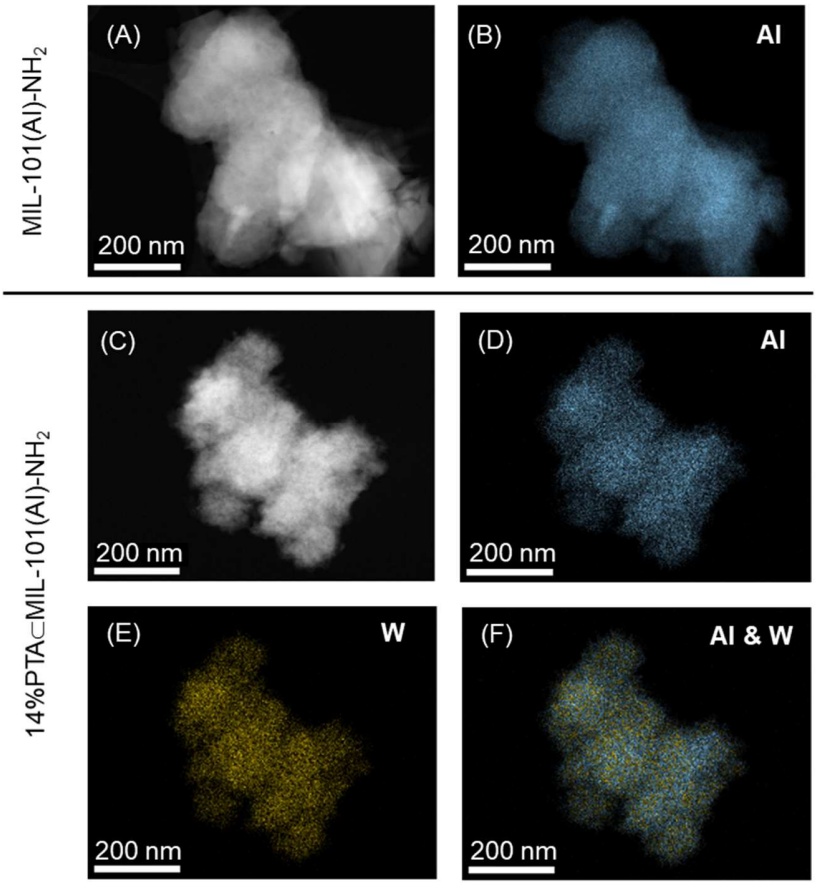
285 During synthesis, the PTA loading was varied from 0.1 to 2.0 g in 30 mL of DMF. To quantify the
286 actual amount of encapsulated PTA, ICP-OES was conducted on encapsulated PTA⊂Al-MOF catalysts. As
287 a control, the bare Al-MOF catalyst contained 11.56 wt.% Al, similar to a reported value [30]. All the

encapsulated PTA⊂Al-MOF catalysts had a W/P molar ratio of 12, which was the same as that in PTA ($H_3PW_{12}O_{40}$) and which confirmed successful PTA encapsulation [83]. As expected, increases in PTA loading during synthesis progressively increased the W content and decreased the Al/W molar ratio. Interestingly, a PTA loading greater than 0.25 g/30 mL (entry 3) during synthesis did not result in a significant increase in encapsulated PTA. These results suggested that there was an optimal PTA loading that could occupy the MOF pores.

Table 1. Physicochemical properties of MOFs with varying PTA content

Entry	PTA loading [g/30mL][a]	Catalyst[b]	Al [wt.%][c]	W [wt.%][c]	PTA [wt.%][c]	Al/W [mol/mol]	B/L[d]	S_{BET} [m^2/g]	Total pore volume [cm^3/g]	Pore diameter (nm)
1	0.00	NH_2-MIL-101(Al)	11.56	-		-	0.37	1487	0.92	2.49
2	0.10	8%PTA⊂NH_2-MIL-101(Al)	9.33	6.2	8.1	10.3	0.53	1375	0.82	2.39
3	0.25	14%PTA⊂NH_2-MIL-101(Al)	9.53	11.03	14.3	5.9	0.78	1276	0.78	2.46
4	0.50	15%PTA⊂NH_2-MIL-101(Al)	9.19	11.51	15.0	5.4	0.96	1061	0.72	2.72
5	1.00	17%PTA⊂NH_2-MIL-101(Al)	9.64	13.00	16.9	5.1	1.04	961	0.59	2.45
6	2.00	18%PTA⊂NH_2-MIL-101(Al)	9.11	13.52	17.5	4.6	1.14	854	0.57	2.69

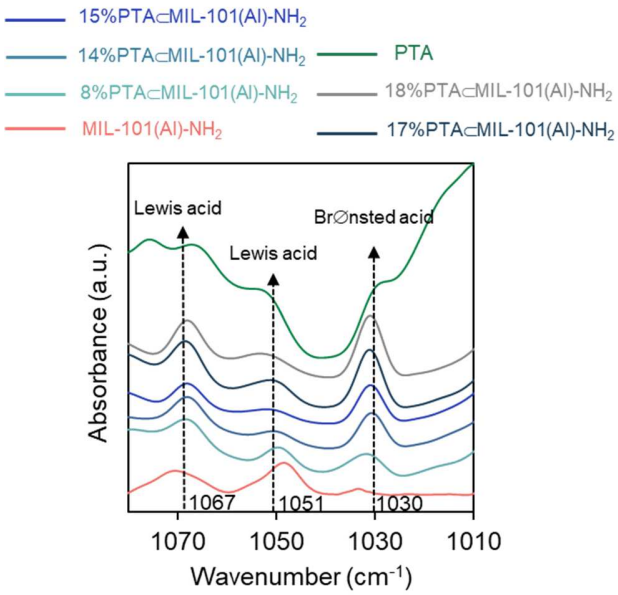
[a]per 30 mL DMF, [b]number before catalyst name indicates the encapsulated PTA measured by ICP-OES, [c]composition measured by ICP-OES, [d]B/L indicates Brønsted acid/Lewis acid site ratio from the area integral by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS).



298

299 **Figure 1.** STEM-HAADF images and corresponding elemental mapping of (A-B) MIL-101(Al)-NH_2 and (C-F)

300 14%PTA⊂MIL-101(Al)-NH_2.



301

302 **Figure 2.** Acid properties of encapsulated PTA⊂Al-MOF catalysts measured by diffuse reflectance

303 infrared Fourier transform spectroscopy (DRIFTS).

304

305 **3.2 Acid properties of the catalysts by diffuse reflectance infrared Fourier transform spectroscopy**

306 Selective glucose conversion to HMF requires a cooperative effect between Lewis and Brønsted acid

307 catalysts for the cascade of glucose isomerization to fructose followed by fructose dehydration to HMF.

308 Hence, it is important to distinguish and quantify the acid sites. To characterize the acid sites of the

309 synthesized MOFs, DRIFTS was performed with adsorbed pyridine. Pyridine was chosen as an in-situ

310 titrant for probing the acid site density of MOFs because of previous success in observation of Lewis acid

311 and Brønsted acid sites in MOFs [84-86]. To avoid degradation of bare Al-MOF and encapsulated

312 PTA⊂Al-MOF catalysts, DRIFTS was performed in a range of 30 - 150°C according to their thermal

313 stability from the TGA result (**Fig. S5**). After pyridine adsorption, the DRIFT spectra of these MOFs

314 demonstrated characteristic bands at 1067, 1051, and 1030 cm^{-1} (**Fig. 2**). The 1067 and 1051 cm^{-1} bands

315 corresponded to the interaction between pyridine and coordinated unsaturated metal sites (cus), i.e.,
316 Lewis acid sites [86, 87]. The band at 1030 cm^{-1} corresponded to the interaction between pyridine and
317 the Brønsted acid sites from encapsulated PTA. Surprisingly, a weak band at 1300 cm^{-1} in the MIL-
318 101(Al)-NH_2 sample was observed, which suggested the presence of Brønsted acidity in MOFs. Similarly,
319 studies by Herbst et al. [88], Halls et al. [89], Vimont et al. [90], and Volkringer et al.[86] showed that
320 MIL- 101(Cr), MIL-100(Cr), and MIL-100(Al) exhibited Brønsted acidity. The origin of Brønsted acidity in
321 MOFs remains the topic of debate. However, its origin was hypothesized to come from the water
322 molecules bound to metal sites [86]. Moreover, this water coordinated to the metal sites was not easily
323 removed during activation of MOFs because a high temperature was required to remove the bound
324 water. The high temperature can cause the structural damage to the MOFs and cause a loss in catalytic
325 activity (*see Supporting Information and Fig. S6 for detail*).
326
327 Next, the Brønsted acid to Lewis acid ratio (B/L) was determined using the area integral of these
328 bands (**Table 1**). An increase in encapsulated PTA loading increased the intensity of the Brønsted acid
329 band at 1030 cm^{-1} and increased the B/L ratio of the catalysts. It should be noted that an increase in
330 encapsulated PTA within MOFs was not proportional to an increase in B/L ratio. The acidic properties of
331 encapsualted catalysts are difficult to be determined because the interaction between encapsulated
332 species and the host support can modify their acidic properties. Juan-Alcañiz et al. showed the
333 interaction between encapsualted PTA and the MIL-100(Cr) framework decreased Lewis acidity [91],
334 which agrees with our finding of an increase in the B/L ratio after encapsulating more PTA becasuse of
335 an increase in Brønsted acid sites and a decrease in Lewis acid sites.
336

337 **3.3 PTA⊂MIL-101(Al)-NH_2-catalyzed glucose dehydration to 5-hydroxymethylfurfural**

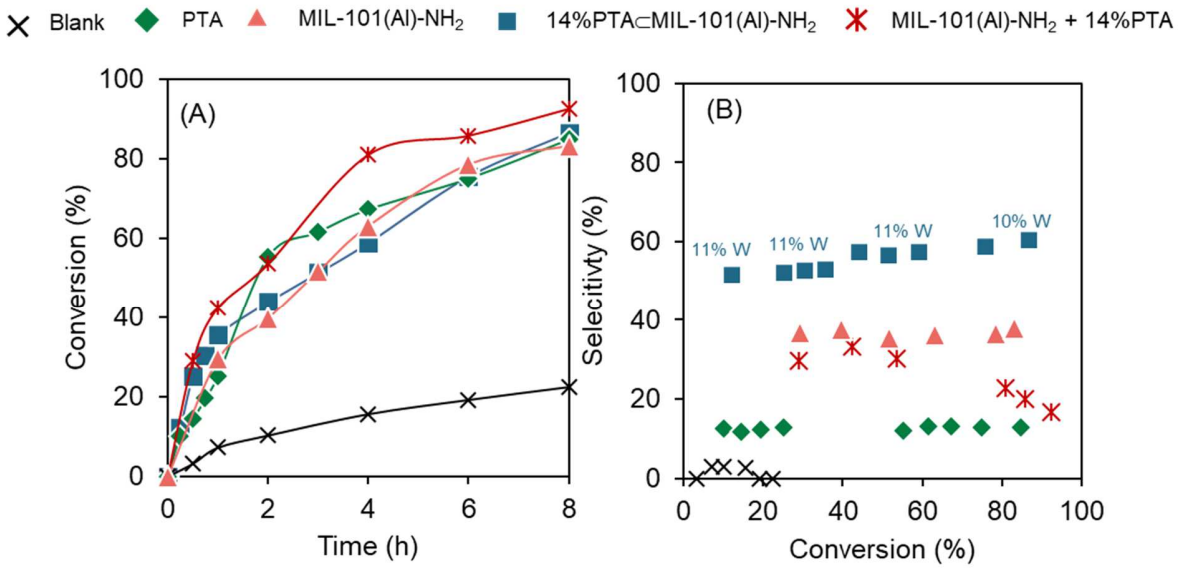
To determine the effect of PTA encapsulation on the catalytic performance, glucose dehydration was performed with encapsulated PTA⊂MIL-101(Al)-NH_2 catalysts (**Fig. 3**). A glucose:Al molar ratio of 25:1 was used in all experiments to normalize the Al content in the catalysts and compare catalytic performance with different encapsulated PTA loadings. As a control, a blank (no added catalyst) did not show any HMF production, which suggested that (1) the reaction is not autocatalytic, and (2) [C_2C_1im]Cl could not catalyze glucose dehydration. All catalysts were active for glucose dehydration in [C_2C_1im]Cl at 120°C (**Fig. 3A**). Another control of using PTA as a catalyst showed a low HMF selectivity of 13% at 43% glucose conversion. Fructose, levulinic acid, or formic acid were not observed as products. These results suggested the PTA catalyst was not selective to HMF as in previous studies [52]. The bare Al-MOF catalyst appeared to be an efficient catalyst for glucose dehydration; however, it was not the most selective for HMF. All encapsulated PTA⊂Al-MOF catalysts were more selective for HMF than MIL-101(Al)-NH_2, which indicated that the encapsulated PTA in the pores of the Al-MOF enhanced HMF selectivity (**Fig. S7**). Moreover, HMF selectivity exhibited a volcano-shaped profile vs. the Brønsted to Lewis acid site ratio (B/L) (**Fig. 4)**. The optimal B/L of 0.78 (14%PTA⊂Al-MOF catalyst) maximized the HMF selectivity of 58% at 44% glucose conversion at 120°C after 2h (**Fig. 3B**). These results suggested that cooperativity between Brønsted acidic PTA and Lewis acid sites of Al-MOF catalyst enhanced HMF selectivity.

To determine the importance of encapsulating PTA, a glucose dehydration reaction was performed with a physical mix of PTA and bare Al-MOF catalyst at the same composition as 14%PTA⊂Al-MOF catalyst. HMF selectivity by the physical mix catalyst was 33%, lower than that of encapsulated 14%PTA⊂Al-MOF catalysts (58%). These results confirmed the importance of PTA encapsulation in maximizing HMF selectivity. Interestingly, the HMF selectivity of the physically mixed catalyst converged to that of PTA alone (**Fig. 3B**). Although the Bronsted acid such as PTA catalyzes fructose dehydration to HMF, the free PTA molecules in the physical mix can catalyze aldol addition and condensation reactions

362 from HMF via 2,5-dioxo-6-hydroxyhexanal [92], which resulted in humin formation. Moreover, the free
363 PTA in the physical mix has a strong interaction with the surface of MOF, partially blocking the channels
364 of MOFs and inhibiting the reactant accessibility to active sites [93, 94]. This blocking effect is the reason
365 why the HMF selectivity of the physical mix was lower than that of encapsulated PTA in MOFs [78]. Thus,
366 the physical mix showed a high glucose conversion with a poor HMF selectivity, in agreement with the
367 study by Zhang et al. [52].

368 To evaluate the stability of PTA in encapsulated PTA⊂MIL-101(Al)-NH_2 catalysts during the
369 reaction, ICP-OES was performed on spent encapsulated 14%PTA⊂ MIL-101(Al)-NH_2 catalyst (**Fig. 3B**).
370 The W content of the encapsulated 14%PTA⊂MIL-101(Al)-NH_2 catalyst remained relatively constant (~11
371 wt.% W), which confirmed the stability of the PTA within the 14%PTA⊂MIL-101(Al)-NH_2 catalyst.

372



373

374 **Figure 3.** Catalytic performance of encapsulated PTA⊂MIL-101(Al)-NH_2 catalysts. (A) Catalyst activity for
375 glucose dehydration as a function of time. (B) HMF selectivity with the W content of the spent catalysts

assessed by ICP-OES. Reaction condition: glucose:Al molar ratio=25:1, 50 mg glucose, 1 g [C_4C_1im]Cl, 120°C. Phosphotungstic acid = 14 wt.% in PTA alone and physical mix between PTA + bare Al-MOF to match the PTA in 14%PTA⊂Al-MOF. The percent of tungsten (%W) in **Figure 3B** indicates the W content in the used catalyst at the specific conversion.

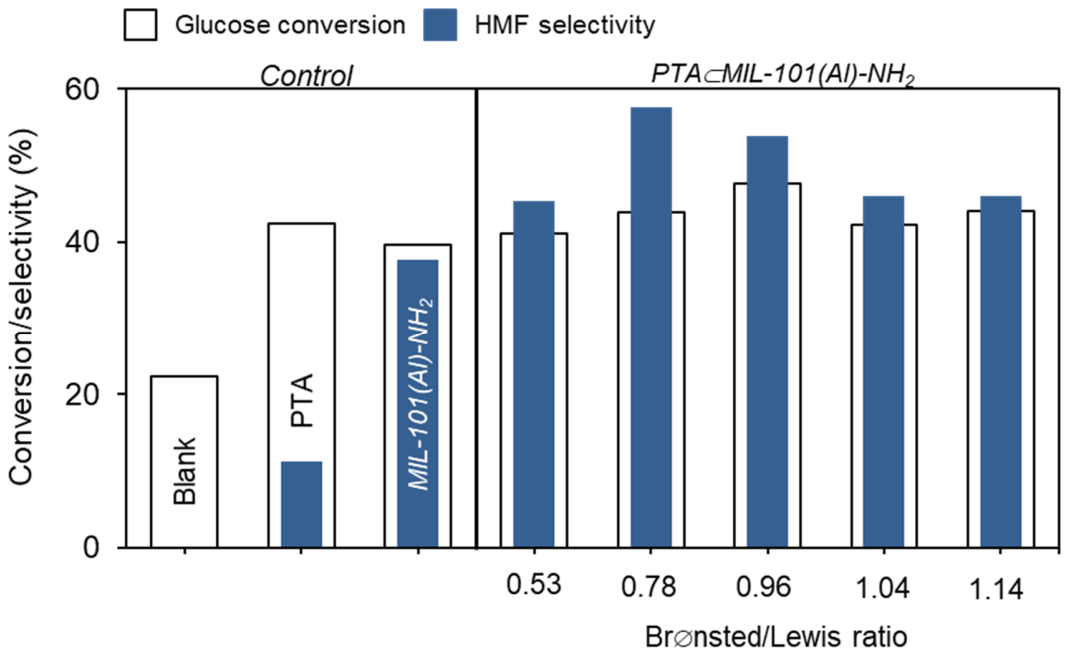


Figure 4. HMF selectivity of encapsulated PTA⊂MIL-101(Al)-NH_2 catalysts at similar glucose conversions. Reaction condition: glucose:Al molar ratio=25:1, 50 mg glucose, 1 g [C_4C_1im]Cl, 120°C, 2h.

3.4 Solvent effect on the glucose dehydration to 5-hydroxymethylfurfural

The solvent affects the rate of reaction, product selectivity, and product stability [95, 96]. A major consideration in catalytic biomass conversion is the stability of reactants, intermediates, and product in the reaction solvent. To investigate the effect of solvent on the stability of these molecules, glucose, fructose and HMF were used as reactants in various solvents. The 14%PTA⊂Al-MOF was chosen as

389 catalyst because it had the greatest HMF selectivity. For glucose, $[C_4C_1im]Cl$ was the best performing
390 solvent as shown by the greatest HMF selectivity at similar conversion to other solvents (**Fig. 5**).
391 However, there was no obvious correlation between the HMF selectivity and solvent properties, such as
392 dielectric constant or donor number.

393 Next, fructose was used as a reactant in $[C_4C_1im]Cl$ (**Fig. 6**). Three solvents, DMA, 2-butanol, and
394 *p*-dioxane, were selected for comparison with $[C_4C_1im]Cl$. Without added catalyst (blank), HMF
395 selectivity was 47% at 96% fructose conversion in $[C_4C_1im]Cl$. The other solvents did not yield HMF and
396 showed <20% fructose conversion. As expected, added 14%PTA⊂MIL-101(Al)-NH_2 catalyst improved the
397 HMF selectivity in all solvents; more specifically, HMF selectivity in $[C_4C_1im]Cl$ was 89% at 94% fructose
398 conversion, two times greater HMF selectivity compared with a reaction without added catalyst.
399 Although added 14%PTA⊂MIL-101(Al)-NH_2 catalyst improved the fructose conversion in DMA, 2-
400 butanol, and *p*-dioxane from <20% to >60%, the HMF selectivity in these three solvents was low (<22%).
401 These results suggested that $[C_4C_1im]Cl$ can act as both acid catalyst [97, 98] and solvent in fructose
402 dehydration reaction. Moreover, the 14%PTA⊂MIL-101(Al)-NH_2 enhanced HMF selectivity from fructose
403 dehydration.

404

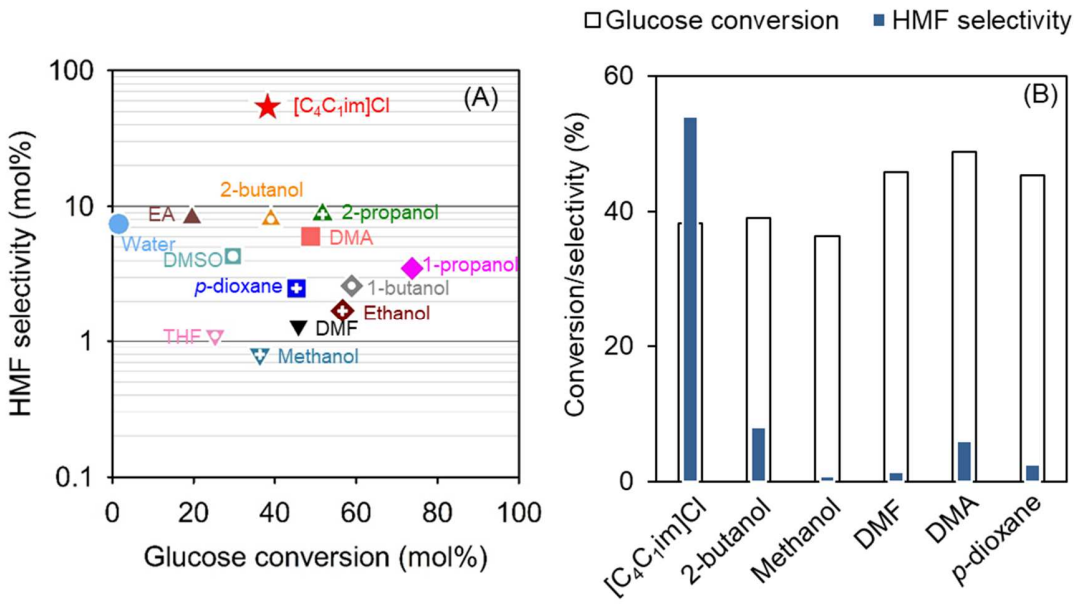
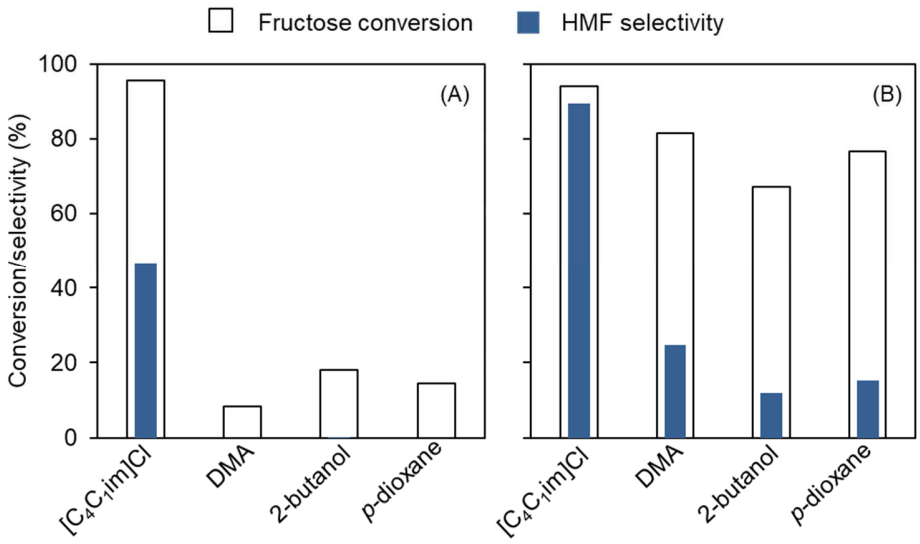


Figure 5. Solvent effect on glucose conversion and HMF selectivity (A) and comparison of conversion and selectivity in selected solvents(B) by using 14%PTA⊂MIL-101(Al)-NH_2 catalyst. Reaction condition: glucose:Al molar ratio=25:1, 50 mg glucose, 1 g solvent, 120°C, 2 h.

Next, HMF was used as a reactant in these four solvents to investigate the HMF stability (**Fig. 7**). Without any catalyst(blank), HMF conversion was 11% in $[C_4C_1im]Cl$, and conversion increased slightly in other solvents. There were no identifiable products which suggests the HMF was likely degraded into humin [99, 100]. The added 14%PTA⊂MIL-101(Al)-NH_2 catalyst enhanced HMF conversion to 15% in $[C_4C_1im]Cl$. The presence of 14%PTA⊂MIL-101(Al)-NH_2 catalyst in other solvents improved the HMF conversion more than in $[C_4C_1im]Cl$. These results suggested that (1) HMF was not stable in these solvents and (2) although the 14%PTA⊂MIL-101(Al)-NH_2 catalyst improved glucose/fructose dehydration to HMF, the catalyst facilitated HMF conversion to humin. Thus, to minimize HMF degradation and maintain the high HMF yield, a reactive HMF extraction process should be considered [101].

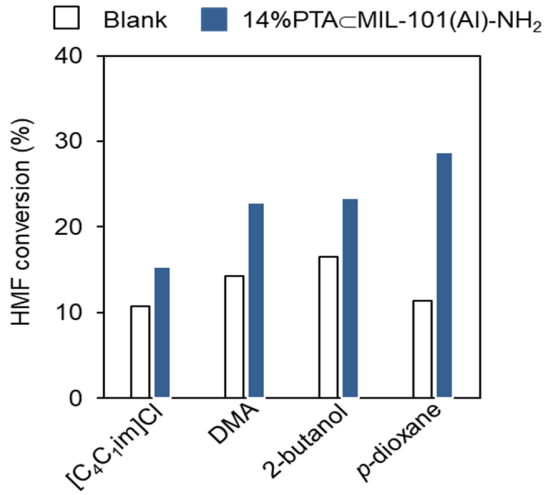


419

420 **Figure 6.** Solvent effect on fructose conversion to HMF (A) without added catalyst and (B) catalytic

421 performance of encapsulated 14%PTA⊂MIL-101(Al)-NH_2. Reaction condition: fructose:Al molar ratio =

422 25:1, 50 mg fructose, 1 g solvent, 120°C, 2h.



423

424 **Figure 7.** HMF conversion in different solvents with/without 14%PTA⊂MIL-101(Al)-NH_2. Reaction

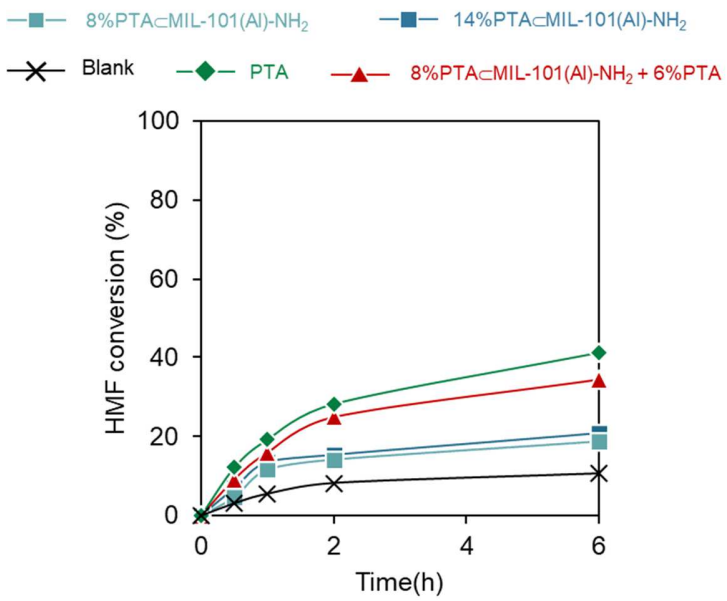
425 condition: HMF:Al molar ratio = 25:1, 50 mg HMF, 1 g solvent, 120°C, 2h.

426

3.5 Stability of HMF in the catalytic system and [C_4C_1im]Cl

To maintain the high HMF selectivity in the reaction, it was important to determine the stability of the HMF under the reaction condition. Thus, HMF was heated in the same experimental condition that was used for glucose dehydration (120°C) in [C_4C_1im]Cl solvent and catalysts. Without catalysts (blank), HMF degradation was ~11% after 6h (**Fig. 8**). Levulinic acid and formic acid were not observed. These results suggested that [C_4C_1im]Cl was not able to rehydrate HMF. With added encapsulated 8% and 14%PTA⊂Al-MOF catalysts, a slight increase in HMF conversion was observed, which reached ~18% after 6h. With PTA alone, the HMF conversion rate was 41%, greater than that of conversion in the presence of encapsulated 8% and 14%PTA⊂Al-MOF catalysts and reaching 19% and 21% after 6h, respectively.

Next, the physical mixture of PTA and 8%PTA⊂MIL-101(Al)-NH_2 catalyst was evaluated to check the HMF stability. The amount of PTA in the physical mixture of PTA and 8%PTA⊂Al-MOF catalyst was maintained at the same level as for the encapsulated 14%PTA⊂Al-MOF catalyst. As expected, the physical mixture increased HMF conversion by 34% at 6h reaction time compared with 21% HMF conversion by 14%PTA⊂Al-MOF catalyst. These results demonstrated that PTA in the bulk solution degraded the HMF and decreased the HMF selectivity, similar to a finding of Zhang et al. [52]. The encapsulation of PTA in the pores of Al-MOF catalyst minimized PTA leaching into the solvent and limited conversion of HMF, which, in turn, maintained the HMF selectivity.



444

445 **Figure 8.** HMF conversion by encapsulated PTA⊂MIL-101(Al)-NH_2. Reaction condition: 50 mg HMF, 30
446 mg catalyst, 1 g solvent, 120°C. Phosphotungstic acid = 14 wt.% in PTA alone and physical mix between
447 6%PTA + 8%Al-MOF to match the PTA in 14%PTA⊂Al-MOF.

448

449 **3.6 Reuse of encapsulated PTA⊂MIL-101(Al)-NH_2 for glucose dehydration**

450 To determine the ability to reuse the encapsulated PTA⊂Al-MOF catalyst, the used catalyst was
451 recovered by centrifugation, washed with water, and dried in a vacuum oven at 130°C to remove
452 moisture, residual products, intermediates, and unreacted glucose. Then, the catalyst was reused four
453 times. The 14%PTA⊂Al-MOF was chosen because it had the greatest HMF selectivity. The 14%PTA⊂Al-
454 MOF catalyst maintained its catalytic performance with HMF selectivity of ~ 55% at 40% glucose
455 conversion after the 4^{th} cycle, <10% decrease in both glucose conversion and HMF selectivity compared
456 with fresh catalyst (**Fig. 9**). In all cycles, the selectivity to HMF was between 55-62%. Next, ICP-EOS was
457 used to measure the Tungsten(W) content in the used catalysts. Only a slight W loss (<3 wt.%) in the

used catalysts was observed after four recycles, which indicated that little to no PTA leached from the 14%PTA⊂Al-MOF catalyst.

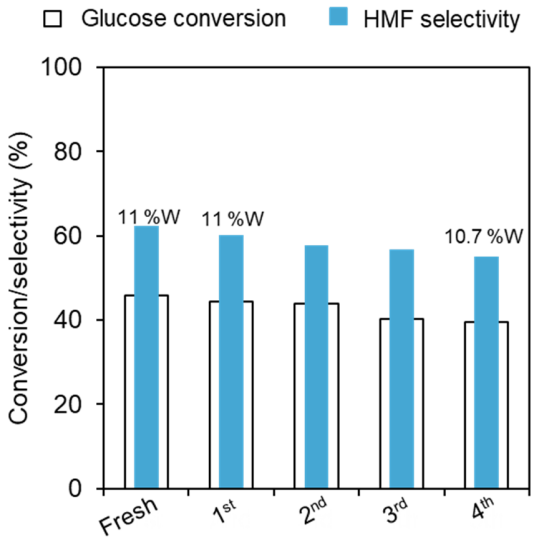


Figure 9. Reuse of 14%PTA⊂MIL-101(Al)-NH_2 for glucose dehydration. Reaction condition: glucose: Al molar ratio = 25:1, 1 g [C_4C_1im]Cl, 120°C, 2 h. Tungsten content (%W) indicates the W content in the used catalyst.

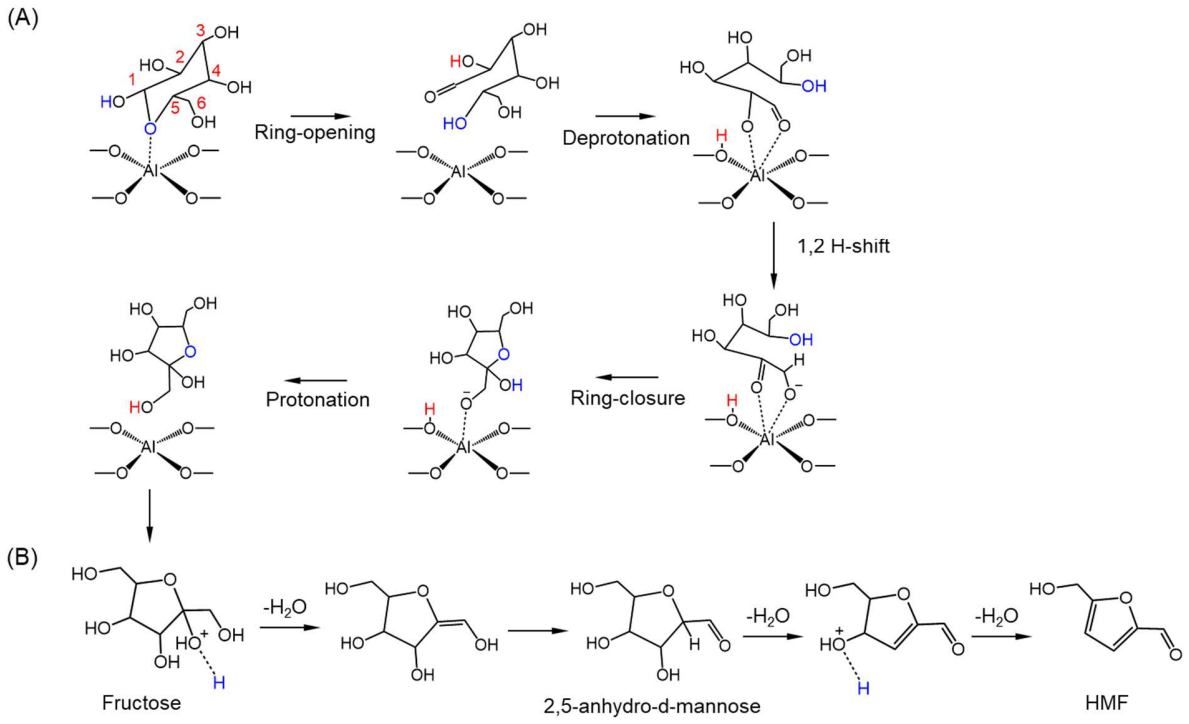
3.7 Proposed chemical pathway for glucose dehydration to HMF by PTA⊂MIL-101(Al)-NH_2

On the basis of the foregoing findings, **Scheme 2** shows a proposed mechanism for glucose dehydration to HMF by PTA⊂MIL-101(Al)-NH_2 catalysts. The reaction proceeds by the synergy between Lewis-Brønsted acid sites: (1) glucose isomerization to fructose by the Lewis acid of MIL-101(Al)-NH_2, and (2) dehydration of resulting fructose to HMF by the Brønsted acid of PTA and/or MIL-101(Al)-NH_2.

The glucose isomerization to fructose by Lewis acid sites consists of a sequence of ring opening, deprotonation, isomerization, protonation, and ring closure processes as shown by Hensen et al. [102-104]. We postulated that glucose initially binds to the Al active site imbedded in the MIL-101 framework

via its ring oxygen atom and followed by the ring opening process to form the acyclic glucose. Subsequently, the deprotonation of the hydroxyl group at C_2 occurred by the metal-oxo clusters. Next, the aldose-ketose isomerization induces the hydride shift from the C_2 to C_1 carbon atom. The reaction undergoes a ring-closure reaction yielding anionic fructofuranose bound to Al site. Finally, the terminal oxygen anionic fructofuranose is protonated to generate fructose.

The fructose undergoes dehydration by Brønsted acid sites to produce HMF by dehydration and tautomerization. First, the hydroxyl group of the fructose at the alpha position is protonated by acidic protons of Brønsted acid catalysts, which resulted in the formation of water. Next, the cyclic enol intermediate is formed and subsequently tautomerized to 2,5-anhydro-d-mannose [105-107]. Then, the reaction proceeds by two sequential dehydrations to form HMF.



Scheme 2. Proposed reaction mechanism for glucose dehydration to HMF over PTA⊂MIL-101(Al)-NH_2. The reaction proceeds by (A) glucose dehydration to fructose, followed by (B) fructose dehydration to HMF.

4. Discussion

A major challenge in selective glucose conversion to HMF is the design of catalysts that possess Lewis and Bronsted acid sites that can act cooperatively [15, 108, 109]. Here, the effect of PTA encapsulation in PTA⊂MIL-101(Al)-NH_2 catalysts (PTA⊂Al-MOF) on glucose conversion to HMF was investigated. The synergy between encapsulated PTA and Al-MOFs enabled the high HMF selectivity. Moreover, the results demonstrated that the encapsulation of PTA in MIL-101(Al)-NH_2 catalysts minimized PTA leaching into the bulk solution, thereby preventing degradation of the HMF product.

The most significant finding was that the HMF selectivity strongly depended on the location of the PTA. Encapsulation of PTA in MIL-101(Al)-NH_2 pores provided two benefits. First, the close proximity between the Lewis acid sites of the Al-MOF and the Brønsted acidic PTA promoted HMF formation. The fructose formed from glucose isomerization by Lewis acid (MIL-101(Al)-NH_2) was dehydrated to HMF by the encapsulated PTA catalyst. Tangsermvit et al. showed that the proximity between Lewis and Brønsted acid sites was important in achieving a high HMF yield [110], a result that agrees with our findings. Second, encapsulated PTA catalysts minimized PTA leaching into the bulk solution and, consequently, prevented HMF degradation. Although Brønsted acids catalyze fructose dehydration to HMF, they also catalyze undesired HMF rehydration to levulinic acid [111] and/or degradation to humin [11]. The MIL-101 structure of the Al-MOF possesses both mesoporous windows (29-34 Å) and microporous windows, the latter corresponding to large hexagonal pores (15-16 Å), and somewhat smaller pentagonal pores (~12 Å) [112-114]. Keggin-type heteropolyacids, ~13-14 Å in size [53], are

larger than the pentagonal pores in MIL-101, thereby the heteropolyacids are preventing from leaching out and causing side reactions (rehydration and/or humin formation). These results explained the retention of HMF selectivity and the ability to recycle the PTA⊂MIL-101(Al)-NH_2 catalyst. Hence, encapsulated Brønsted acidic PTA in the pores of MIL-101(Al)-NH_2 not only provided Brønsted acidity for fructose dehydration but also prevented PTA leaching into the bulk solution, that otherwise had the potential to degrade HMF.

Another significant finding was the discovery of the high selectivity of PTA⊂Al-MOF for glucose dehydration. Many investigators used solid Lewis acid catalysts (Sn-containing β-zeolites [20] and Nb_2O_5 [18]) with homogeneous catalysts such as HCl to maximize HMF selectivity (**Table S3**). Their results suggested that the cooperative effect between Lewis acid and Brønsted acid species was critical in maximizing HMF selectivity in glucose dehydration. Qu et al. impregnated SO_4^{2-} on ZrO_2 by H_2SO_4 acid [115]. Although the SO_4^{2-}/ZrO_2 in biphasic THF/H_2O system reached a high HMF selectivity of 67% at 93% glucose conversion, both HMF selectivity and glucose conversion dropped ~10% after the 4th catalyst recycling due to leaching of SO_4^{2-} [115]. The ability to create the solid bifunctional Lewis-Bronsted catalysts will enhance the commercial feasibility of HMF production. Zhang et al. encapsulated PTA in MIL-101(Cr) to produce the bifunctional acid catalysts with PTA as a Brønsted acid and MIL-101(Cr) as a Lewis acid [52]. The PTA⊂MIL-101(Cr) catalysts were selective toward HMF in fructose dehydration. However, they were not selective toward HMF in glucose dehydration and gave only 10% HMF selectivity at 21% glucose conversion at 100°C after 3h. Compared with MOF-derived catalysts for glucose dehydration, the PTA⊂Al-MOF catalysts described in this report were superior to other MOF-derived catalysts in terms of HMF selectivity (**Table S3**).

These findings demonstrate that PTA⊂Al-MOF catalyst was a selective and recyclable catalyst for glucose dehydration to HMF. The PTA⊂MIL-101(Al)-NH_2 catalyst was easy to synthesize compared

530 with other solid acid catalysts for selective glucose conversion to HMF, such as modified β-zeolites [116].
531 Moreover, the ability to control the ratio of numbers of Brønsted acid sites to Lewis acid sites in PTA⊂Al-
532 MOF catalysts provides opportunities to use the catalysts in various organic reactions, such as
533 esterification [117], alkylation [118], and benzylation [119].

534 Although PTA⊂Al-MOF catalyst is promising for selective glucose conversion to HMF, the
535 interactions between the framework, metal nodes, and PTA (acidic protons) that affect the acid
536 properties and catalytic performance has not been extensively investigated. Juan-Alcañiz et al. reported
537 the partial W substitution by Cr^{3+} of MIL-101(Cr) at high temperatures [53]. The W-substituted
538 heteropolyacids and/or the formation of W-Al complex metal nodes might be the active sites for this
539 reaction. Additional studies should identify the interaction between W in PTA and Al in Al-MOF by ^{27}Al
540 Magic Angle Spin (MAS) Nuclear Magnetic Resonance (NMR). The knowledge will help in designing
541 selective catalysts and systems for glucose dehydration.

542

543 **5. Conclusion**

544 Phosphotungstic acid encapsulated MIL-101(Al)-NH_2 catalyst (PTA⊂MIL-101(Al)-NH_2) was developed for
545 selective glucose conversion to HMF. The encapsulation of Brønsted acidic phosphotungstic acid in the
546 pores of MIL-101(Al)-NH_2 provided the proximity between Brønsted acid sites and Lewis acid sites of
547 MIL-101(Al)-NH_2 for the efficient cascade of glucose isomerization and fructose dehydration. The
548 synergistic effect of Brønsted and Lewis acid sites in the phosphotungstic acid encapsulated MIL-101(Al)-
549 NH_2 catalyst is the key contributor to the high HMF selectivity and glucose conversion; this synergy
550 cannot occur if the agents are introduced separately. Moreover, the encapsulated phosphotungstic acid
551 was stable in the pores of MIL-101(Al)-NH_2, which minimized leaching of PTA into the bulk solution and
552 reaction with the HMF to generate undesired products. As a result, the encapsulated PTA⊂MIL-101(Al)-

553 NH_2 catalyst maintained its catalytic performance after recycling four times. These results underscore
554 the importance of phosphotungstic acid encapsulation to provide the cooperative effect between
555 Brønsted and Lewis acidic sites for maximizing the HMF formation and minimizing subsequent HMF
556 conversion/degradation. This encapsulated metal-organic framework catalyst should be applicable to
557 other acid-catalyzed biomass transformations.

558

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566

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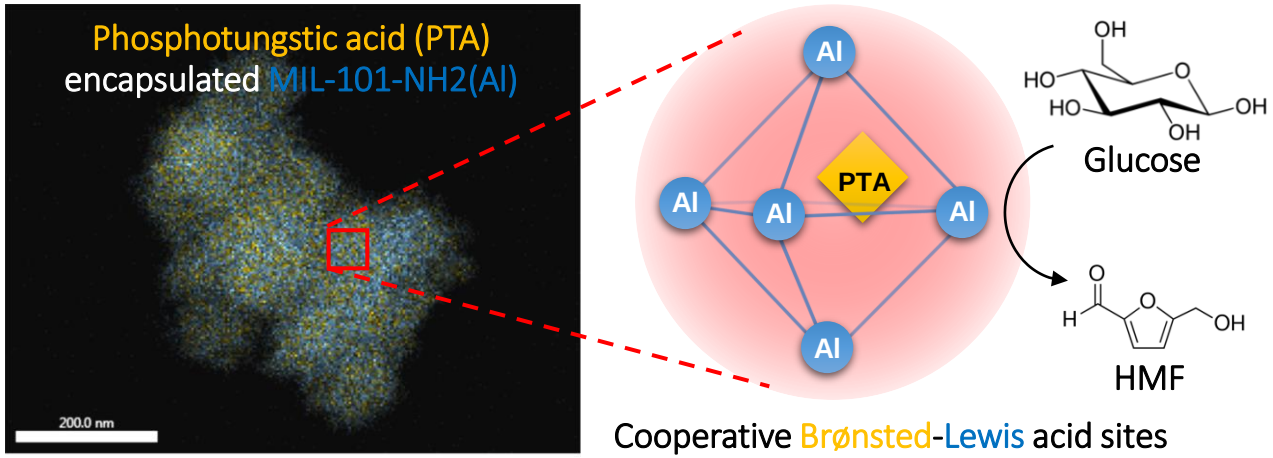
Phosphotungstic acid (PTA)
encapsulated MIL-101-NH2(Al)
200.0 nm
Al
Al
Al
Al
Al
PTA
OH
HO
HO
O
OH
OH
Glucose
O
H
O
OH
HMF
Cooperative Brønsted-Lewis acid sites