Article

Phosphazene-Based Covalent Organic Framework as an Efficient Catalyst (COF-1) for the Dehydration of Fructose to 5-HMF

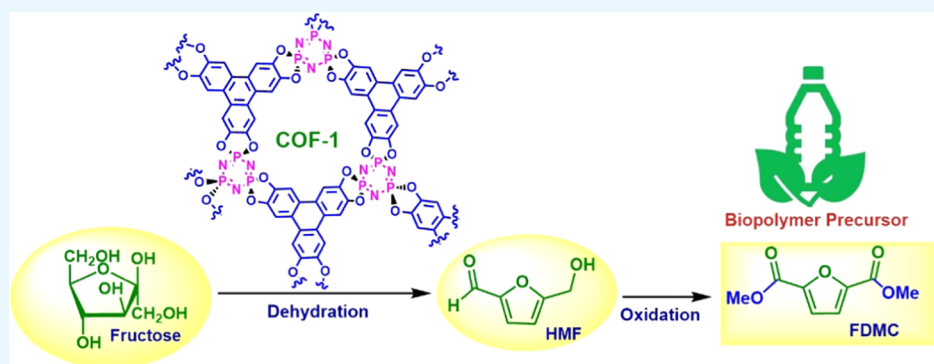Saravanan Saranya and Seenuvasan Vedachalam*

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ABSTRACT: 5-Hydroxymethylfurfural (HMF) is a promising organic platform for producing value-added chemicals. In this work, we focused on using a covalent organic framework (COF-1) as a heterogeneous catalyst for the dehydration of fructose to 5-HMF. The unique phosphazene unit-functionalized pores of COF-1 are essential active sites for catalytic performance. The results show that under the optimized reaction conditions, a maximum yield of 90% was obtained within 1.5 h at 120 °C. Furthermore, the effects of the catalyst load, reaction temperature, and usage of solvents for the improvement of reaction yield were investigated. The catalyst recyclability results showed that the yield of HMF did not change appreciably (90−82%) over five consecutive recycling runs. This work provides a viable strategy by applying phosphazene-based COF-1 for the efficient synthesis of HMF from renewable biomass. The synthesized HMF was further used for the synthesis of the biopolymer monomer furan-2,5-dimethylcarboxylate (FDMC) through N-heterocyclic carbene (NHC)-catalyzed oxidative esterification.

■ INTRODUCTION

Due to the extensive utilization of fossil fuels and combined environmental pollution, it has become an important issue to solve the problem of energy scarcity in modern society. The production of sustainable fine chemicals and transportation fuels from renewable biomass feedstocks is an excellent substitute for fossil fuel resources.[1,2] In recent years, research has mainly focused on developing efficient methods to convert biomass into biobased platform commodities, which is of great importance to biorefinery. 5-Hydroxymethylfurfural (HMF) is a value-added platform molecule, derived from lignocellulosic biomass and is considered to be a promising primary renewable building block for various biorefinery processes.[3] It is also an important source for other furan-based chemical intermediates, such as 2,5-furan dicarboxylic acid, 2,5-furandicarbaldehyde, and levulinic acid (LA), which have also been used for biopolymer and biofuel development.[4,5] HMF is primarily produced by the dehydration of monosaccharides. Among these, fructose is usually selected for this study, which is known for its high selectivity and efficiency. On the other hand, using aldohexoses like glucose and mannose led to lower yields of HMF, primarily due to their stable ring

structures.[6,7] Generally, the dehydration reaction for the biomass conversion of C6-sugars into HMF was carried out by acid catalysts, such as H_3PO_4, HCl, H_2SO_4,[8] methanesulfonic acid, and p-toluenesulfonic acid.[9,10] However, there are several drawbacks in using these systems. The key issues among them are the corrosion of the reactor, difficulties in the separation of homogeneous acid catalysts from the reaction mixture, and the high toxicity of acids. Therefore, the development of convenient and more environmentally friendly heterogeneous catalysts, such as heteropolyacids, ion-exchange resins, phosphates, ionic liquids, and metal oxides is highly desirable.[11−13] However, sulfonated carbonaceous materials, such as β-zeolite,[14,15] PVP/propyl sulfonic acid-modified ordered mesoporous silica, and polymer-bound sulfonic acids
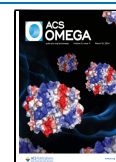
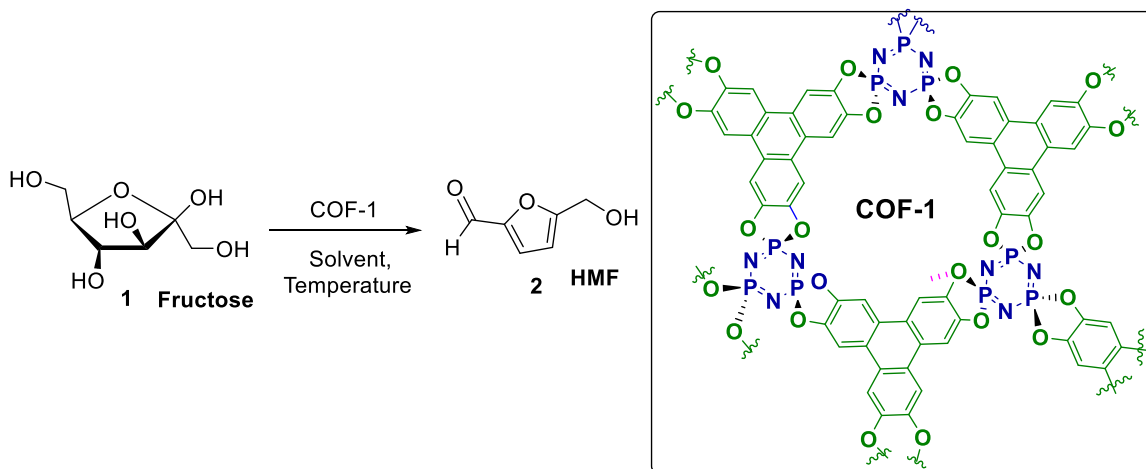**Scheme 1. Dehydration of Fructose to HMF**

enhanced the selectivity of HMF from the dehydration of fructose.[16] Materials of a polymeric heterogeneous catalyst, such as sulfonyl diphenol-supported polyphosphazene,[17] ammonium polymeric resin,[18] polystyrene-containing sulfonic acid,[19] metal−organic frameworks,[20] and COFs are extensively considered to show ambitious activity and reusability for converting carbohydrates into HMF in the recent years. Among them, COF-based catalysts have exhibited promising potential for the dehydration of fructose to HMF formation.[21]

Covalent organic frameworks (COF) are an emerging class of crystalline, porous polymeric frameworks constructed through covalent bonds. Small organic building blocks encompass light elements, leading to robust frameworks that extend in two or three dimensions.[22] Due to their permanent porosity, high surface area, facile synthesis, thermal stability, presence of active centers, and accessible voids, they show wide potential in catalysis, gas and energy storage, chemical sensing, photocatalysis, electronic devices, drug delivery, and so forth. In catalysis, COFs can be used as heterogeneous catalysts because of their unique functionality, uniform tunable pore sizes, and recoverability, which are more suitable for achieving excellent selectivity and catalytic activity than homogeneous catalysts.[23,24] Several functionalized COFs and metal−organic frameworks (MOFs) have also been active in the synthesis of HMF, especially from fructose.[4,25] But these are mainly encompassed by sulfonated acid groups; for instance, in 2015, the sulfonated 2D COF (TFP-DABA-COF-SO$_3$H) was reported by Peng et al. Due to the π-extended TFP-DABA network and the Brønsted acidity of −SO$_3$H groups, fructose was enhanced toward dehydration into 97% HMF in DMSO.[21] Subsequently, in 2019, Babaei et al. developed a sulfonated triazine-based COF, which was supported on SBA-15 to synthesize a Brønsted acidic MAM-CNC-COF-SO$_3$H/SBA-15, and it led to a yield of HMF 78% in DMSO at 120 °C.[26] In 2019, Sun et al. synthesized a more interesting PVP-modified and sulfonated three-component COF (PVP/TAPB-DMTA-DHTA-COF-SO$_3$H) by a condensation reaction. The adaptable PVP chains within COF can function as a pseudosolvent, which encapsulates fructose through hydrogen-bonding interactions, promoting the dehydration of fructose in THF with an excellent yield at 100 °C.[27] Interestingly, the polyphosphazene nanoparticles were investigated by Xu et al., which exhibited good catalytic activity, selectivity, and recyclability. Nevertheless, nanoparticles have

also been grafted by the sulfonic acid group.[17] In recent years, covalent organic frameworks have shown more catalytic applications in various transformations. With the outcome of this research field, we envision the catalytic application of our previously developed COF-1[28,29] for fructose to HMF conversion. Herein, we report phosphazene COF-1 as a catalyst for the dehydration of fructose (1) into HMF (2), and the reaction produced a remarkable yield, with good recyclability and selectivity under mild reaction conditions (Scheme 1).

Furan-2,5-dimethylcarboxylate (FDMC) is a biomass-derived monomeric unit of biopolymers, such as polyethylene furoate (PEF).[30] The synthesis of FDMC from HMF by oxidative esterification has attracted attention in recent years. The production of FDMC from HMF via various catalytic approaches, including the use of metal catalysts with oxygen or MnO$_2$ oxidants has been explored. Noble metal catalysts have been demonstrated to exhibit excellent catalytic activity in various oxidation reactions under a molecular oxygen atmosphere. First, Christensen et al. reported Au−TiO$_2$ for HMF oxidative esterification, resulting in 98% FDMC in 3 h, using sodium methoxide (MeONa) as a base additive.[31] Also, non-noble metal catalysts were used for FDMC synthesis by Xu et al. using CoO$_x$-N/C with α-MnO$_2$ as a multicatalytic system for HMF oxidative esterification, which could give high FDMC yields (95.6%),[32] and a series of other non-noble metals (Cr, V, Co, Mo, Ca, Al) doped into MnO$_2$, which also results in considerable yield of FDMC.[33] N-heterocyclic carbene (NHC)-catalyzed oxidative esterification of aldehydes with alcohols has become a prominent strategy for the formation of esters.[34] Earlier, Liu et al. developed NHC-catalyzed esterification of aldehydes with alcohol in the presence of MnO$_2$ as an oxidant at 70 °C.[35,36] To demonstrate the applicability of HMF in FDMC monomer synthesis, we adopted a similar protocol for the esterification of HMF by using a benzimidazolium NHC (C1) catalyst.

■ RESULTS AND DISCUSSION

COF-1 was synthesized by the condensation reaction between the addition of hexachlorophosphazene and tris(2,3,6,7,10,11-hexahydroxytriphenylene) (HHTP) to form five-membered polymeric rings as a black solid according to our earlier report.[28,29] COF-1 was characterized by SEM images at different magnifications (Figure 1a,b) of a polymeric frame-
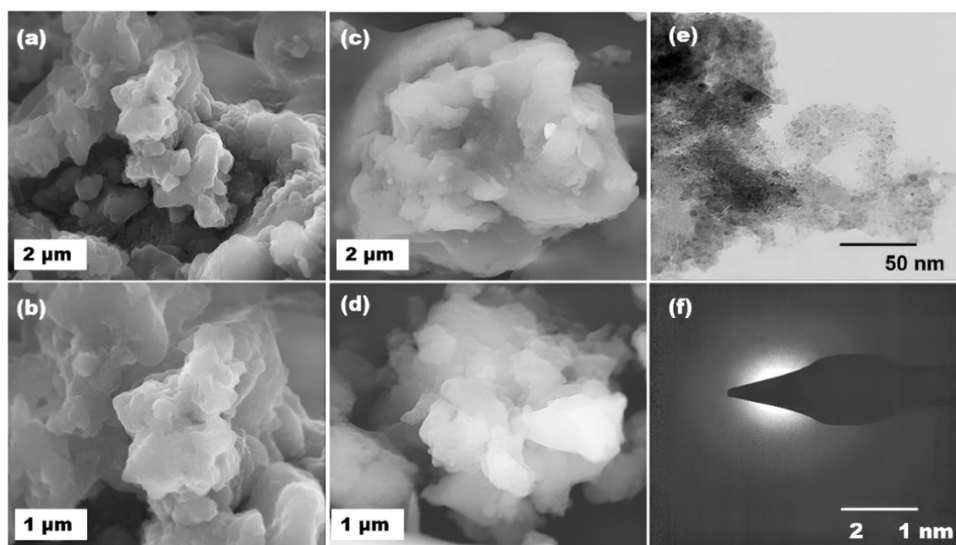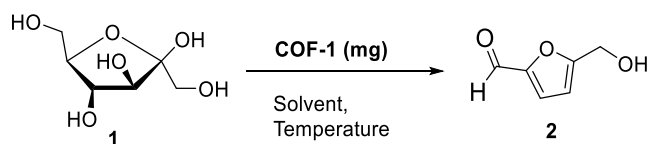
Figure 1. (a, b) SEM images of COF-1 at different magnifications. (c, d) Recovered catalyst of COF-1 after 5 cycles. (e, f) TEM and SAED images of COF-1.

## Table 1. Optimization of Dehydration of Carbohydrates to HMF

sI. no.	carbohydrate[a]	catalyst (mg)	temperature (°C)	solvent	time (h)	HMF[b] yield (%)
1	fructose	5	120	DMSO	2	69
2	fructose	10	120	DMSO	1.5	82
3	fructose	15	120	DMSO	1.5	90, 89, 90[c]
4	fructose	20	120	DMSO	1.5	85
5	fructose	30	120	DMSO	1.5	78
6	fructose	40	120	DMSO	1.5	65
7	fructose	none	120	DMSO	24	nd
8	fructose	15	100	DMSO	1.5	76
9	fructose	15	110	DMSO	1.5	84, 86, 84[c]
10	fructose	15	130	DMSO	1.5	87
11	fructose	15	140	DMSO	1.5	75
12	fructose	15	150	DMSO	1.5	72
13	fructose	15	120	DMSO/H_2O	1.5	81
14	fructose	15	120	DMF	1.5	70
15	fructose	15	120	dry DMSO	1.5	92
16	fructose	15	80	EtOH	2	32
17	fructose	15	90	EtOH/H_2O	2	55
18	fructose	15	100	IPA	5	38
19	fructose	15	100	H_2O	5	20
20	fructose	15	65	1,4-dioxane	5	40
21	fructose	15	80	MeOH	5	nd
22	fructose	15	65	THF	8	nd
23	fructose	15	120	DMSO	0.5	45
24	fructose	15	120	DMSO	3	87
25	glucose	15	120	DMSO	6	40
26	galactose	15	120	DMSO	6	25
27	mannose	15	120	DMSO	6	10

[a]Carbohydrate (200 mg, 1.1 mmol), solvent (2 mL). [b]Isolated yield. [c]he same reaction was repeated 3 times.

work showing two-dimensional sheet-like morphology, and the synthesis of COF-1 was also confirmed by EDX analysis showing peaks corresponding to the elements making up the composition of COF-1 (Figure S1a). Moreover, the elemental mapping analysis results for COF-1 show a uniform distribution of all elements (Figure S2). The porous nature of COF-1 was confirmed by TEM analysis, which showed the presence of small voids on the polymer surface. In addition,

Scheme 2. Proposed Mechanism for HMF Formation
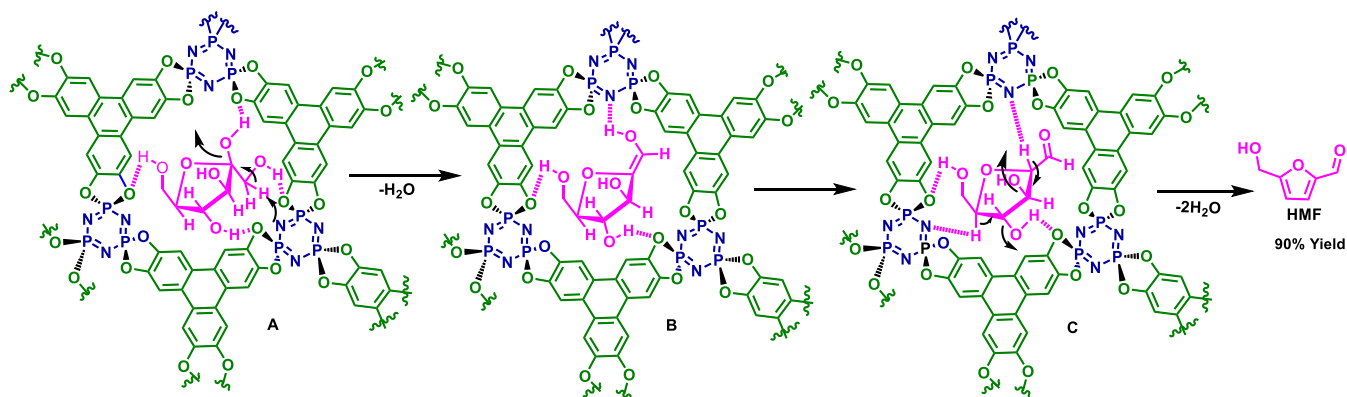
selected area electron diffraction (SAED) studies revealed a diffused ring pattern, which may be attributed to the polymer's polycrystalline nature (Figure 1e,f). The FT-IR spectrum of COF-1 reveals the presence of PO_2C_2 rings with characteristic Ar−O−P bands at 931 and 1075 cm^{-1} and broad O−H bands at 3000−3600 cm^{-1}. The stretching frequencies of P=N, P= N−C, and C=C (benzene ring) were detected at 1180, 1400, and 1630 cm^{-1}, respectively (Figure S3).

The presence of a 2D uniform microporous polymeric backbone in COF-1 prompted us to investigate its potential as a catalyst for the dehydration of fructose to HMF. Preliminary studies reveal that COF-1 is a suitable catalyst for this conversion. First, the reaction was carried out with 1.1 mmol of fructose and 5 mg (2.5% w/w) of catalyst in 2 mL of DMSO at 120 °C for 1.5 h, affording HMF with an isolated yield of 69%. Furthermore, the reaction was optimized under various conditions, such as the catalytic amount, temperature, solvents, and reaction time. Increasing the catalyst amount from 5 to 10 mg (5% w/w) resulted in an HMF yield of up to 82% (Table 1, entry 2). A catalytic amount of 15 mg (7.5% w/w) furnishes a 90% yield of HMF under the same reaction conditions (Table 1, entry 3). In addition, when the catalytic amount was increased to 20 mg (10% w/w), 30 mg (15% w/w), and 40 mg (20% w/w), the yield of HMF decreased to 85, 78 and 65%, respectively (Table 1, entries 4−6). For comparison, a control experiment was conducted without the addition of a catalyst, revealing that no detectable HMF was formed within 2−3 h. However, after 18−24 h, a trace amount of HMF was observed, indicating the importance of the COF-1 catalyst (Table 1, entry 7). The catalytic performance, based on the effect of the reaction temperature on the synthesis of HMF, was evaluated under standard conditions (Table 1, entry 3), with modifications to the temperature ranging from 100 to 150 °C. The results are presented in Table 1 (entries 8−12). The findings indicated that HMF yields were reduced to 76 and 86% at 100 and 110 °C, respectively (Table 1, entries 8−9). Conversely, as the reaction temperature increased beyond 120 °C, the HMF yield gradually decreased, ranging from 130 to 150 °C (Table 1, entries 10−12). Hence, 120 °C was selected as the optimal reaction temperature for the conversion of fructose into HMF using COF-1 as the catalyst. The catalytic activity of COF-1 for the dehydration of fructose was examined in different solvents, and the results are shown in Table 1 (entries 13−20).

The use of polar solvents, such as DMSO, DMSO/H_2O, and DMF, afforded HMF in 90, 81, and 70% yields, respectively (Table 1, entries 3, 12−14). When dry DMSO was used, the

HMF yield increased from 90 to 92% (Table 1, entry 15). Furthermore, polar protic solvents like EtOH, EtOH/H_2O, isopropyl alcohol, and H_2O were also investigated, resulting in lower isolated yields of 32, 55, 38, and 20%, respectively (Table 1, entries 16−19). The use of 1,4-dioxane gave a 40% yield in 5 h (Table 1, entry 20), and HMF formation was not detected when MeOH and THF were used as solvents (Table 1, entries 21−22). Overall, DMSO was found to be the most suitable solvent for the conversion of fructose to HMF under mild reaction conditions. DMSO is commonly used for dehydration reactions due to its ability to enhance conversion rates and selectivity. To evaluate the HMF yield over time, the reaction was conducted for 0.5 and 3 h, resulting in yields of 45% and 87%, respectively (Table 1, entries 23 and 24). The catalytic activity of COF-1 was also investigated for other carbohydrates, namely, glucose, galactose, and mannose, under the optimized reaction conditions, as shown in Table 1. Glucose yielded 40% HMF in 6 h (Table 1, entry 25), suggesting a potential two-step reaction involving glucose to fructose isomerization and subsequent dehydration of fructose to HMF. In contrast, galactose and mannose afforded HMF in 25 and 10% isolated yields, respectively, in 6 h (Table 1, entries 26−27). These results indicate that COF-1 can convert fructose into HMF in a higher yield than other carbohydrates under standard conditions (Table 1, entry 3). This indicates that COF-1 was more active and chemoselective in the conversion of fructose into HMF. Hence, COF-1 exhibited high catalytic performance, producing HMF from fructose in a 90% isolated yield under standard conditions (Table 1, entry 3). We examined the pH of the reaction mixture before and after completion of the reaction (1.5 h), and observed a neutral pH value of 7. Based on GC-MS analysis, we confirmed that HMF was the only observed product, without the formation of any other byproducts (Figures S4 and S16). This was further confirmed by HPLC analysis, which showed more than 99% purity of HMF by direct injection of the reaction mixture in 30 min and 1.5 h (Figure S15). The calibration curve for the formation of HMF using GC-MS was studied with various concentrations of HMF and 1 mmol of internal standard dodecane, which predicted 92% HMF formation in the reaction mixture. Additionally, the formation of HMF was confirmed by ^1H and ^{13}C NMR analyses (Figures S6 and S7). To the best of our knowledge, earlier reports on COFs have been supported by sulfonic acid groups that convert fructose into HMF. Our findings demonstrate that the nonacidic nature of our COF-1 facilitated the conversion of fructose into HMF in 90% isolated yield. Based on the observed results, a possible

catalytic mechanism of COF-1 in the dehydration of fructose is depicted in Scheme 2. Initially, fructose diffuses onto the surface of the COF-1 catalyst, and the methylene hydroxy protons of fructose form a hydrogen bond with oxygen (−P−O−) (A) at the active site of COF-1, resulting in the formation of the 2-hydroxymethyl-5-hydroxylmethylene-tetrahydrofuran-3,4-diol (HTFD) intermediate (B). The reaction is further activated by the N atom (−P=N−), which is protonated to produce an enol intermediate, followed by the dehydration of the water molecule (C). Due to the instability of HTFD, it tautomerizes into 3,4-dihydroxy-5-(hydroxymethyl)-tetrahydrofuran-2-carbaldehyde (DHTC) (C). Finally, HMF is generated by the loss of two water molecules from the catalyst surface (Scheme 2).[37,38]

COF-1 was examined for heterogeneity and recyclability, and the results are compiled in Figure 2. Upon completion of
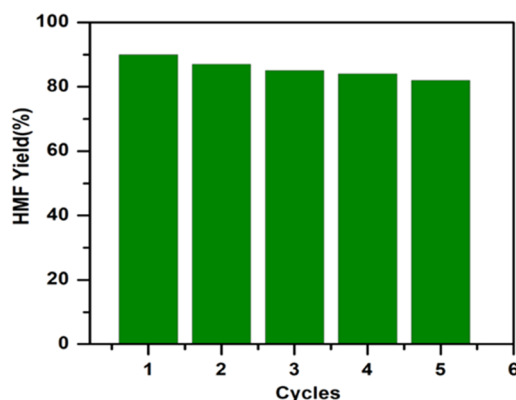

Figure 2. Recyclability of COF-1 for fructose to HMF conversion.

each run, COF-1 was recovered by centrifugation, washed with ethyl acetate and ethanol, and dried at 60 °C for 12 h before reuse. COF-1 was reused five times with a slight reduction in its catalytic activity from 90 to 82%. The recovered COF-1 was analyzed after 5 cycles using FT-IR, SEM, and EDX analysis. FT-IR (Figure S3) and SEM (Figure 1c,d) analyses showed no prominent changes in the structure. However, the incorporation of DMSO may be responsible for the presence of a sulfur atom, as shown in the EDX elemental analysis data of the recovered catalyst (Figure S1b).

Application for the Synthesis of FDMC. To the best of our knowledge, most FDMC syntheses from HMF have been catalyzed by noble and non-noble metal catalysts, often with high-pressure oxygen or oxidants. Previous studies by Liu et al. identified dibenzyl benzimidazolium bromide NHC (C1) as an effective catalyst for the conversion of aldehydes into esters, using MnO$_2$ as an oxidizing agent.[36] According to these results, we intended to synthesize FDMC from HMF, using C1 (0.3 equiv), DBU (0.3 equiv), MeOH (2.5 equiv) as alcohol, and MnO$_2$ (5 equiv) in the presence of dry THF at 70 °C (Scheme 3). However, under these conditions, the obtained product was monoesterified with HMFCE in 65% yield, and the product was confirmed by GC-MS analysis (Figure S5), ^{1}H, and ^{13}C NMR analyses (Figures S10 and S11). Based on these findings, we synthesized DFF from a literature procedure[35] by using MnO$_2$ as an oxidizing agent to give an 80% yield, and the product was characterized by ^{1}H and ^{13}C NMR spectroscopy (Figures S8 and S9). Subsequently, we proceeded with the NHC-catalyzed esterification reaction under the same conditions to synthesize biobased FDMC from DFF using C1 (0.3 equiv), MeOH (2.5 equiv), MnO$_2$ (5 equiv), and DBU (0.3 equiv) in dry THF (3 mL) at 70 °C (Scheme 3). Within 2 h, FDMC afforded 75% yield, and the product formation was confirmed by ^{1}H,^{13}C NMR, and HRMS (Figures S12−S14).

Mechanistically, the NHC-catalyzed reaction proceeds through the Breslow intermediate, as proposed in Scheme 4. The catalytic cycle is initiated by the generation of free NHC (II) from the precatalyst (I) in the presence of a base. The nucleophilic addition of NHC (II) to the aldehyde formed a tetrahedral intermediate (III), which was further converted into a hydroxyenamine intermediate (IV). This intermediate was then oxidized to acyl benzimidazolium intermediate (V) using MnO$_2$. Subsequently, the nucleophilic addition of methanol furnished the desired ester.

■ CONCLUSIONS

The synthesized COF-1 has unique structural features with a high surface area, pore size, and active catalytic sites, owing to its significant synergistic catalytic activity for the dehydration reaction of fructose to HMF in 90% yield. COF-1 has a unique phosphazene backbone and is nonacidic, facilitating interactions with fructose through hydrogen bonds and selective

Scheme 3. NHC Catalyzed Oxidative Esterification of HMF and DFF[a]
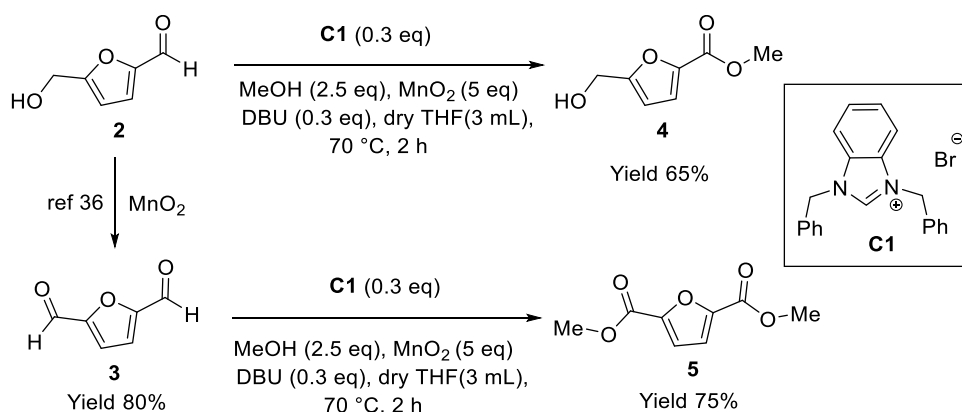
[a]Reaction conditions: HMF (1 equiv, 0.792 mmol), NHC catalyst (0.3 equiv), DBU (0.3 equiv), THF (3 mL), MnO$_2$ (5 equiv), MeOH (2.5 equiv), 70 °C, and 2 h.

Scheme 4. Proposed Mechanism of Oxidative Esterification of Aldehydes

Breslow intermediate
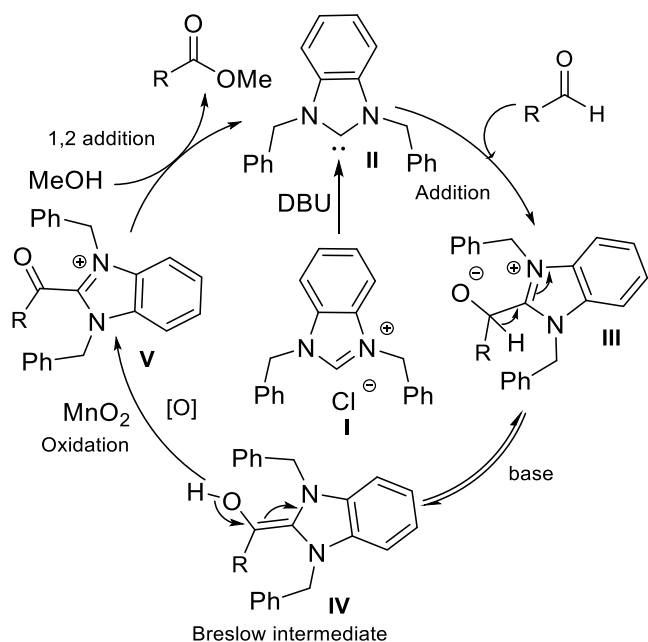
dehydration at the active sites. Moreover, COF-1 demonstrates good heterogeneity after five reaction cycles without significant loss in catalytic activity. Furthermore, we present the transformation of HMF into FDMC, the monomer of a bioplastic material, using an NHC catalyst in the presence of MnO$_2$. In conclusion, we successfully developed the conversion of fructose to HMF using the covalent organic framework (COF-1) as a neutral heterogeneous catalyst for this biomass transformation.

■ EXPERIMENTAL SECTION

Materials and Instrumentation. For descriptions of the instrumentation, sources of materials, and additional characterization data for the catalysts, see Section S2.

Synthesis of COF-1.[28,29] A sealed pressure tube was charged with a mixture of tris (2,3,6,7,10,11-hexahydroxytriphenylene) (1 g, 3.08 mmol), hexachlorophosphazene (1 g, 2.88 mmol), and 5 mL of mesitylene-dioxane solution (1:1, v/v) under a N$_2$ atmosphere at 120 °C for 5 days. The resulting dark gray solid was isolated via filtration, washed with acetone (3 × 30 mL), and dried under vacuum for 24 h. The yield of the product was 1.4 g (71%).

Catalytic Conversion of Fructose into HMF[39] (2). An oven dried sealed tube was charged with D-fructose (200 mg, 1.10 mmol, 1 equiv) and catalyst COF-1 (15 mg, 7.5% w/w) was dissolved in DMSO (2 mL). The tube was purged with N$_2$ gas and then placed into a preheated oil bath at 120 °C for 1.5 h. The progress of the reaction was monitored by using TLC. The reaction mixture of the obtained brown liquid was cooled to room temperature, and COF-1 was recovered by centrifugation, washed with ethanol followed by acetone, dried for 12 h at 50 °C, and reused directly in the next run by adding fresh fructose and DMSO. After the separation of the catalyst, the reaction mixture was diluted with ethyl acetate (20 mL), washed with water (3 × 10 mL) and brine (2 × 5 mL), dried over Na$_2$SO$_4$, and evaporated under reduced pressure. The resulting residue was subjected to GC/MS analysis. The

residue was then purified by column chromatography on silica gel, and the product was obtained as a pale brown liquid: 126.5 mg, 90% yield; ^{1}H NMR (400 MHz, CDCl$_3$): δ 9.51 (s, 1H), 7.20 (d, J = 3.6 Hz, 1H), 6.48 (d, J = 3.2 Hz, 1H), 4.67 (s, 2H), 3.21 (s, 1H); ^{13}C NMR (400 MHz, CDCl$_3$): δ 177.8, 161.0, 152.1, 123.4, 110.0, 57.0.

Product Analysis (Purity). The purity of HMF was determined by using HPLC, equipped with a C-18 column and a PDA detector. The column temperature was maintained at 35 °C, and 10 μL of aliquot was injected into the mobile phase (water/methanol; 70:30) at a flow rate of 1.0 mL/min. The peaks of HMF were quantified, and it showed >99% purity by injecting the reaction mixture directly into HPLC for 30 min and 1.5 h (Figure S15). The purity of the crude reaction mixture was confirmed by GC-MS analysis and a single chromatogram peak. The formation of HMF was calculated from the calibration curves of various concentrations of HMF and the internal standard (dodecane) on the chromatograms (Figure S16).[10] The conversion of the substrates and the concentrations of HMF formation from the reaction mixture were calculated from the standard calibration curves with a premixture of dodecane and 92% of the GC yield.

Synthesis of DFF (4).[40] An oven-dried 50 mL sample of RB was charged with HMF (500 mg, 3.96 mmol, 1 equiv) and MnO$_2$ (3.5 g, 39.6 mmol, 10 equiv) in 25 mL of toluene. Then, the reaction mixture was refluxed for 6 h. Product formation was assessed by TLC. After completion of the reaction, the solvent was evaporated, and the product was purified by column chromatography on silica gel. The product was obtained as a pale-yellow solid: 79 mg, 80% yield; m.p.: 105−110 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 9.84 (s, 2H), 7.29 (s, 2H); ^{13}C NMR (400 MHz, CDCl$_3$): δ 119.36, 154.35, 179.30.[41]

Preparation of the Dibenzylbenzimidazolium Bromide (C1) Catalyst.[41] To a 50 mL flask charged with benzimidazole (1.18 g, 10 mmol), 10 mL of 30% NaOH (aq) and 1.5% equiv of Bu$_4$-N$^+$Br$^-$ (TBAB) (50 mg, 0.15 mmol) were added, followed by 1.2 equiv of benzyl bromide (1.4 mL, 12 mmol) at room temperature. The mixture was stirred at 55 °C for 3 h, poured into 50 mL of water, and extracted with toluene (20 mL × 3). The toluene extracts were dried with Na$_2$SO$_4$, filtrated and added to a solution of benzyl bromide (2.4 mL, 20 mmol) in a 100 mL flask. The mixture was refluxed for 6 h and slowly cooled to room temperature to give dibenzylbenzimidazolium bromide as a white powder, which was further purified by recrystallization from CH$_2$Cl$_2$ to give colorless crystals (1.9 g, 60%).

Synthesis of a Biobased Ester of HMFCE[42] (3). In an oven-dried sealed tube, HMF (100 mg, 0.792 mmol, 1 equiv), NHC catalyst **C1** (71 mg, 0.237 mmol, 0.3 equiv), MeOH (155 μL, 1.98 mmol, 2.5 equiv), MnO$_2$ (34 mg, 0.396 mmol, 5 equiv), and a catalytic amount of DBU (35 μL, 0.237 mmol, 0.3 equiv) were dissolved in dry THF (2 mL) under a N$_2$ atmosphere. The resulting solution was stirred at 70 °C in a preheated oil bath for 1 h. The progress of the reaction was monitored using TLC; upon completion, the reaction mixture was diluted with ethyl acetate (10 mL), washed with water (3 × 10 mL) and brine (2 × 5 mL), and dried over Na$_2$SO$_4$. The solvent was evaporated under reduced pressure, and the product was then purified by column chromatography on silica gel using ethyl acetate/hexane as the eluent. The product was obtained as pale-yellow liquid: 81 mg, 65% yield; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.06 (d, J = 4.5 Hz, 1H), 6.35 (d, J = 4.0

Hz, 1H), 4.61 (s, 2H), 3.82 (s, 3H), 2.38 (s, 1H); ^{13}C NMR (500 MHz, CDCl$_3$): δ 159.2, 158.4, 143.9, 118.8, 109.3, 57.4, 51.9.

Synthesis of DFF[39] (4). DFF was synthesized following a procedure from the literature.[40] The product was obtained as a pale-yellow solid: 79 mg, 80% yield; m.p.: 105–110 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 9.84 (s, 2H), 7.29 (s, 2H); ^{13}C NMR (400 MHz, CDCl$_3$): δ 119.36, 154.35, 179.30.

Synthesis of FDMC[42] (5). In an oven-dried sealed tube, DFF (100 mg, 0.805 mmol, 1 equiv), NHC catalyst **C1** (72.3 mg, 0.241 mmol, 0.3 equiv), MeOH (158.12 μL, 2.012 mmol, 2.5 equiv), MnO$_2$ (349.8 mg, 4.025 mmol, 5 equiv), and a catalytic amount of DBU (36 μL, 0.241 mmol, 0.3 equiv) were dissolved in dry THF (4 mL) under a N$_2$ atmosphere. The resulting solution was stirred at 70 °C in a preheated oil bath for 1–3 h. The progress of the reaction was monitored using TLC; upon completion, the reaction mixture was diluted with ethyl acetate (10 mL), washed with water (3 × 10 mL) and brine (2 × 5 mL), and dried over Na$_2$SO$_4$. The solvent was evaporated under reduced pressure. The product was then purified by column chromatography on silica gel using ethyl acetate/hexane as eluent. The product was obtained as a white solid: 112 mg, 75% yield; m.p.: 110–115 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.15 (s, 1H), 3.86 (s, 3H); ^{13}C NMR (400 MHz, CDCl$_3$): δ 158.4, 146.6, 118.5, 52.4. HRMS (ESI) m/z: calculated, 207.0269 [C$_8$H$_8$O$_5$Na]; found, 207.0269 [C$_8$H$_8$O$_5$Na].

ASSOCIATED CONTENT

Ⓢⁱ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.3c08763.

EDX, FT-IR, GC-MS, NMR, HRMS analysis. (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

ABBREVIATIONS

COF	covalent organic framework
MnO$_2$	manganese dioxide
NHC	N-heterocyclic carbene
HMF	5-hydroxymethylfurfural
H$_3$PO$_4$	phosphoric acid
HCl	hydrochloric acid
H$_2$SO$_4$	sulfuric acid
FDMC	furan-2,5-dimethylcarboxylate
DFF	2,5-diformylfuran
PEF	polyethylene furanoate
HMFCE	methyl 5-(hydroxymethyl)furan-2-carboxylate
DMSO	dimethyl sulfoxide
Na$_2$SO$_4$	sodium sulfate
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
THF	tetrahydrofuran
TLC	thin layer chromatography

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