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Diels-Alder Conversion of Acrylic Acid and 2,5-Dimethylfuran to para-Xylene over Heterogeneous Bi-BTC Metal-Organic Framework (MOF) Catalysts under Mild Conditions

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Supporting information for this article is given via a link at the end of the document.

Abstract: Heterogeneous Bi-BTC successfully catalyzed a promising yield (92%) of para-xylene from bio-based 2,5-dimethylfuran and acrylic acid conversion, under relatively mild conditions (160 ºC, 10 bar) with a low reaction energy barrier (47.3 kJ/mol). The proposed reaction strategy also demonstrated remarkable versatility for furan derivatives such as furan and 2-methylfuran.

p-Xylene (PX) is one of the most industrially important precursors with an estimated annual demand of 37 million tons in 2014,[1] mainly for the production of polymers such as polyethylene terephthalate (PET).[2-5] PX is conventionally obtained from petroleum-derived naphtha; however, production of PX from lignocellulosic biomass renders a more sustainable process.[6, 7] Lignocellulosic biomass, composed of cellulose, hemicellulose, and lignin,[8] is a promising candidate to substitute current petrochemical precursors in the production of value-added chemicals.[9, 10] Hydrolysis of cellulose and hemicellulose followed by the dehydration can produce fundamental furan molecules such as furfural (FAL), 2-methylfuran (MF), 5-hydroxymethylfuran (HMF) and 2,5-dimethylfuran (DMF)[11, 12] that belong to the top-12 bio-derived platform chemicals listed by the U.S. Department of Energy.[13] These furan platform molecules can be further converted into aromatics such as PX through Diels–Alder cycloaddition, followed by dehydration with alkene such as ethylene over acidic catalysts under high temperature and pressure conditions (typically at 250 ºC, 62 bar).[14-17] However, since most alkenes are still derived from

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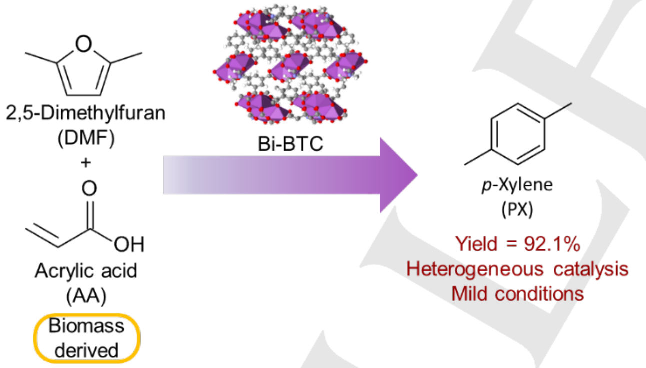
petroleum sources, the process compromises sustainability.[14-17]

To replace alkenes with sustainable feedstocks, the production of PX has been reported by reacting DMF with bio-derived sources such as ethanol[18] and acrylic acid (AA)[19] over acid catalysts. Teixeira et al.[18] demonstrate that zeolite can catalyze the dehydration of ethanol to produce ethylene, which then undergoes Diels-Alder reaction with DMF since both reactions are catalyzed by acidic sites. These results demonstrate that ethanol can act as a dienophile source for furan cycloaddition with substantially higher rates and lower reaction barriers than those of ethylene.[18] However, this method produced a relatively low yield of PX (56%) and was conducted under severe reaction conditions (300 °C, 40 bar). Synthesis of PX from DMF and AA through ionic liquid catalysis at room temperature has been reported,[19] but it had a relatively low yield of p-xylene (45%). Additionally, the involvement of ionic liquid inevitably introduces additional processes in catalyst separation and product recovery. Therefore, to develop an effective heterogeneous catalytic system that can facilitate catalyst recovery and achieve a high yield of PX from renewable feedstocks under milder reaction conditions than those in current industrial practice (250 °C, 62 bar) is a compelling desire. Very recently, the Al-Naji group demonstrated the successful production of PX with a high yield of 83% from PX and AA over a heterogeneous Beta zeolite (Si/Al=150) under a relatively high reaction temperature (200 °C).[20] This pioneering study clearly showed that heterogeneous catalysts can be effective in lowering the reaction temperature while achieving a high product yield.



Scheme 1. Schematic illustration of Bi-BTC catalyzed Diels-Alder reaction of DMF and AA to PX.

MOFs are organic−inorganic hybrids composed of metal ions (or clusters) and organic ligands. Unlike a simple mixture of metal ions and organic compounds, MOFs exhibit unique properties such as tunable functionalities and various molecular structures, which advance the development of efficient catalysts.[21-30] MOF catalysts typically outperform other heterogeneous catalysts due to their uniform porosity and high density of catalytic active sites.[31-33] Moreover, MOFs can tailor an array of material owing to their composition of organic ligands and metal clusters, which have exhibited excellent catalytic performances in various liquid phase reactions.[34]

In this work, we demonstrate a viable and scale-up possible technology for PX production from bio-based sustainable feedstocks, DMF, and AA under mild conditions (160 °C, 10 bar) as a comparison to current industrial practice. Heterogeneous Bi-BTC catalyst is applied for the Diels-Alder reaction in this study as illustrated in **Scheme 1**. The highest yield of PX (92%) can be obtained under optimized reaction conditions, and the catalyst demonstrates stable performance for at least six runs. Moreover, the proposed reaction has one of the lowest apparent reaction activation energies (47.3 kJ/mol) reported in existing DMF to PX reactions. The applicability of this Diels-Alder reaction protocol can also extend to other furan derivatives with AA.

The synthesis of Bi-BTC is modified from the procedure reported by Wang et al,[35] where the synthesis details are described in Supporting Information. To further confirm the structure and purity of the sample, Powder X-ray diffraction (XRD) was carried out. The XRD patterns of the as-synthesized Bi-BTC and simulated Bi-BTC are displayed in **Fig. 1a**. The XRD pattern of the as-synthesized Bi-BTC shows well-defined diffraction peaks (2θ) of 9.8°, 10.6°, 11.8°, 12.8°, and 17.8°, which indicates precise structural agreement with the simulated result based on the single crystal structure. This result confirms the formation of the Bi-BTC structure during the synthesis. In addition, the strong intensities of the diffraction peaks suggest the as-synthesized Bi-BTC possesses a high crystallinity. The SEM images (**Fig. 1b**) indicate that the Bi-BTC is a quadrangular prism crystal with a grain particle size of 14.3 μm (counted by 41 particles, **Fig. S10**). The SEM-EDS mapping reveals that bismuth is homogeneously dispersed on the samples, confirming the purity of the Bi-BTC particles.

To evaluate the thermal stability of Bi-BTC, TG/DTA was conducted under air condition from 30 to 800 °C. As shown in **Fig. 1c**, weight losses are observed at around 100 and 400 °C, while one weight gain is observed at around 315 °C. The gradual weight loss (13.3%) from 100 °C to 280 °C corresponds to the loss of water molecules. The modest weight gain from 280 °C to 315 °C may be assigned to the oxidation of partial bismuth metal nodes of the Bi-BTC second building unit (SBU) from Bi^{+3} to Bi^{+5} under air condition. The drastic weight loss (35.5%) from 315 °C to 400 °C is ascribed to the decomposition of MOF structure and mineralization of the trimesic acid into CO_2.

The Bi-BTC was analyzed by N_2 adsorption and desorption isotherm to determine the specific surface area and pore size distribution (**Fig. 1d**). The combination of Type I and IV isotherms indicate microporous and mesoporous structures of the as-synthesized Bi-BTC, which is also confirmed by the microporous and mesoporous size distribution (**Fig. 1d**). The specific surface area of the Bi-BTC is 186.2 m^2/g. As dominated by mesopores, the specific surface area of the as-synthesized Bi-BTC was smaller than other microporous MOFs in the literature.

In the catalytic evaluation tests (**Fig. 2a**), the 2,5-dimethylfuran (DMF) was consumed in every reaction entry, while p-xylene (PX) and 2,5-dimethylbenzoic acid (DMCA) were only obtained when Bi^{3+} species were in the systems

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(i.e., Bi_2O_3, Bi-BTC, $Bi(NO_3)_3\cdot5H_2O$+BTC and $Bi(NO_3)_3\cdot5H_2O$). These results indicate that the Diels-Alder reaction of DMF to PX was catalyzed by Bi^{3+} species. The total yields of Diels-Alder reaction products (PX and DMCA) were 96%, 84%, 19% and 57% for the reaction catalyzed by Bi-BTC, $Bi(NO_3)_3\cdot5H_2O$+BTC, Bi_2O_3 and $Bi(NO_3)_3\cdot5H_2O$, respectively. Addition of BTC to $Bi(NO_3)_3\cdot5H_2O$ significantly enhanced the product yield from 57% to 84%, which can be ascribed to the π-π interaction between BTC and Diels-Alder cycloadduct intermediate.[36] The gas chromatography mass spectrometry (GC-MS) identified the other products in addition to PX and DMCA in the reaction mixture were 4-methyl-3-penten-2-one, 2,5-hexanedione, phorone, and 2-methoxyfuran in the blank test and in the presence of bare BTC. Inferring by the structures, these products probably resulted from self-polymerization of AA and degradation of DMF (**Fig. S8**).

These side reactions could be eliminated by using acidic catalysts to facilitate the Diels-Alder cycloaddition of AA and DMF. In the catalysis by Bi-BTC, DMF was converted to a particularly high yield of 92% PX, where AA polymerization and DMF degradation were suppressed as indicated by the GC-MS results (**Fig. S9**). The catalytic activity of Bi-BTC for the Diels-Alder reaction was verified using density functional theory (DFT) calculations, which show that the barrier of the Diels-Alder reaction of AA and DMF can be significantly decreased with the mediation of Bi-BTC (**Fig. S12**). The results of DFT also suggest that the organic ligands of BTC

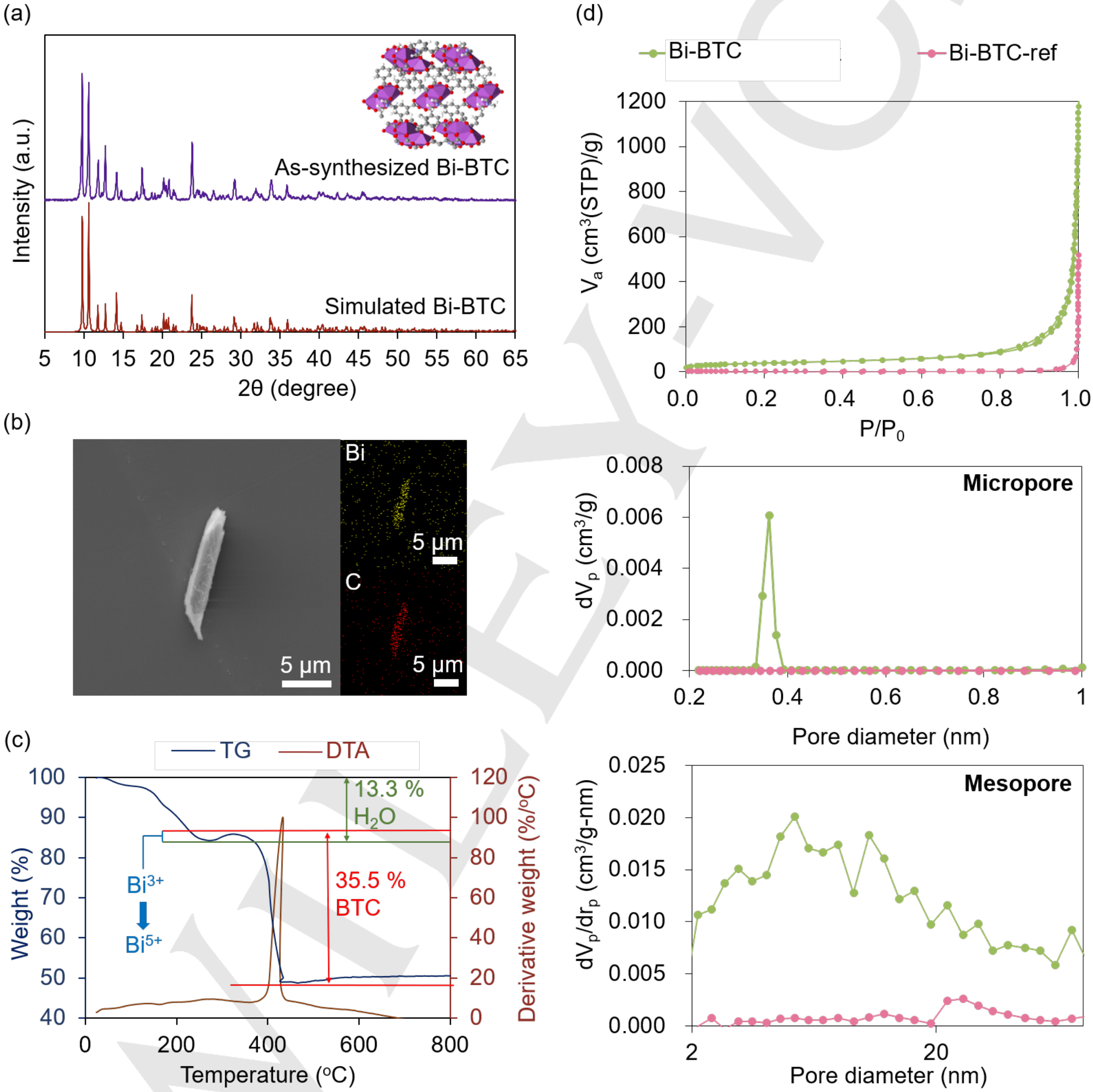

Figure 1. Characterization of Bi-BTC. (a) XRD pattern of as-synthesized Bi-BTC and simulated Bi-BTC, (b) SEM and SEM-EDS images of Bi-BTC, (c) TGA-DTA analysis of Bi-BTC, (d) Adsorption and desorption isotherm, micropore size distribution and mesopore size distribution of Bi-BTC and Bi-BTC-ref.

have a role in stabilizing the reactive species of the Diels-Alder reaction since removing the organic ligands from the Bi-BTC cluster model increases the calculated barrier for Bi-BTC (**Fig. S12**).

Catalysts reported for Diels-Alder conversion of DMF and ethylene including Y-zeolite,[14] H-BEA,[15] ZSM-5,[16] and $SnPO_4$[17] were also tested for DMF and AA conversion in this study for comparison. The results showed that PX yielded less than 32% for all these tested catalysts under full conversion (**Fig. S15**), which highlighted the excellent performance of Bi-BTC in Diels-Alder conversion for PX production.

DMF undergoes Diels-Alder, decarboxylation and dehydration to produce PX.[19] The Diels-Alder,[37] decarboxylation[38] and dehydration[39] reactions can be catalyzed by Lewis acid, which is the Bi^{3+} species in Bi-BTC.[40, 41] Therefore, a Lewis-acid-catalyzed mechanism is proposed (**Fig. S4**). The Bi^{3+} species in Bi-BTC acting as Lewis acid could promote the Diels–Alder reaction by a diminished Pauli repulsion between the *p*-electron systems of diene and dienophile.[37] Based on the fact that excess of AA is needed to optimize PX yield as explained below, the deprotonated AA removes a proton from the carboxylic acid, followed by a removal of carbon dioxide via decarboxylation. A lone pair of the oxygen of the bridging ether then binds to the Lewis-acid site in Bi-BTC, and through a proton transfer the bridging ether becomes an epoxide. At last, the epoxide ring opens and transforms to an alcohol group, which is then removed through dehydration. The DFT calculated reaction energies and structures of the proposed intermediates can be found in the Supporting Information (**Fig. S4**).

The yield of PX was further examined in various solvent environment, including acetone, hexane, and methanol as shown in **Fig 2b**. The reaction in acetone produced the highest yield of PX (92%) with minor yield of DMCA (4%). Lower yield of PX were obtained in reactions conducted in hexane and methanol. The yields of 52% PX with 7% DMCA, and 43% PX with 5% DMCA were obtained in hexane and methanol, respectively. The lower selectivity to the Diels-Alder reaction products (PX and DMCA) in hexane and methanol can be attributed to the stronger solvation of DMF and AA in these solvents (**Table S2**). Introducing an appropriate solvent for DMF and AA decreases the loading of these species in the MOF catalyst, resulting in a lower probability for forming the Diels-Alder adduct, i.e., a higher barrier for the Diels-Alder reaction (**Table S2**).

Since the Diels-Alder reaction is reversible, increase of the portion of one reactant could right-shift the equilibrium. Meanwhile, excess of DMF could react with water produced in the dehydration step to lower PX selectivity.[42] The yields of PX increased from 19% to 92% when the molar ratio of DMF/AA decreased from 1/1 to 1/6 (**Fig. S5**). Further decreasing the DMF/AA ratio to 1/7 and 1/8 showed negligible difference in PX yield (89% and 91%, respectively), which is one of the highest PX yields in the reported DMF and AA Diels-Alder reaction. These results reveal the optimized molar ratio of DMF/AA determined in this study is 1/6. We propose that the increasing conversion observed in decreasing DMF/AA ratio from 1/1 to 1/6 is due to higher AA concentration in reaction mixture. The increase of AA concentration accelerates DMF consumption rate and enhances DMF conversion. Further decreasing DMF/AA ratio to 1/7 and 1/8 (*i. e.* increase of AA concentration) no longer improves DMF conversion since >99% conversion has been reached at a DMF/AA ratio of 1/6. The unreacted AA is recovered by water extraction followed by rotatory evaporation to remove the water and the dissolved acetone. The recovered AA with fresh DMF resulted in 88.6% of PX under the optimized reaction conditions. Details of AA recovery procedures are provided in the Supporting Information. Examination of the catalyst dosage shows that PX yield increased from 13% (Conv. = 13%) to 92% (Conv.> 99%) when the catalyst amount increased from 5 mg to 20 mg (**Fig. S6**). Minor improvement was observed when the catalyst dosage was increased to 25 mg. These results indicate that 20 mg Bi-BTC is the optimal catalyst dosage in this study.

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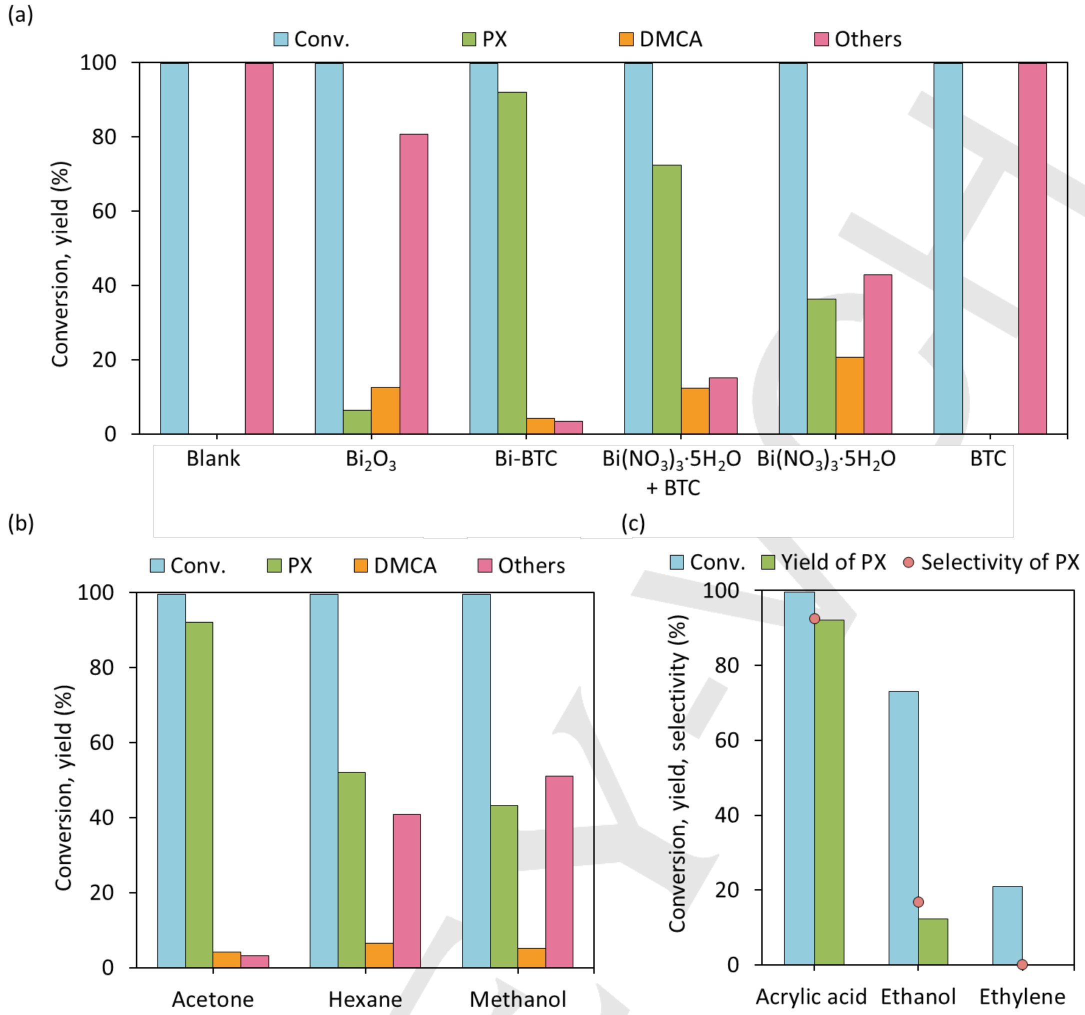
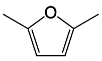
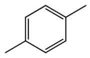
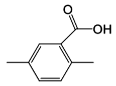
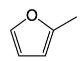
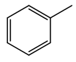
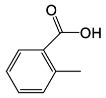
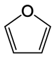
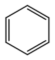
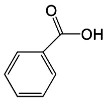
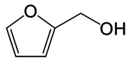
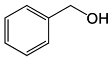
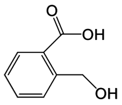
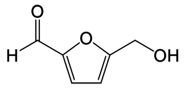
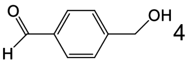
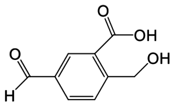


Figure 2. (a) Catalyst evaluation test, (b) the solvent effect and (c) carbon source effect of DMF to PX reaction. All the reactions are conducted in a 20-mL glass pressure tube with 20 mg catalyst, 200 µL solvent, 3.0 mmol dienophile, 0.5 mmol DMF at 160 °C for 24 h.

Different Diels-Alder dienophiles including acrylic acid, ethanol, and ethylene were investigated in the Diels-Alder reaction of DMF conversion to PX under the optimized reaction conditions (i.e., 20 mg Bi-BTC, 200 µl acetone, 3.0 mmol dienophile, and 0.5 mmol DMF at 160 ºC for 24 h) as indicated in **Fig. 2c**. The yields of 92% (Selectivity: 92%), 12% (Selectivity: 17%) and 0% PX are obtained when acrylic acid, ethanol, and ethylene act as the dienophile, respectively. These results highlight that acrylic acid demonstrates a favorable component in the conversion of DMF to PX with high yields under a mild reaction condition (160 ºC). The kinetic studies of DMF conversion to PX were conducted at various temperatures (i.e., 140, 150 and 160 ºC) to determine the apparent activation energies of the reactions. The details and related assumptions are listed in the Supporting Information. The obtained results reveal that Bi-BTC catalysis of DMF to PX reaction has one of the lowest reported apparent activation energy. The apparent activation energies of DMF to PX (Ea_{PX}) and DMF to DMCA (Ea_{DMCA}) were measured as 47.3 kJ mol^{-1} and 32.1 kJ mol^{-1}, respectively. The Ea_{PX} is slightly lower than the activation energy of DMF to PX Diels-Alder reaction with ethylene catalyzed by H-Beta zeolite[15] (54.3 kJ mol^{-1}), with ethanol catalyzed by zeolite[18] (55.8 kJ mol^{-1}), and with acrylic acid catalyzed by Brønsted acid in ionic liquid[19] (64.8 kJ mol^{-1}). Therefore, Bi-BTC serves as an effective catalyst in Diels-Alder reaction of DMF to PX with the one of the lowest activation energies.

Our Bi-BTC also shows good recyclability. As shown in **Fig. S7**, the Bi-BTC catalyst maintained high catalytic activity and selectivity for six runs with minor loss under the optimized conditions. The inductively coupled plasma-mass spectrometer results (**Table S3**) indicated minimal changes of Bi^{3+} amount on Bi-BTC, and undetectable Bi^{3+} leaching (detection limit 1 ppb) to the reaction mixture in the six reaction runs. Both the fresh and used Bi-BTC materials showed two peaks at around 164.2 eV and 158.9 eV in the X-ray photoelectron spectroscopy (XPS) analysis (**Fig. S2**), which were assigned to $Bi4f_{5/2}$ and $Bi4f_{7/2}$, respectively.[43] These XPS peaks clearly revealed the Bi^{3+} species in the Bi-BTC materials, which were well retained in the reaction. Similar to fresh Bi-BTC, the used Bi-BTC was in the morphology of quadrangular prism crystal revealed by SEM images (**Fig. S13**). Furthermore, the XRD pattern of used Bi-BTC (**Fig. S14**) was the same as that of fresh Bi-BTC (**Fig. 1a**). These results demonstrate that Bi-BTC is stable under

Table 1. Results of reaction with different furan derivative feedstocks.

Reactant		Conv.	Yield					
			Targeted Diels-Alder Aromatics			Main Diels-Alder side Aromatic products		
	DMF	≥ 99%		PX	92%		DMCA	4%
	2-MF	≥ 99%		Toluene	65%		2-MBA	23%
	Furan	≥ 99%		Benzene	37%		Benzoic acid	43%
	FOL	≤ 0%		PMOL	Trace		2-HMBA	Trace
	HMF	≤ 0%		4-HMBA	Trace		5-FHMBA	Trace

2-MF: 2-methylfuran, 2-MBA: 2-methylbenzoic acid, FOL: furfuryl alcohol, PMOL: phenylmethanol, 2-MBA: 2-(hydroxymethyl)benzoic acid, HMF: 5-hydroxymethyllfurfural, 4-HMBA: 4-(hydroxymethyl)benzaldehyde, 5-FHMBA: 5-formyl-2-(hydroxymethyl)benzoic acid.

the reaction conditions and offers consistent performance in the recycling tests

To demonstrate the industrialization potential, scale-up reaction was conducted (reaction details in the Supporting Information). In the gram-scale reaction, 90% yield of PX with full conversion and 6% yield of DMCA were obtained, which were similar to those obtained in the milligram-scale reaction (92% yield PX, 4% yield DMCA, full conversion). These results reveal that Bi-BTC catalyst is capable of upscaling reactions. Since metal species disperse in MOFs atomically,[44] the turnover frequency (TOF) and turnover number (TON) can be calculated as 0.62 h^{-1} and 89.96 based on the molecule formula of Bi-BTC ($C_{17}H_{25}BiN_2O_{10}$).

In addition, Bi-BTC is active in the catalysis of various furan derivatives for BTX production (i.e., benzene, toluene and xylene) by means of Diels-Alder reaction (**Table 1**), for instance, DMF and 2-MF were converted into high yields of PX (92%) and toluene (65%), respectively. Furan can also be transformed to benzene in this reaction, where 37% yield of benzene was obtained accompanied with a major product of benzoic acid (43%). The Bi-BTC is not able to catalyze the conversion of FOL and HMF due to the steric hindrance of hydroxyl group and aldehyde group. Nevertheless, in consideration of the outstanding yields of PX (92%), toluene (65%) and benzene (37%) from furan derivatives, Bi-BTC is a promising catalyst for the Diels-Alder reaction of furan derivatives with acrylic acid in a sustainable route.

In conclusion, a remarkable yield of PX (92%) from Diels-Alder reaction with sustainable feedstocks DMF and AA was reported by heterogeneous Bi-BTC catalysts in this study. The low activation energy of DMF to PX (47.3 kJ/mol) facilitated the reaction under a mild condition (160 ˚C, 10 bar). In addition, the Bi-BTC works for various furan derivatives to produce valuable BTX compounds. This work provides a promising route to replace traditional catalytic reforming of BTX from petroleum source with catalytic conversion of bio-based DMF and AA.

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Keywords: Metal-organic framework • Bi-BTC • acrylic acid •2,5-dimethylfuran • *para*-xylene

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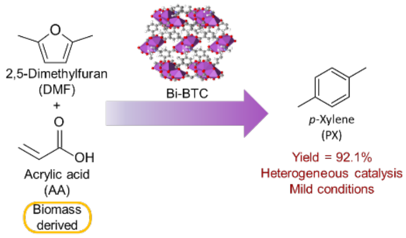

Heterogeneous Bi-BTC can catalyze conversion of bio-based 2,5-dimethylfuran and acrylic acid into a promising yield (92%) of para-xylene under relatively mild conditions (160 ºC, 10 bar).