Supporting Information

Synergistic Fe(III) and Acid Sites in SiW@MIL-100(Fe) Catalyst Prompt the Synthesis of p-Xylene from Biomass Derivatives

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Experimental Section

Materials

All reagents were purchased from chemical companies (Adamas, Macklin, and Sinopharm Chemical) without secondary purification.

$Fe(NO_3)_3 \cdot 9H_2O$ (>98%), benzene (>99%), methylbenzene (>99.5%), and benzaldehyde (99%) were purchased from Sinopharm Chemical Reagent Co., Ltd. $H_4[Si(W_3O_{10})_4] \cdot xH_2O$ and $H_3O_{40}PW_{12} \cdot xH_2O$ were purchased from Shanghai Macklin Biochemical Technology Co., Ltd. All the other organic reagents were purchased from Adamas-beta LTD.

Catalyst preparation

Synthesis of MIL-100(Fe)

The synthesis of MIL-100(Fe), SiW@MIL-100(Fe), and PW@MIL-100(Fe) were modified from the procedure reported by Guan and co-workers.[29] Trimesic acid (5 mmol) and ferric nitrate nonahydrate (6.0 mmol) were fully dissolved in 25 mL water. The mixture was placed into a Teflon liner and sealed with a stainless-steel jacket. The reactor was heated at 130 ^{o}C for 3 days and then cooled down to room temperature. The light orange sediment was obtained and washed alternately with ultrapure water and methanol, then dried at 60 ^{o}C in the air.

Synthesis of SiW@MIL-100(Fe)

The synthesis of SiW@MIL-100(Fe) was similar to MIL-100(Fe) besides the addition of POM in the synthesis process. Typically, trimesic acid (5 mmol), ferric nitrate nonahydrate (6.0 mmol), and $H_4[SiW_{12}O_{40}]$ (0.6 mmol) were fully dissolved in 25 ml water, then the solution was transferred to a 50 mL Teflon bottle, and heated at 130 ^{o}C for 3 days. The obtained sediment product was named SiW@MIL-100(Fe)-1. When 0.9, 1.2, and 1.8 mmol of SiW were used in synthesis, the obtained solid products were referred to as SiW@MIL-100(Fe)-2, -3, and -4, respectively.

Synthesis of PW@MIL-100(Fe)

The synthesis of PW@MIL-100(Fe) was similar to SiW@MIL-100(Fe). Trimesic acid (5 mmol), ferric nitrate nonahydrate (6.0 mmol), and $H_4[PW_{12}O_{40}]$ (0.6 mmol) were fully dissolved in 25 ml water, then the solution was transferred to a 50 mL Teflon bottle, and heated at 130 ^{o}C for 3 days. The obtained product was named PW@MIL-100(Fe).

Characterization

Powder X-Ray diffraction (PXRD) data were collected on the Rigaku 2550V X-ray diffractometer with Cu Kα radiation. The images of the scanning electron microscope (SEM) and transmission electron microscopy (TEM) were captured by Hitachi SU-8220 Field emission scanning electron microscope and JEM-2100F Field emission transmission electron microscope, respectively. Thermogravimetric analysis (TGA) was obtained under flowing Ar on an SDT Q600 V8.3 Build 101 thermal analysis device with a temperature-increasing rate of 5 ^{o}C/min in Ar. N_2 sorption experiments were performed on a Micromeritics ASAP2460 aperture analyzer. Fourier transform infrared (FTIR) spectra were recorded on a Lambda FTIR-7600 spectrometer over 4000-400 cm^{-1} with a resolution of 4 cm^{-1}. Pyridine infrared spectra (Py-IR) were obtained on PerkinElmer Frontier. The pellets were placed in an in-situ cell equipped with ZnGe windows. The inductively coupled plasma optical emission spectroscopy (ICP-OES, Agilent 5110) was used to determine the SiW. Electron paramagnetic resonance (EPR) spectra were obtained from a Bruker EMXnano EPR spectrometer (9.828 GHz, X-band). Solid-state NMR experiments were performed on a Bruker Avance III HD 400WB (9.4 T) spectrometer equipped with a 3.2 mm CPMAS probe at spinning speeds of 15-24 kHz. ^{1}H MAS NMR spectra were acquired with a $\pi/2$ pulse of 3 μs and a recycle time of 2 s, processed with background subtraction, and were referenced to adamantane at 1.9 ppm (relative to TMS at 0 ppm). $^{13}C\{^{1}H\}$ MAS NMR spectra were acquired with a ^{13}C $\pi/2$ pulse of 3.57 μs, a ^{1}H decoupling field strength of 80 kHz, and a recycle time of 2 s. The ^{13}C chemical shifts were referenced externally to glycine COOH at 176.2 ppm.

Synthesis of p-xylene from furan derivatives with acrylic acid over the catalysts

Typically, 2,5-dimethylfuran (DMF, 5 mmol) and acrylic acid (AA, 30 mmol) were added into a glass pressure tube with a given mass of catalysts, n-heptane as an internal standard, and the experiment was performed under 140 °C for 24 h in CO_2 atmosphere. After the reaction, the reactor was cooled to room temperature, and the liquid products were analyzed using Gas Chromatography (GC). The yields and selectivity of products were analyzed by GC 2060 with a SE-54 column and a flame ionization detector (FID). The products of CO_2 and p-Tolyl-2,5-xylylmethane were analyzed by GC (Tianmei 7900) with a TDX-01 column and an FID. Then identifications of them were performed by Gas Chromatography-Mass Spectrometer (GC-MS) (Agilent 7890A-5975C) equipped with an HP-5MS column and an FID.

Catalyst sample treatment method for solid-state NMR test

A certain mass of catalyst sample was suspended and stirred in a probe solution (such as acetone, 2,5-dimethylfuran, or H_2O) for 30 minutes. The resulting sample was collected by centrifugation at 12000 rpm for 3 min and dried in an oven at 60 °C overnight, then used for solid-state NMR tests.

Quantitative calculation

$$Conversion\ of\ DMF = \frac{moles\ of\ DMF\ reacted}{initial\ moles\ of DMF} \times 100\ \%$$

$$Selectivity\ of\ product = \frac{moles\ of\ product}{moles\ of DMF\ reacted} \times 100\ \%$$

$$Yield = Conversion \times Selectivity$$

TOF calculation

$$\text{TOF (mol (mol SiW or Fe(III)*h)}^{-1}\text{)} = \frac{Num.\ of\ reacted\ DMF\ (mol)}{Num.\ of\ POM\ or\ Fe\ loading\ (mol) \times Time(hour)}$$

The loading of POM or Fe was calculated regarding the ICP results.

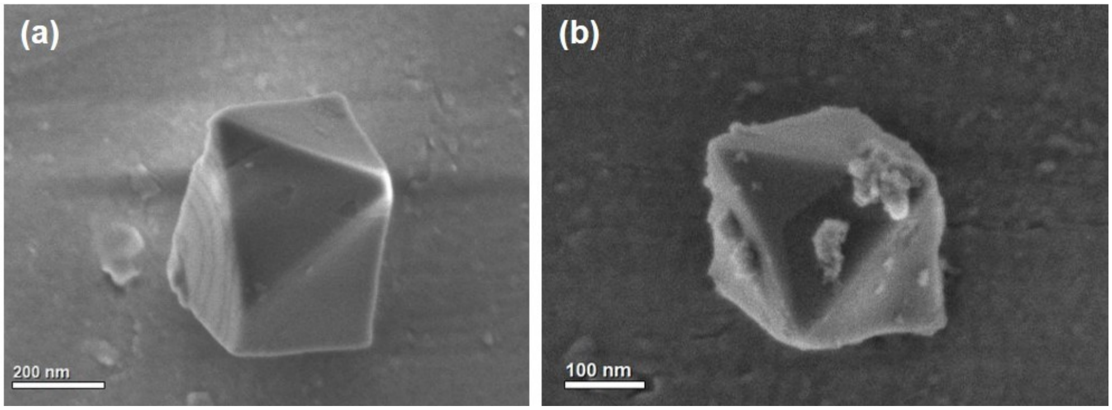


Figure S1. SEM images of (a) MIL-100(Fe) and (b) SiW@MIL-100(Fe)-3.

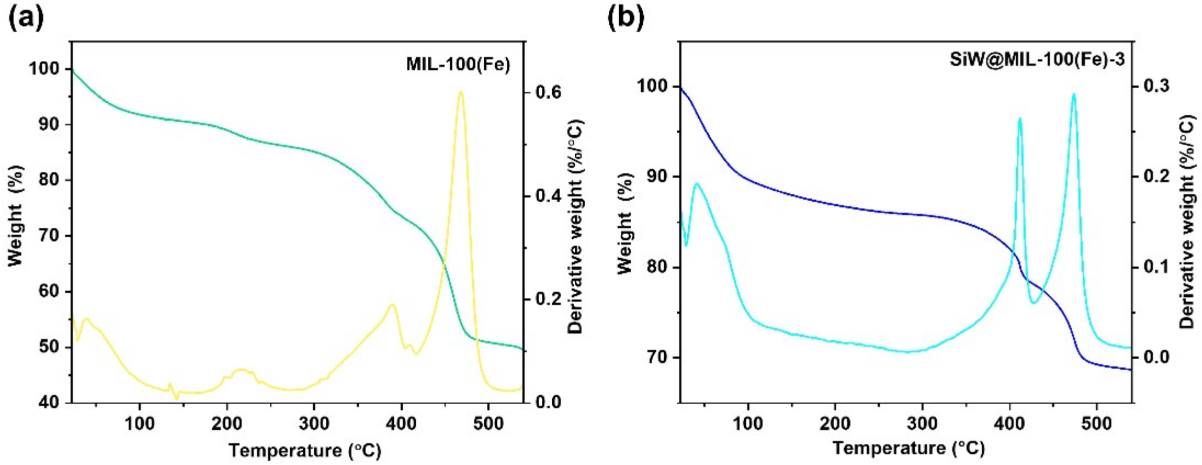


Figure S2. TGA-DTA analysis of (a) MIL-100(Fe) and (b) SiW@MIL-100(Fe)-3.

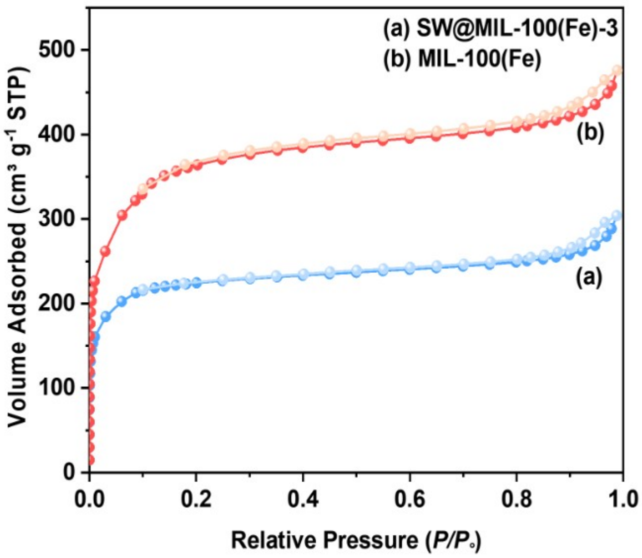


Figure S3. Absorption and desorption isotherm of MIL-100(Fe) and SiW@MIL-100(Fe)-3.

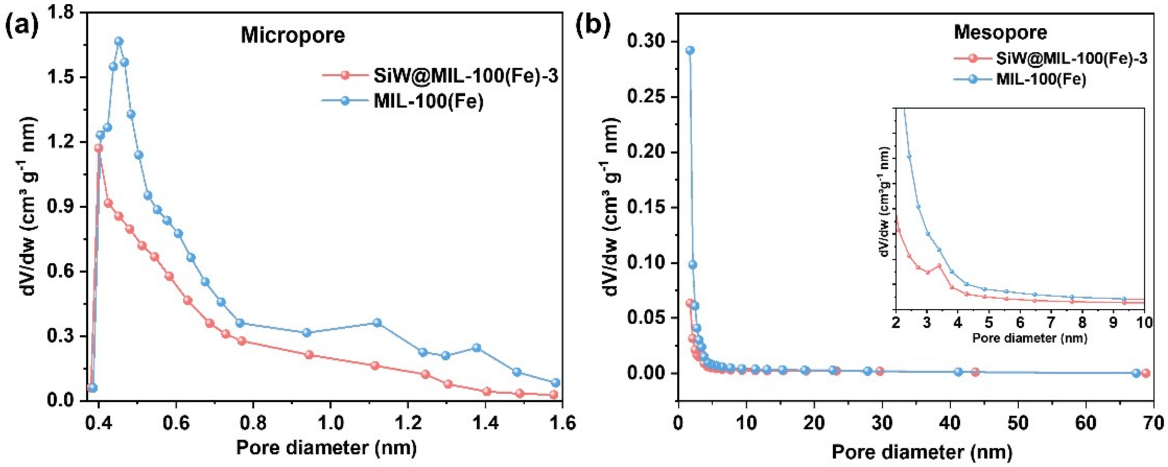
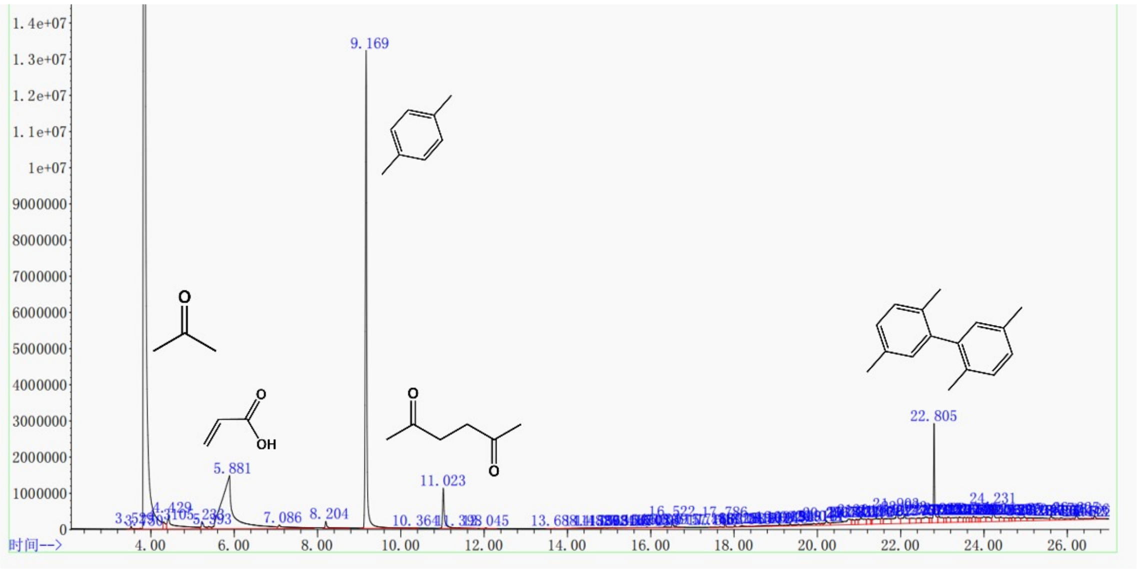


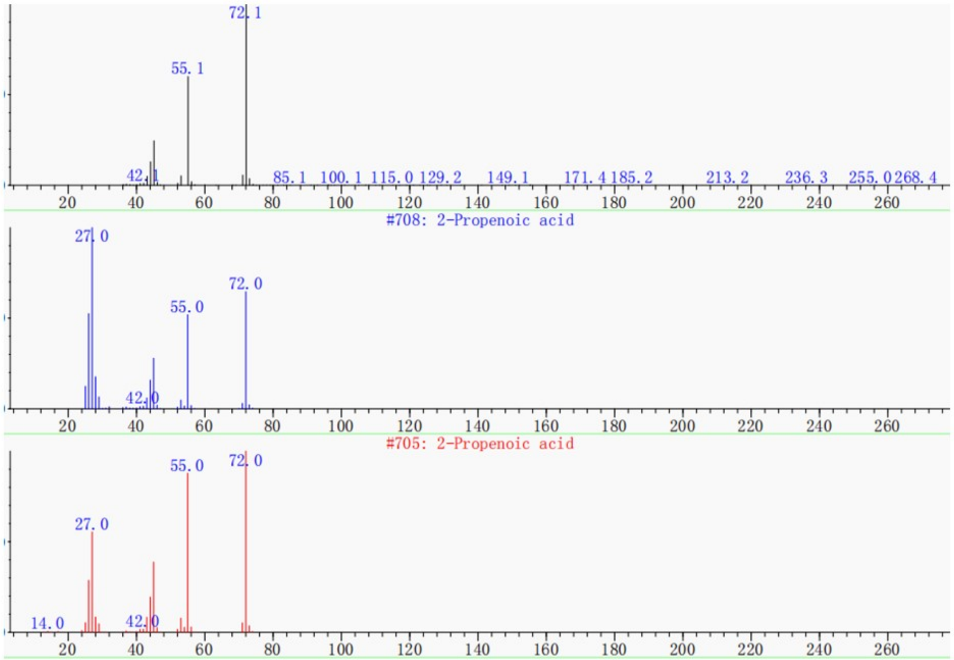
Figure S4. (a) Micropore size and (b) mesopore size distribution of MIL-100(Fe) and SiW@MIL-100(Fe)-3.

GC-MS details

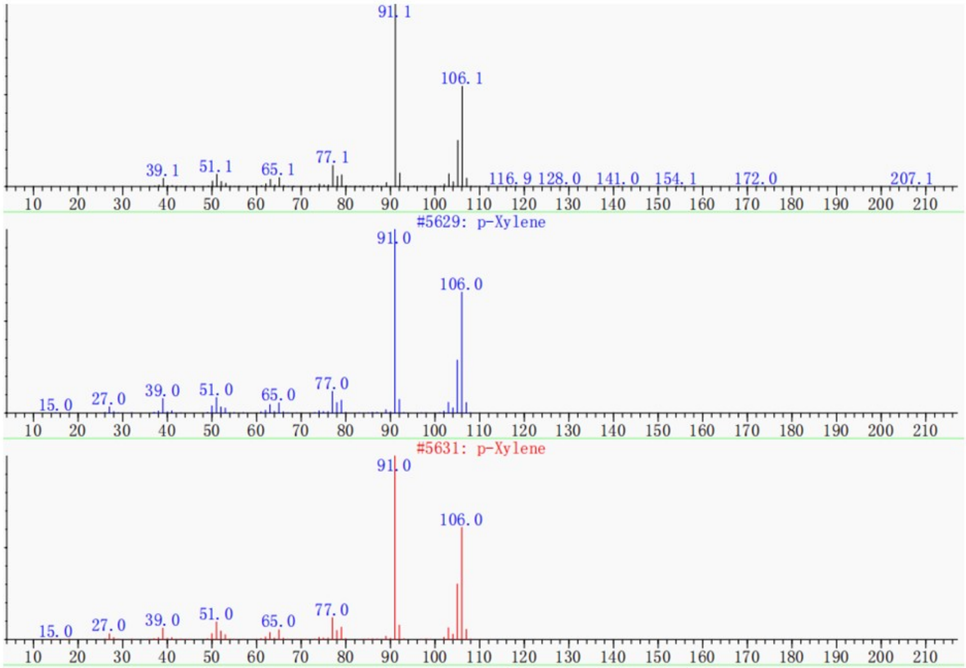
The results from GC-MS (Table 1, entry 3) is shown in Figure S4, and the major peaks at retention time 3.8, 5.8, 9.1, 11.0, and 22.8 minutes stand for acetone (as diluent), AA, PX, 2,5-hexanedione, and p-tolyl-2,5-xylylmethane, respectively.



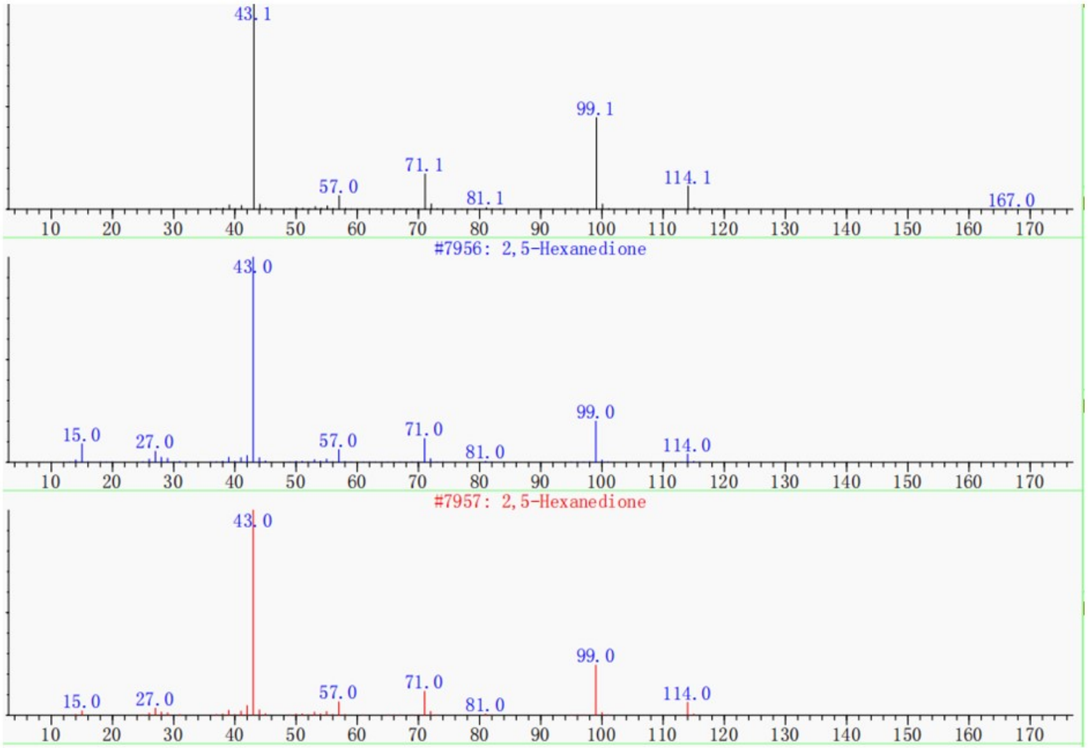
propenoic acid (5.8 min)



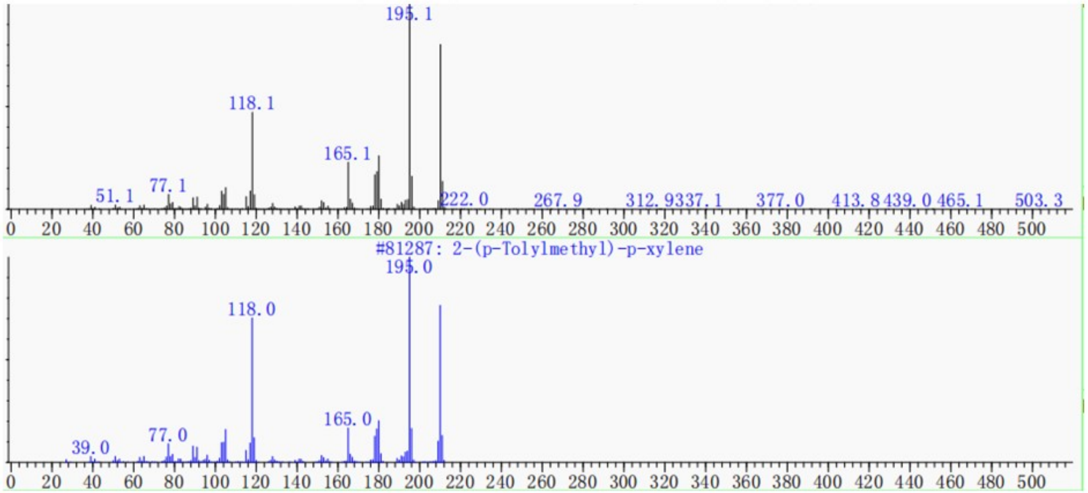
p-xylene (9.1 min)



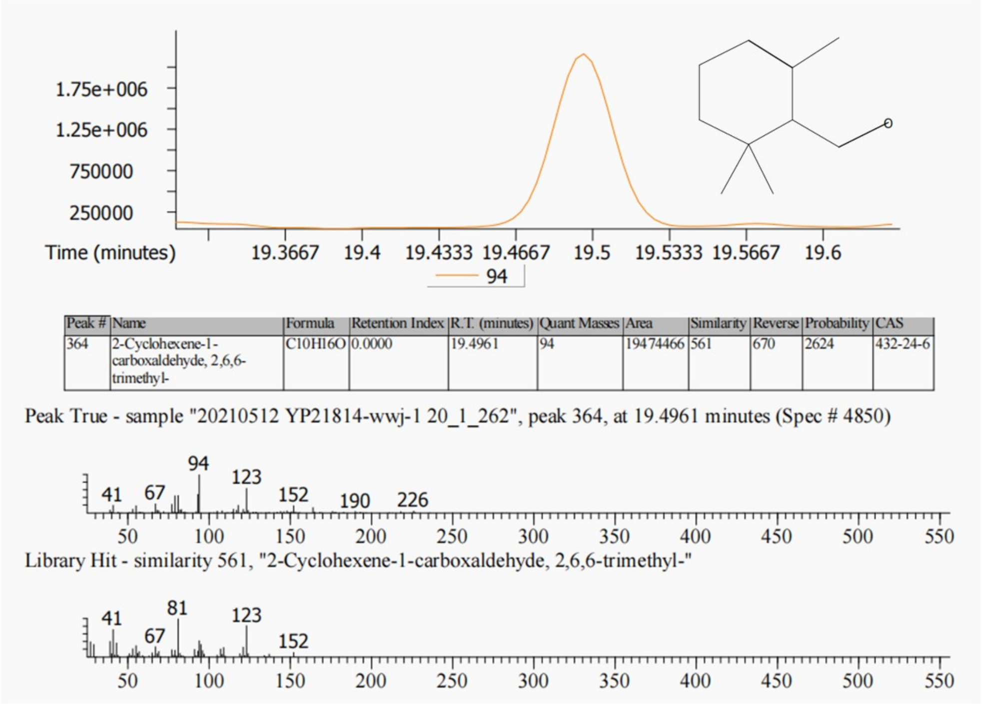
2,5-hexanedione (11.0 min)



p-tolyl-2,5-xylylmethane (22.8 min)



Possible intermediates 1

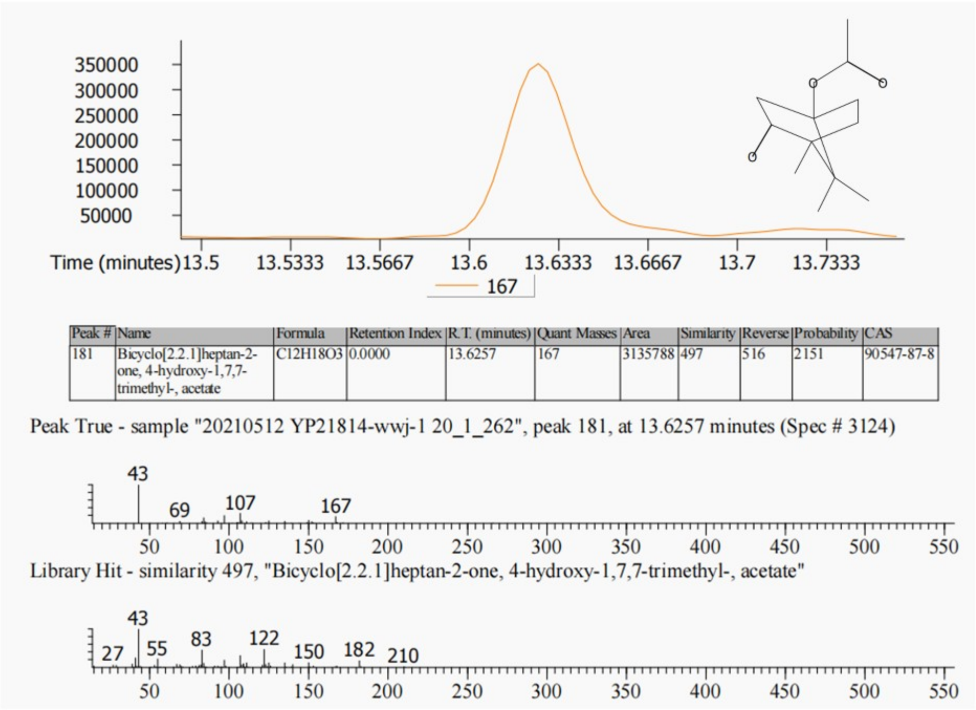


Peak #	Name	Formula	Retention Index	R.T. (minutes)	Quant Masses	Area	Similarity	Reverse	Probability	CAS
364	2-Cyclohexene-1-carboxaldehyde, 2,6,6-trimethyl-	C10H16O	0.0000	19.4961	94	19474466	561	670	2624	432-24-6

Peak True - sample "20210512 YP21814-wwj-1 20_1_262", peak 364, at 19.4961 minutes (Spec # 4850)

Library Hit - similarity 561, "2-Cyclohexene-1-carboxaldehyde, 2,6,6-trimethyl-"

Possible intermediates 2



Peak #	Name	Formula	Retention Index	R.T. (minutes)	Quant Masses	Area	Similarity	Reverse	Probability	CAS
181	Bicyclo[2.2.1]heptan-2-one, 4-hydroxy-1,7,7-trimethyl-, acetate	C12H18O3	0.0000	13.6257	167	3135788	497	516	2151	90547-87-8

Peak True - sample "20210512 YP21814-wwj-1 20_1_262", peak 181, at 13.6257 minutes (Spec # 3124)

Library Hit - similarity 497, "Bicyclo[2.2.1]heptan-2-one, 4-hydroxy-1,7,7-trimethyl-, acetate"

Figure S5. The products of the test (Table 1, entry 3) by GC-MS. (GC-MS Agilent 7890A-5975C equipped with HP-5MS column and an FID)

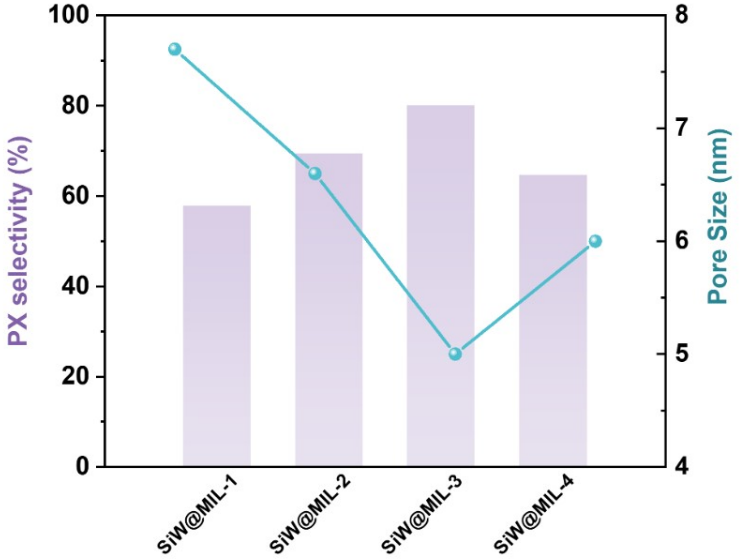


Figure S6. The correlation trend between catalytic performance and pore size.

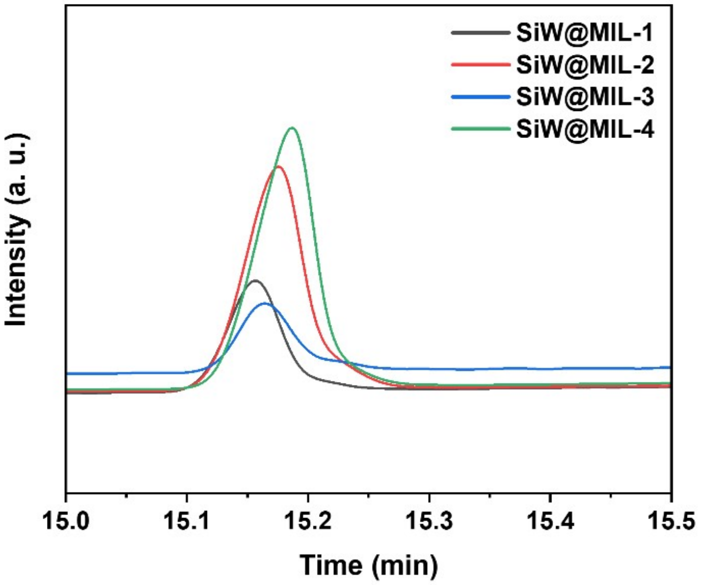


Figure S7. The GC signals of of the by-product PTX, dimer of PX, over SiW@MIL-100(Fe)-n (n =1-4) catalysts. (GC 2060 with SE-54 column and a FID).

Decarboxylation step

The proposed hypothesis was confirmed by the following methods. Firstly, signals of carbon dioxide and ethylene (decarboxylation product of AA) were detected during the reaction with N_2 atmosphere **(Figure S8)**. Specifically, ethylene and carbon dioxide were detected when the mixture of AA and SiW@MIL-100(Fe)-3 was heated to 140 °C (**Figure S8**). Secondly, no undecarboxylated products such as 2,5-DMBA were detected during the reaction analyzed by GC-MS (**Figure S5).**

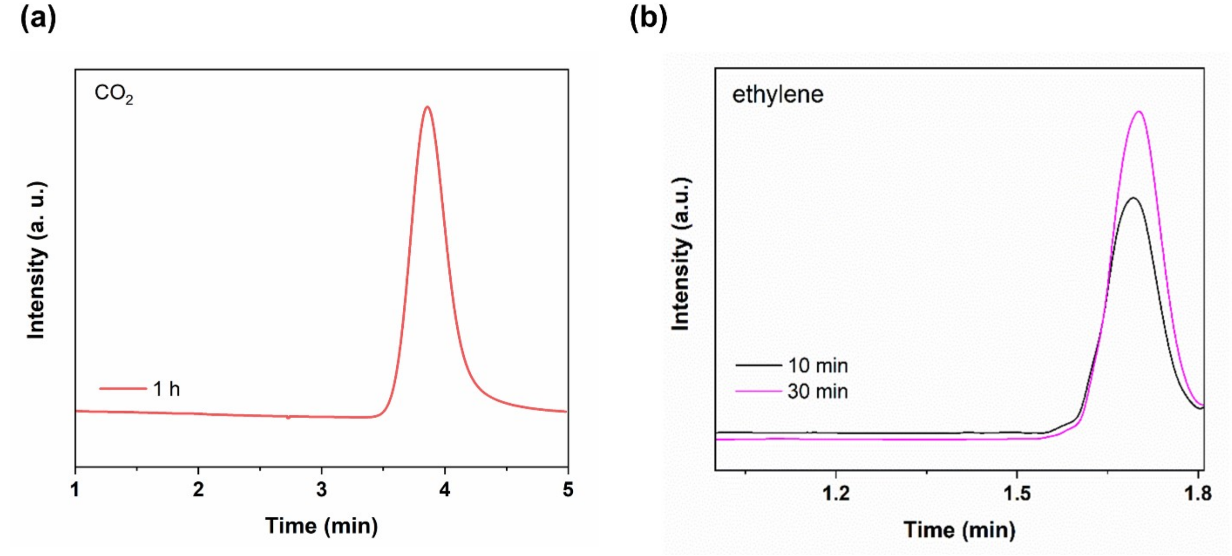


Figure S8. (a) The carbon dioxide signals and (b) ethylene (with retention time 1.70 min and 3.8 min, respectively) of reaction detected by GC (Tianmei 7900) with a TDX-01 and SE-54 column and a FID. Reaction conditions: 30 mmol AA, SiW@MIL-100(Fe)-3, 400 mg, 140 ^{o}C in N_2.

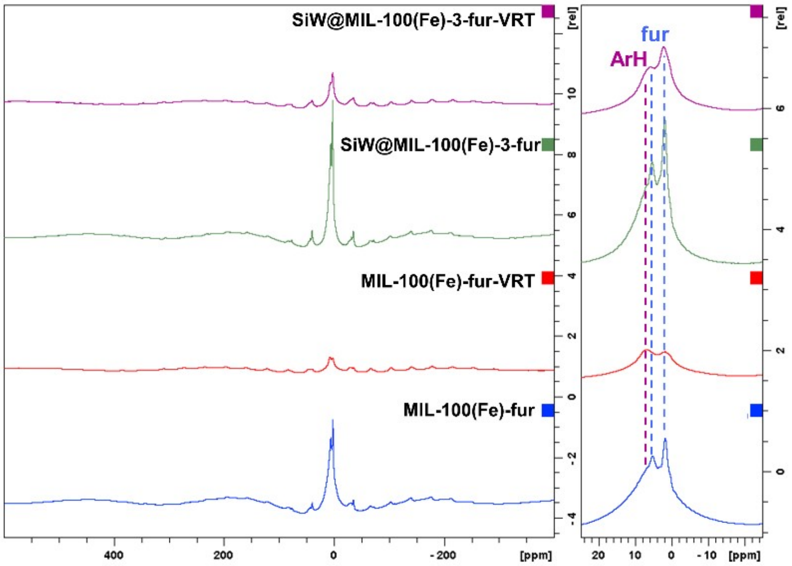


Figure S9. ^{1}H spectra of MIL-100(Fe)-fur and SiW@MIL-100(Fe)-3-fur with and without vacuum treatment at 25 ^{o}C. (SS =15kHz)

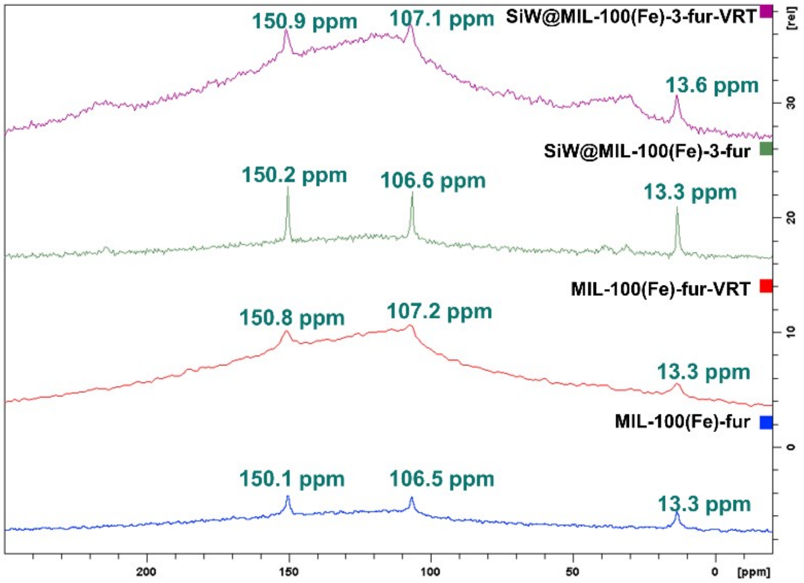


Figure S10. ^{13}C {^{1}H} spectra of MIL-100(Fe)-fur and SiW@MIL-100(Fe)-3-fur with and without vacuum treatment at 25 ^{o}C. (SS =15kHz)

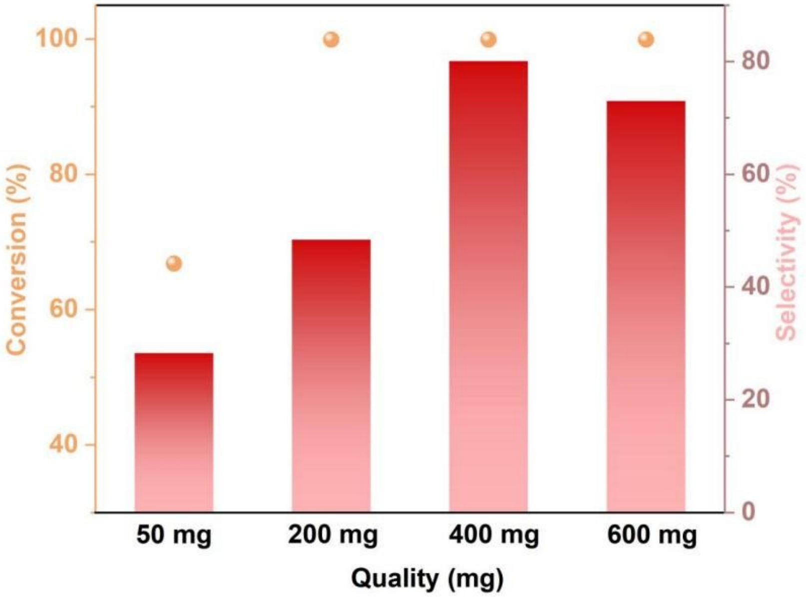


Figure S11. The quality effect of DMF and AA to PX with SiW@MIL-100(Fe)-3.

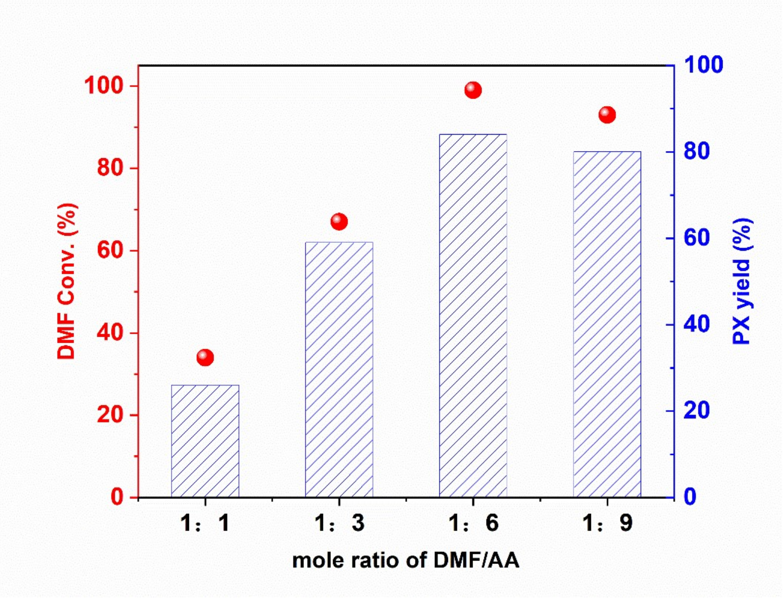


Figure S12. The effects of DMF/AA molar ratios. Reaction conditions: 5 mmol DMF, 30 mmol AA. 140 °C, 24 h, 1 bar CO_2, 400 mg catalyst.

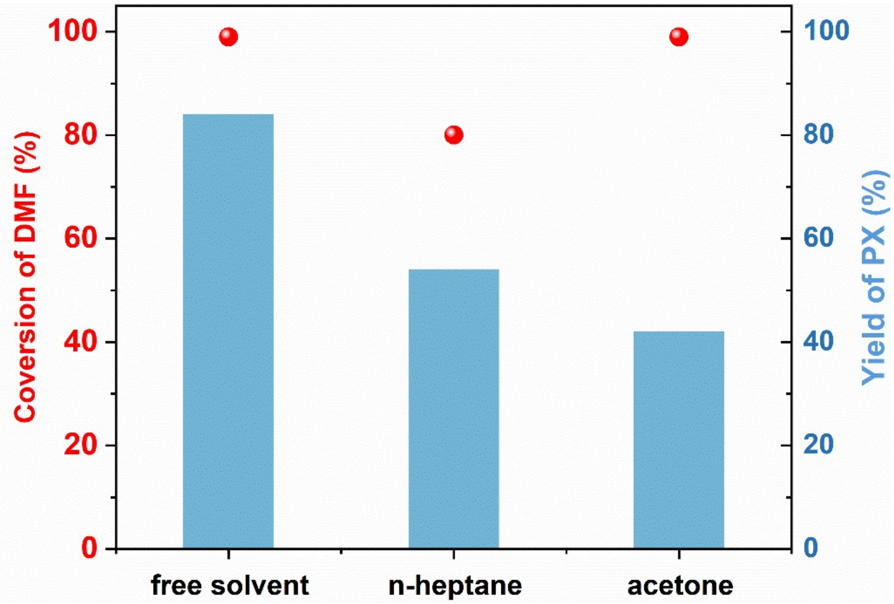


Figure S13. The solvent effects of DMF and AA to PX reaction. Reaction conditions: 2 mL additional solvent was added.

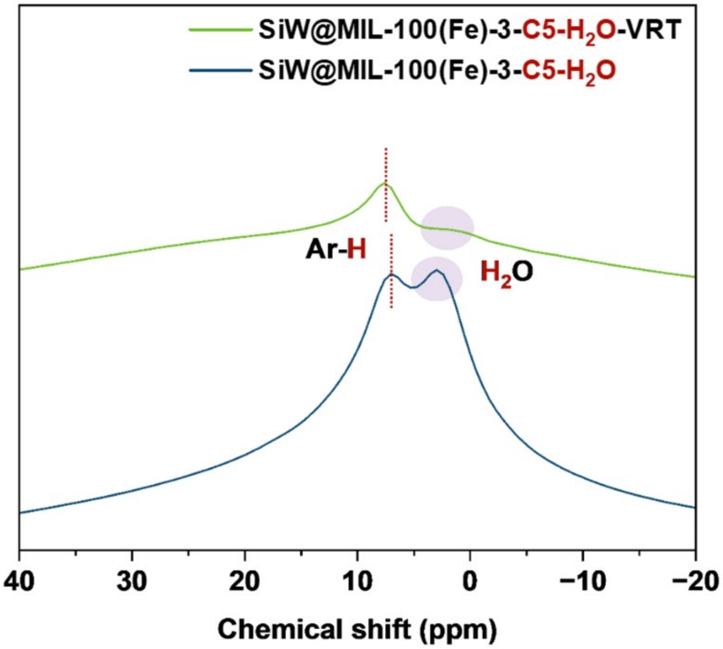


Figure S14. ^{1}H MAS NMR spectra of SiW@MIL-100(Fe)-3-H_2O-C5 with and without vacuum treatment at 25 ^{o}C. (SS =15kHz)

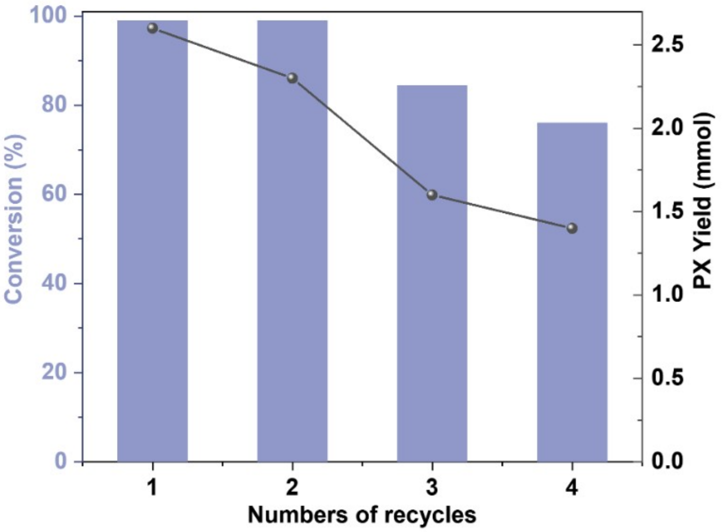


Figure S15. The cycle performance of SiW@MIL-100(Fe)-3-ace-C4 (scrubbed by acetone). (Reaction condition: 5 mmol DMF, 30 mmol AA, 140 ^{o}C, 1h, 400 mg SiW@MIL-100(Fe)-3 as the catalyst. Reaction yields were determined by gas chromatography using n-heptane as an internal standard.)

Stability of SiW@MIL-100(Fe)-3

To verify the stability of SiW@MIL-100(Fe)-3, we characterized the recovered catalyst by XRD and TEM. The XRD pattern showed some amorphization (in the range of 3-10 degree) after reaction and the peak at 20 degree shifted slightly towards lower angles (**Figure S16**), which might be a result of the adsorbed acrylic acid. Similar phenomena of a shift of diffraction peak caused by adsorbed molecules have been reported.[1] That acrylic acid coordinated with Fe sites was verified by the diffuse reflection curve of the catalyst (**Figure S17**). UV-vis diffuse reflection spectra (UV-vis DRS) showed that the absorption curve of the SiW@MIL-100(Fe)-3 with adsorption of acrylic acid was red-shifted. Similarly, the curve of the recovered catalysts showed the same shift. In addition, the TEM images before and after the reaction were shown in **Figure S18**, and there is no significant change in the morphology of the catalyst.

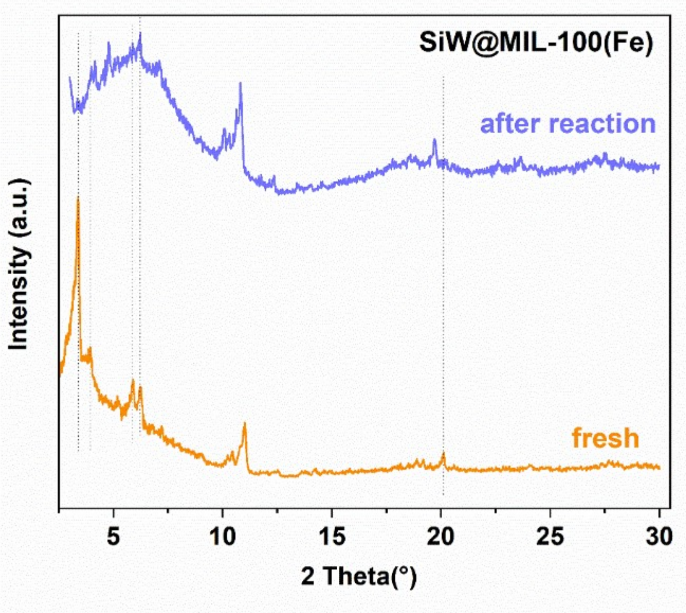


Figure S16. XRD patterns of SiW@MIL-100(Fe)-3 and recovered SiW@MIL-100(Fe)-3.

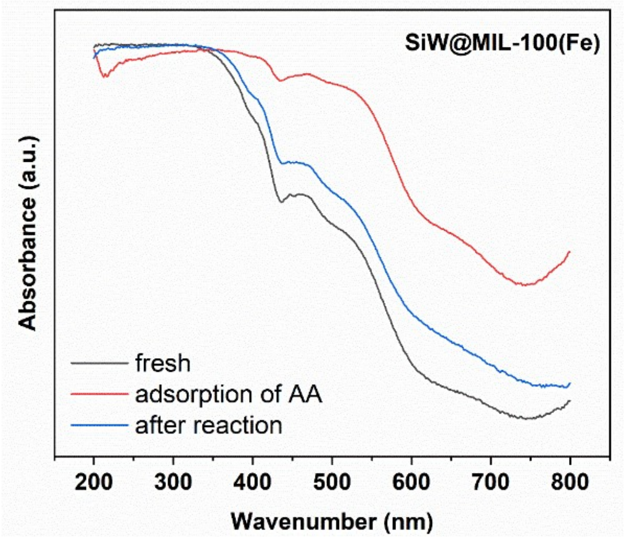


Figure S17. UV-vis DRS of SiW@MIL-100(Fe)-3 and recovered SiW@MIL-100(Fe)-3.

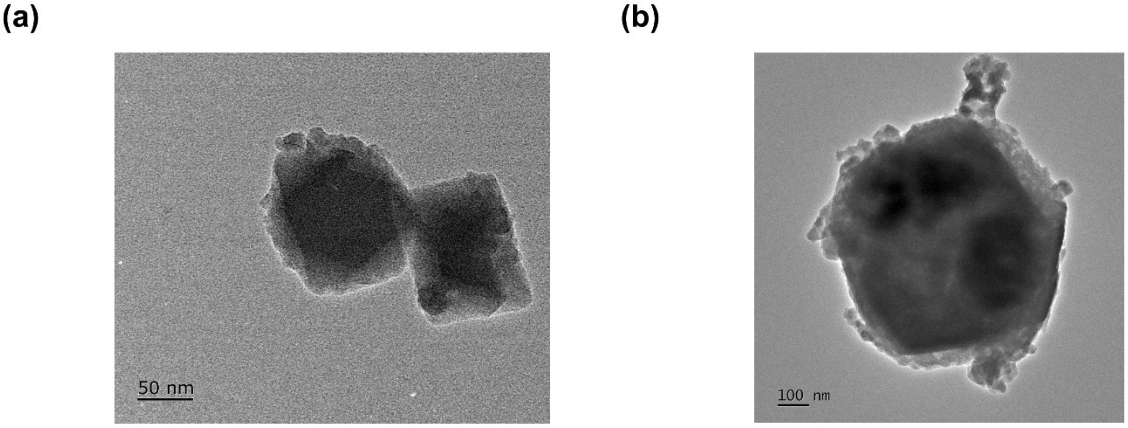


Figure S18. TEM images of (a) SiW@MIL-100(Fe)-3 and (b) used SiW@MIL-100(Fe)-3.

Table S1. The specific data of the pore canal of the samples.

	Surface Area ($m^2 \cdot g^{-1}$)	Pore Volume ($m^2 \cdot g^{-1}$)	Pore Size (nm)
MIL-100(Fe)	1,394.1	0.73	3.1
SiW@MIL-100(Fe)-1	757.0	0.49	7.7
SiW@MIL-100(Fe)-2	707.3	0.43	6.6
SiW@MIL-100(Fe)-3	849.8	0.47	5.0
SiW@MIL-100(Fe)-4	637.5	0.36	6.0

Table S2. The composition of catalysts calculated from ICP-OES.

	Fe (wt %)	W (wt %)
SiW@MIL-100(Fe)-1	13.22	13.19
SiW@MIL-100(Fe)-2	12.13	14.49
SiW@MIL-100(Fe)-3	11.46	25.09
SiW@MIL-100(Fe)-4	12.06	21.67

Table S3. Summary of the references on the synthesis of PX over heterogeneous catalysts.

Catalyst	Dienophile	T (°C)	P (bar)	Time (h)	DMF Conv. (%)	PX Yield (%)	Ref.
H-Y zeolite	ethylene	300	57	-	~90	68	[2]
Mesoporous MFI	ethylene	250	50	24	~99	76	[3]
Dealuminated H-Beta Zeolites	ethylene	300	40	20	99	96	[4]
Beta(Si/Al=150)	acrylic acid	200	30	0.17	100	83	[5]
SAPO-34	ethylene	250	20	24	84	63	[6]
SiO_2-SO_3H	ethylene	250	45	6	67	60	[7]

SnPO	ethylene	250	<20	18	~99	93	[8]
ZrP grafted SBA-15	ethylene	250	20	2	83	79	[9]
WOx/SiO_2	ethylene	300	54	6	62	45	[10]
NbOx/MCM	ethylene	250	40	10	~99	96	[11]
Bi-BTC	acrylic acid	160	10	24	99	92	[12]
[Bmim]HSO_4/Cu_2O/4,7-diphenyl-1,10-phenanthroline/1-methyl-2-pyrrolidinone/quinoline	acrylic acid	25/210	1	1+4	87	72.2	[13]
$Sc(OTf)_3$+H_3PO_4/Cu_2O/4,7-diphenyl-1,10-phenanthroline/1-methyl-2-pyrrolidinone/quinoline	acrylic acid	15/210	1	1+4	90	56.7	[14]
SiW@MIL-100(Fe)-3	acrylic acid	140	1	24	99	84	This work

Yield=Conversion×selectivity×100%

References:

1. J. Ethiraj, F. Bonino, J. G. Vitillo, K. A. Lomachenko, C. Lamberti, H. Reinsch, K. P. Lillerud and S. Bordiga, *ChemSusChem.,* 2016, **9**, 713-719.
2. C. L. Williams, C. C. Chang, P. T. M. Do, N. Nikbin, S. Caratzoulas, D. G. Vlachos, R. F. Lobo, W. Fan and P. J. Dauenhauer, *ACS Catal.*, 2012, **2**, 935-939.
3. J. Kim, R. Ryoo, M. V. Opanasenko, M. V. Shamzhy and J. Čejka, *ACS Catal.*, 2015, **5**, 2596-2604.
4. R. Zhao, Z. Zhao, S. Li, A. Parvulescu, U. Müller and W. Zhang, *ChemSusChem.*, 2018, **11**, 3803-3811.
5. J. A. Mendoza Mesa, F. Brandi, I. Shekova, M. Antonietti and M. Al-Naji, *Green Chem.*, 2020, **22**, 7398-7405.
6. Z. Gao, Y. Feng, L. Zhang, X. Zeng, Y. Sun, X. Tang, T. Lei and L. Lin, *ChemistrySelect.*, 2020, **5**, 2449-2454.
7. X. Feng, C. Shen, C. Tian and T. Tan, *Ind. Eng. Chem. Res.*, 2017, **56**, 5852-5859.
8. X. Feng, Z. Cui, K. Ji, C. Shen and T. Tan, *Appl. Catal. B.*, 2019, **259**, 118108.
9. S. Kasipandi, J. M. Cho, K. S. Park, C. Shin and J. Wook Bae, *J Catal.*, 2020, **385**, 10-20.
10. Z. Cui, X. Feng, H. Li and T. Tan, *Chem. Eng. Sci.*, 2020, **227**, 115942.
11. Y. Zhao, K. Wang, Z. Sun, Q. Zhang, Z. Wang, Y. Liu, H. He and Y. Cao, *Green Chem.*, 2022, **24**, 4095-4107.
12. J. Yeh, S. S. Chen, S. Li, C. H. Chen, T. Shishido, D. C. W. Tsang, Y. Yamauchi, Y. Li and K. C. W. Wu, *Angew. Chem. Int. Ed.*, 2021, **60**, 624-629.
13. L. Ni, J. Xin, K. Jiang, L. Chen, D. Yan, X. Lu and S. Zhang, *ACS Sustain. Chem. Eng.*, 2018, **6**, 2541-2551.
14. L. Ni, J. Xin, H. Dong, X. Lu, X. Liu and S. Zhang, *ChemSusChem.*, 2017, **10**, 2394-2401.