Electronic Supplementary Material (ESI) for Chemical Communications.

Phenolics isolation from bio-oil using the metal-organic framework MIL-53 as highly selective adsorbents

Experimental section

Material All reagents and solvents were purchased from commercial sources and used without further purification

Synthesis of Materials. The hydrothermal synthesis of MIL-53(Al)-as (as-synthesized) was based on a literature procedure[1]. Typically, 15 g of $Al(NO_3)_3 \cdot 9H_2O$ (Riedel-de Haën, 98%), 3.2 g of terephthalic acid (Acros, 99+%), and 30 mL of H_2O were mixed in a 250 mL Teflon-lined stainless steel autoclave, which was heated at 220°C for 3 days. After cooling down, washing with H_2O, and drying at 60°C, the white powder was calcined in shallow beds in a muffle furnace in air at 300°C for 24 hours to remove the terephthalic acid residing in the pores. The obtained material had a pore volume of 0.50 mL g^{-1} and a specific surface of 1293 m^2 g^{-1}(see Figure S4). XRD revealed a single-phase material before adsorption. Crystals between 2 and 10 μ m were observed with scanning electron microscopy (SEM).

The hydrothermal synthesis of MIL-53(Cr)-as was based on a literature procedure [2]. Typically, 12 g of $Cr(NO_3)_3 \cdot 9H_2O$ (Acros, 97%), 4.85 g of terephthalic acid (Acros, 99+%), 6mL of HF (48 wt. % in H_2O) and 150mL of H_2O were mixed in a 250 mL Teflon-lined steel autoclave, which was heated at 220°C K for 3 days. Calcination of MIL-53(Cr)-as was typically performed by treating 20 mg of the material in a 1.8 mL GC vial in a muffle furnace in air at 300°C for 40 h to remove the occluded terephthalic acid from the pores. The obtained material had a pore volume of 0.26 mL g^{-1} and a specific surface of 915 m^2 g^{-1}(see Figure S4). XRD revealed a single-phase material before adsorption.

The hydrothermal synthesis of MIL-47(V)-as was based on a literature procedure [3]. Typically, 12.2 g of VCl_3 (Acros, 97%), 3.2 g of terephthalic acid (Acros, 99+%), and 140mL of H_2O were mixed in a 250 mL Teflon-lined steel autoclave, which was heated at 200 °C for 4 days. Calcination of MIL-47(V)-as was typically performed by treating the material in a muffle furnace in air at 300°C for 40 h to remove the occluded terephthalic acid from the pores and to oxidize V^{III} to V^{IV}. XRD revealed a single-phase material before adsorption. The obtained material had a pore volume of 0.39 mL g^{-1} and a specific surface of 814 m^2 g^{-1} (see Figure S4).

Characterization

Powder x-ray diffraction (PXRD) patterns for samples were taken on a Stoe COMBI P diffractometer equipped with Cu Kα radiation (λ= 0.15405 nm). Thermogravimetric analysis (TGA) was performed under

O_2 atmosphere with the heating rate of 5 °C min^{-1} on a TQA 500 of TA Instruments. FTIR spectra were recorded on a Nicolet Nexus spectrometer with an extended KBr beam splitting device and a MCT cryo-detector in the range of 4000-400 cm^{-1} (around 6 mg samples were diluted with 200 mg KBr). N_2 physisorption measurements were performed on a Micrometrics 3Flex surface analyzer at liquid nitrogen temperature (77 K). Prior to the measurements, the samples (50-100 mg) were outgassed under 0.1 mbar vacuum at 200℃ for 5 hours. Surface area calculations were performed by using the 3Flex Version1.01 program. Uptakes from water methanol mixture were directly calculated from HPLC output data recorded on an Agilent SL1200 binary system equipped with a ZORBAX RRHD SB-C18 column and a UV detector (λ =240 nm). Uptakes from methanol and real bio-oil mixture were calculated from the GC-FID (gas chromatography-flame ionization detector) output data recorded on a Shimadzu GC-2014 equipped with CP-sil 5CB 60mm column. The identification of the real bio-oil mixture was performed on a Agilent 6890N GC-5973N MSD gas chromatograph (GC-MS) equipped with a 100% dimethylpolysiloxane column (HP-1MS 30 mx 0.25mm ID ×0.25um). Scanning electron microscopy (SEM) images were obtained using a Philips XL 30 FG. The Al content of the solution after adsorption (from 0.05 M aqueous solution) on MIL-53(Al) was determined by ICP-OES analysis using a Varian 720-ES equipped with a double-pass glass cyclonic spray chamber, and a Sea Spray concentric glass nebulizer.

Adsorption Experiments

Liquid-phase batch adsorption experiments for mimic bio-oil were carried out at 298 K in 1.8 mL glass vials filled with 0.020 g adsorbent and a solution of methanol or methanol : water (v : v 1 : 1) containing target molecules following a literature procedure. Uptakes from methanol were directly calculated from GC output data recorded on a gas chromatography-flame ionization detector (GC-FID) with the CP-sil 5CB 60mm column. Uptakes from methanol : water (v : v 1 : 1) were directly calculated from HPLC output data recorded on an Agilent SL 1200 binary system equipped with a ZORBAX RRHD SB-C18 column and a UV detector. From both GC and HPLC analysis, equilibrium and initial concentrations of guest molecules were determined. The differences between these pairs of concentration values were used directly for the calculation of adsorbed amounts, expressed as weight percentages (wt.%).

Desorption of 4-MeG from MOFs

After the adsorption experiment, the MOF was firstly rinsed with water in order to remove the 4-MeG absorbed on the surface of the material, afterwards the absorbent (~20 mg) was immersed in 10 mL (7.92 g / 20 mg)of methanol solution. The mixture was stirred for 1 hour, followed by recovery through centrifugation. The supernatant was characterized by HPLC and the MOF was characterized by PXRD.

Breakthrough experiment

A breakthrough experiment was performed according to reference [4]. It was conducted with an HPLC pump and a 5 cm stainless-steel column filled with MOF material (0.3 g). A feed of methanol : water mixture containing 4-MeG and Furfuryl alcohol(both with concentration of 0.05 M), was through the column packed with MIL-53(Al)-lt, at a rate of 0.137 mL/min. The column outlet (every two minutes) was manually sampled and afterward analyzed by HPLC.

Adsorption and desorption performed on real pyrolysis oil

Adsorption experiments for crude bio-oil were performed in 10 mL glass vials filled with MOF (100 mg) and 5 mL bio-oil at room temperature. The mixture was allowed to be stirred under room temperature for 3 hours. After that the mixture was centrifuged (2500 r/min, 5 min) and rinsed with methanol to remove the compounds absorbed on the surface of MOFs. 5 mL of methanol was added with stirring at room temperature for about 3 hours to desorb the adsorbed components from the MOFs. This procedure was repeated twice until the supernatant became transparent. We collected the supernatant and evaporated the methanol prior to analysis.

In order to identify the compounds, crude bio-oil and the extracted fractions were analyzed with a Agilent 6890N GC - 5973N MSD gas chromatograph (GC-MS). A 100% dimethylpolysiloxane column was used (HP-1MS 30 mx0.25 mm ID × 0.25 μ m. The column temperature was maintained at 50 °C for 2 minutes then to 200°C at a rate of 5 °C per minute and then set to hold 2 minute at 200 °C, finally to 300 °C at a rate of 30 °C per minute. The initial assignment of each compounds peak was established by comparison to NIST MS Spectral library (v. 2.2) 2008.

For quantitative analysis, the same crude bio-oil and the extracted fractions used in GC-MS were re-analyzed, with dichlorobenzene(when pyridine was used as solvent) and toluene (when methanol was used as solvent) as internal standards, using gas chromatography-flame ionization detector (GC-FID) with a similar column (CP-sil 5CB 60mm) and similar conditions as used in GC-MS. After matching each identified phenolic peak via GC-MS with the peaks on GC-FID, the relative response factor (RRF) of each phenolic compound identified was calculated using the effective carbon number (ECN) method, which was then used to evaluate concentrations of the identified species by comparison with the reference compound (toluene). A description in more detail is enclosed in Table S1 by using Equations S1 and 2. The identified compounds are summarized in Table S2.

In order to see the signals for carboxylic acid, alcohols and sugars, silylation of the oil in pyridine was conducted by using N,O-Bis(trimethylsilyl)trifluoroacetamide (BSTFA). Typically, 600 μl of BSTFA was

added to the pyridine dissolved bio-oil and then the mixture was heated at 60° for 1 hours. Afterwards, the mixture was analyzed by GC-MS and GC-FID. In this stage, all of the observed acids, alcohols and sugars were silylated. In their mass spectrograms, the fragment [M-73] was observed, resulting from the cleavage of the t-butyl moiety and one hydrogen (mass count 73). The identified compounds are summarized in Table S3.

Table S1 ECN reduction values by functional group used for analysis in this experiment.

Functional group	*ECN reduction*
Phenol	*0.83*
Ether	*1*
Olefinic C	*0.95*
Carbonyl	*1*
Carboxyl	*1*
Primary Alcohol	*0.5*
Secondary Alcohol	*0.75*
Ester	*1*

$$Fw = \frac{\mathrm{Mc}\times\mathrm{ECNi}}{\mathrm{Mi}\times\mathrm{ECNc}} \quad \text{Equation S1}$$

$$Mc = \frac{\mathrm{Ac}\times\mathrm{ECNi}\times\mathrm{Mi}}{\mathrm{Ai}\times\mathrm{ECNc}} \quad \text{Equation S2}$$

Fw is the response factor, ECN is the effective carbon number, M is the concentration, A is the peak area. The subscript *i* indicates the internal standard, c indicates the compound.

Table S2 Identification and quantification of each compound in crude bio-oil.

	detected molecules	number of carbons	carbon reduction	ECN(theoretical)	Mw	Concentration (mg/ml)
Internal standard	toluene	7	7	7	91	8.7
1	2-cyclopenten-one	5	1+0.05x2	3.9	98	5.15
2	Furfuryl alcohol	5	1+0.5+0.05x2	3.4	130	1.68
3	2 5-dimethyltetrahydrofuran	6	1+1+1	3	132	7.96
4	2-methyl-cyclopenten-1-one	6	1+0.05x2	4.9	96	1.35
5	2-Acetylfuran	6	2+0.05x4	3.8	110	0.81
6	2-methyl-cyclopenten-1-one	6	1+0.05x2	4.9	96	1.36
7	2-pentenal-2-methyl	6	1.1	4.9	98	0.83
8	2-furan-2-yl-2-methoxy-ethanol	7	1+1+0.5+0.05x4	4.3	142	0.27
9	phenol	6	0.83	5.17	94	2.26
10	3-methyl-1,2-cyclopentanedione	6	1x2	4	112	8.24
11	2,3-dimethyl-2-cyclopenten-1-one	7	1+0.05x2	5.9	110	0.26
12	Hexanal dimethyl acetal	8	2	6	146	1.10
13	2,3-dimethyl-5-hydroxy-2-cyclopenten-1-one	7	1+0.05x2+0.25	5.65	126	0.61
14	p-cresols	6	0.83	5.17	108	1.36
15	2,3-dimethyl- Cyclohexanol	8	0.75	7.25	128	2.35

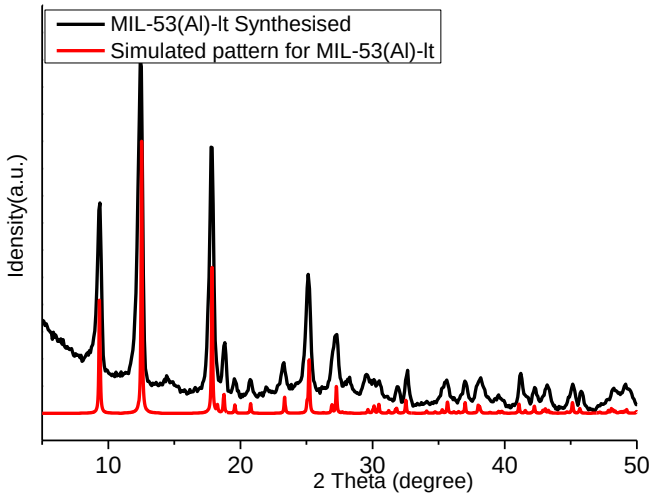
16	o-cresols	6	0.83	5.17	108	1.74
17	guaiacol	7	0.83+1	5.17	124	4.46
18	3-ethyl-2-hydroxy-2-cyclopeten-1-one	7	1+0.25+0.05*2	5.17	126	1.10
19	3,5-dimetylphenol	7	0.83	6.17	122	0.56
20	2-ethylphenol	7	0.83	6.17	122	1.90
21	4-methylguaiacol	8	0.83+1	6.17	138	2.86
22	catechol	6	0.83x2	4.34	110	4.45
23	3-methoxycatechol	7	0.83x2+1	4.34	140	0.73
24	3-methylcatechol	7	0.83x2	5.34	124	0.45
25	4-ethylguaiacol	9	0.83+1	7.17	152	0.40
26	4-methylcatechol	7	0.83x2	5.34	124	3.08
27	4-tert-butyl-phenol	10	0.83	9.17	150	2.02
28	2,6-dimethoxyphenol	8	0.83+1x2	5.17	154	0.91
29	2-methyl hydroquinone	7	0.83x2	5.34	124	1.58
30	2-methoxy-4-(1-propenyl)-,(E)-phenol	10	0.83+1+0.05x2	8.07	164	1.04
31	2-methyoxy-4-propylphenol	10	0.83+1	8.17	166	0.66
32	vaniline	8	0.83+1+1	5.17	152	1.31
33	4-ethylcatechol	8	0.83x2	6.34	138	0.90
34	Eugenol	10	0.83+1+2x0.05	8.07	164	0.48
35	1,2,3-trimethoxy benzene	9	3	6	168	0.77
36	2-methoxy-4-(1-propenyl)-,(Z)-phenol	10	0.83+1+2x0.05	8.07	164	0.46
37	1-(4-hyroxy-3-methyoxyphenyl)-2-ethanone	9	0.83+1+1	6.17	166	0.53
38	1-(4-hyroxy-3-methyoxyphenyl)-2-propanone	10	0.83+1+1	7.17	180	0.52
39	2,3,5-Trimethoxyamphetamine	12	3+0.5	8.5	182	1.14
40	4-(3-hydroxy)-(propenyl)-2-methoxy-phenol	10	1+0.83+0.5+0.05x2	7.57	180	8.75
41	4-(2-propenyl)-2,6-dimethyoxyphenol	11	0.83+1x2+0.05x2	8.07	194	1.83
42	2-ethyoxy-4-(methyoxymethyl)phenol	10	0.83+1+1	7.17	182	1.07
43	4-(2-propenyl)-2,6-dimethyoxyphenol	11	0.83+1x2+0.05x2	8.07	194	0.60
44	1-(4-Hydroxy-3,5-dimethoxy-phenyl)-ethanone	10	3+0.83	6.17	196	0.35
45	Desaspidinol	11	2+0.83x2	7.34	210	0.18

Table S3 Identification and quantification of each compounds in silylated bio-oil by using GC-MS and GC-FID.

	Target compound	Mw	MW C-TMS	ECN-C-TMS	concentration (mg/ml)
Internal standard	1,3-dichlorobenzene	146	146	6	12.28
1	propanol	60	132	5	0.69
2	acrylic acid	72	144	4.9	0.67
3	1,3-pentanediol	104	248	9	0.07

4	propionic acid	74	146	5	2.15
5	butanol	74	146	6	12.36
6	2-methyl propionic acid	88	160	6	1.72
7	2-ethoxyethanol	90	162	2.5	0.92
8	1,2,5-pentanetriol	120	336	5	1.38
9	pentanol	88	160	7	2.51
10	pentanoic acid	102	174	4	0.42
11	glycol	62	206	6	6.60
12	1,2-propanediol	148	220	7	1.05
13	phenol	94	166	8	2.12
14	2-Hydroxy-propionic acid	90	234	7	0.74
15	glycolic acid	76	220	6	6.53
16	4-0xo-pentanoic acid	116	188	6	0.89
17	o-cresol	108	180	9	0.73
18	p-cresol	108	180	9	1.64
19	m-cresol	108	180	9	0.74
20	3-Hydroxy-propionic acid	90	234	7	0.20
21	3,7,11,15,18-Pentaoxa-2,19-disilaeicosane	236	380	12	0.21
22	4-Hydroxy-4-methyltetrahydro-2H-pyran-2-one	130	202	6	0.67
23	octanoic acid	144	216	10	1.67
24	3-Methyl-cyclohex-1-enol	112	184	8.9	8.57
25	glycerol	92	308	9	0.57
26	3,3-Dimethyl-cyclohex-1-enol	126	198	9.9	0.54
27	4-Hydroxy-benzaldehyde	122	194	6	0.42
28	guaiacol	124	196	8	2.11
29	2,6-dimethyl phenol	122	194	10	0.69
30	4-Hydroxy-benzaldehyde	122	194	8	1.03
31	glycol	62	206	6	0.60
32	4-Hydroxy-butyric acid	104	248	8	0.86
33	3,3-Dimethyl-cyclohex-1-enol	126	198	9.9	2.00
34	[1,4]Dioxane-2,5-diol	120	308	6	1.58
35	2-[2-(2-Hydroxy-ethoxy)-ethoxy]-ethanol	150	294	8	4.07
36	[1,4]Dioxane-2,5-diol	120	308	6	4.17
37	glycerol	92	308	9	0.74
38	4-(2-Aminoethyl)-2-methoxyphenol	167	308	9.5	1.43
39	catechol	110	254	10	6.42
40	2-Methyl-succinic acid	132	276	9	0.45
41	3,3-Dihydroxy-propionic acid	130	274	8.9	0.58
42	2-Hydroxy-butyric acid	106	322	9	0.64
43	2-Deoxy-α-D-erythro-pentofuranose	134	350	10	1.32
44	2,4,5-trimethoxy-Benzaldehyde	134	350	10	1.43

45	vaniline	150	224	8	0.70
46	orcinol	124	268	11	3.74
47	resorcinol	110	254	10	2.36
48	D-Erythrose	120	226	12	0.31
49	2,3,4-Trihydroxy-butyraldehyde	220	336	9	1.90
50	Pentane-1,2,3,5-tetraol	140	424	12	1.51
51	2-Hydroxy-heptanoic acid	146	290	11	2.94
52	2-methoxy-4-(1-propenyl)-phenol(E)	164	236	9.9	1.27
53	orcinol	124	268	11	2.21
54	3,6-Bis-hydroxymethyl-[1,4]dioxane-2,5-diol	180	468	12	2.22
55	Butane-1,2,3,4-tetraol	130	410	12	2.99
56	4-Hydroxy-butyric acid	104	248	8	1.14
57	2,3,4-Trihydroxy-butyraldehyde	202	482	12	1.52
58	4-Hydroxy-butyric acid	92	308	9	0.37
59	2-methoxy-4-(1-propenyl)-phenol(Z)	164	236	9.9	2.91
60	D-Erythro-Pentopyranose	152	224	8	5.63
61	β-D-Mannopyranoside	134	350	10	0.90
62	D-xylopyranose	150	438	12	1.03
63	D-Ribofuranose	134	350	10	0.62
64	β-DL-Lyxopyranose	150	438	12	2.81
65	β-DL-Arabinopyranose	150	438	12	1.40
66	Arobinose	150	438	12	1.87
67	D-Ribopyranose	150	438	12	1.46
68	D-altro-2-heptulose	162	378	10	6.20
69	Levoglucosan	210	642	18	22.17
70	D-Xylose	150	438	12	2.82
71	D-Ribose	150	438	12	2.73


MIL-53(Al)-lt Synthesised
Simulated pattern for MIL-53(Al)-lt
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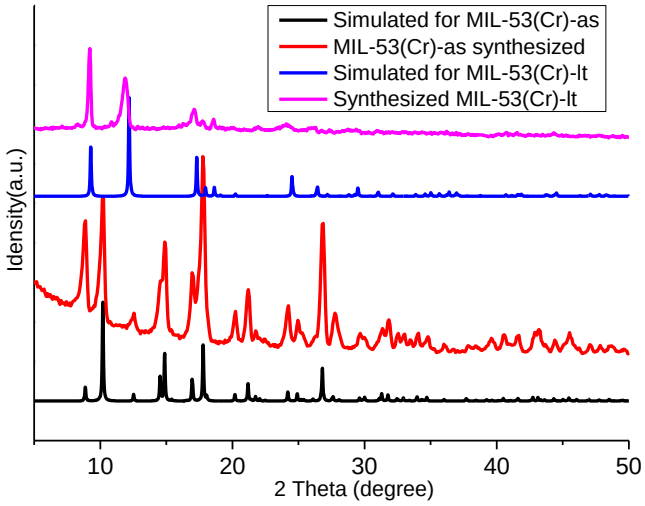
10
20
30
40
50
2 Theta (degree)


Simulated for MIL-53(Cr)-as
MIL-53(Cr)-as synthesized
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10
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50
2 Theta (degree)

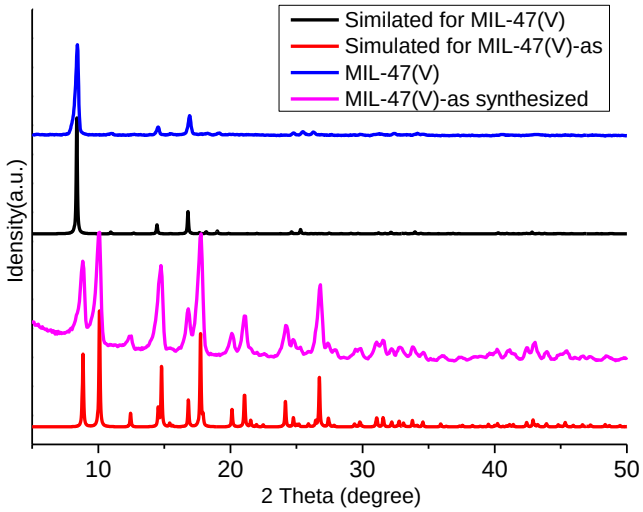

Figure S1 PXRD patterns, from top to bottom, for MIL-53(Al), MIL-53(Cr) and MIL-47(V).

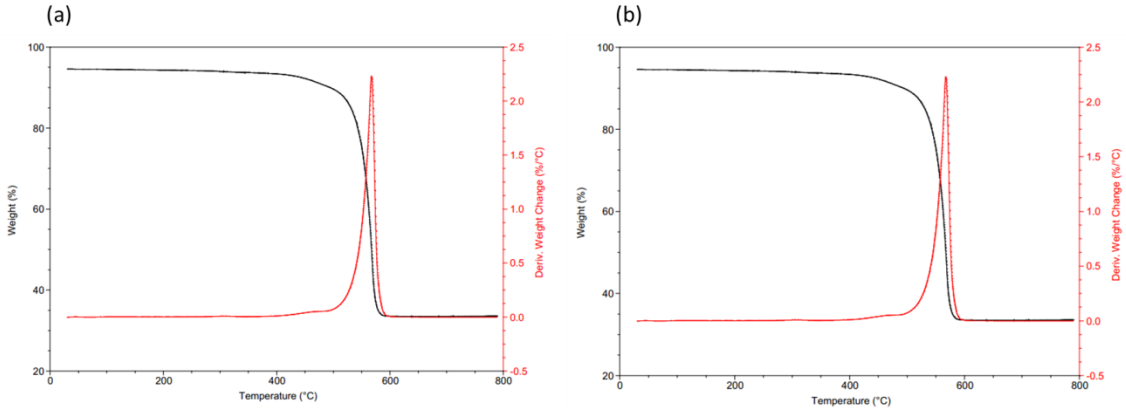

Figure S2 TGA profile for (a) MIL-53(Al); (b) MIL-53(Cr).

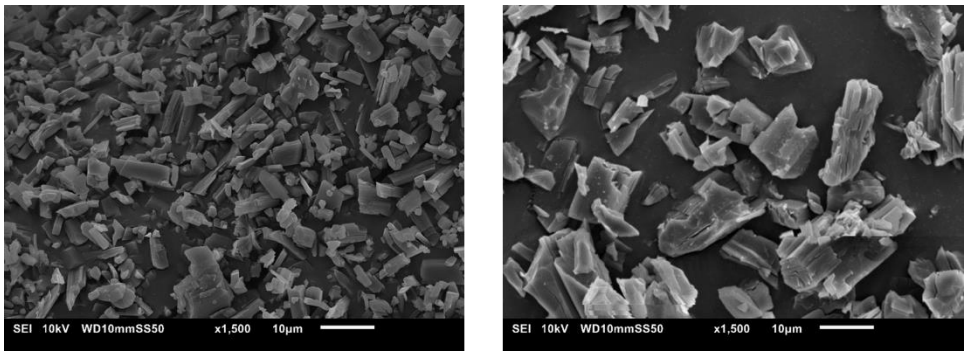

Figure S3 SEM image of MIL-53(Al)-lt (left) and MIL-53(Cr)-lt (right).

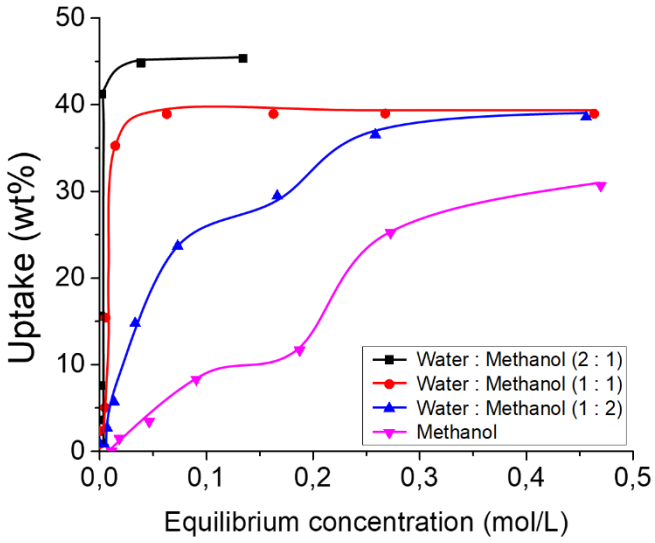

Figure S4 Single compound adsorption isotherms of 4-MeG on MIL-53(Al)-lt from methanol : H_2O (v : v 1:2), methanol : H_2O (v : v 1:1), methanol : H_2O (v : v 2:1) and from pure methanol. Initially the 4-MeG was supplied in the solution with concentrations of 0.5, 0.3, 0.2, 0.1, 0.05, 0.02, 0.01 and 0.001 M, respectively.

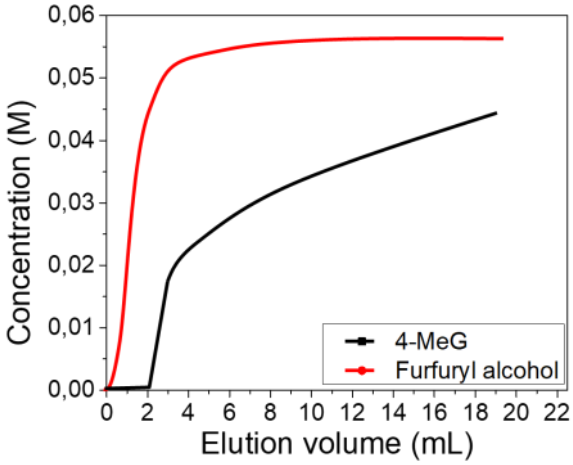

Figure S5 Breakthrough experiment on MIL-53(Al)-*lt* column at 298 K with a 0.05 M solution of FA and 4-MeG in a water-methanol mixture.

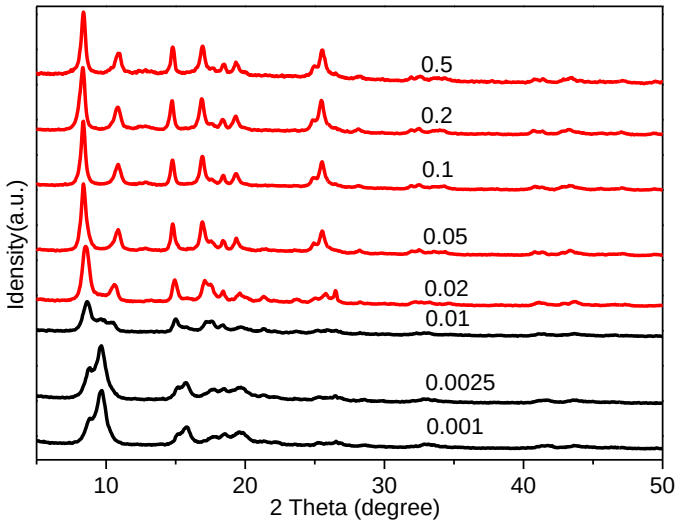

Figure S6 The PXRD patterns of **Basolite A100** after uptake 4-methylguaiacol from different methanol water mixed solution (v : v = 1 : 1) concentrations.

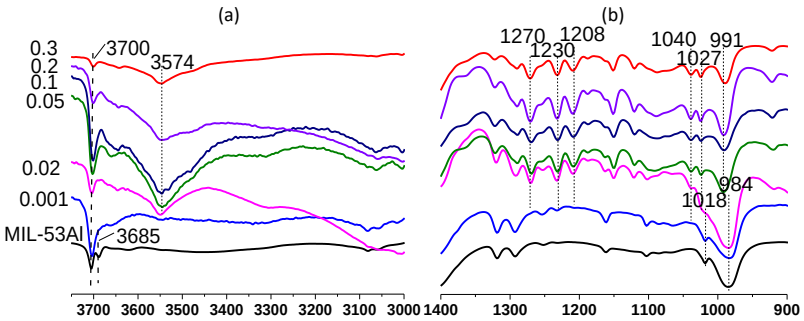

Figure S7 FTIR spectra of MIL-53(Al)-lt, before and after adsorption of 4-MeG from water-methanol solutions with initial 4-MeG initial concentrations of 0.001, 0.02, 0.05, 0.1, 0.2 and 0.3 M. Samples were outgassed for 1 hour under vacuum at room temperature prior to measurements.

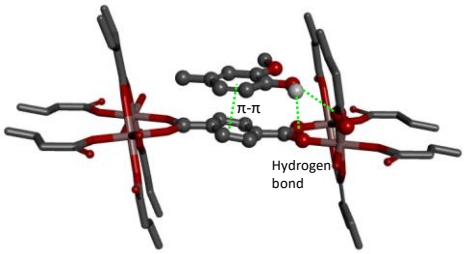

Figure S8 Possible interactions between MIL-53(Al) and 4-MeG.

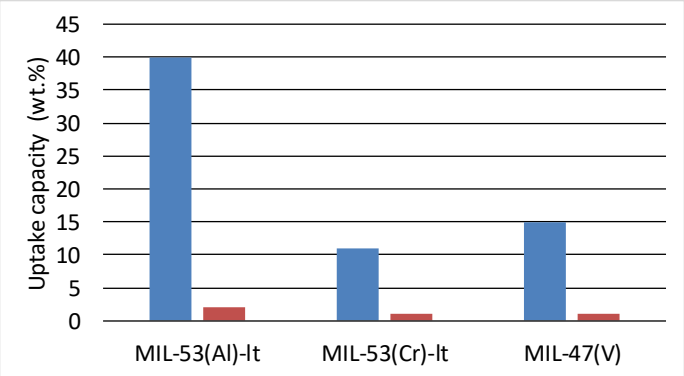

Figure S9 Single compound adsorption from water-methanol solution on MIL-53(Al)-lt, MIL-53(Cr)-lt and MIL-47(V). Initially 4-MeG and Furfuryl alcohol (FA) were supplied with 0.05M concentration, and 20 mg of absorbent was treated with 1.8mL of initial solution.

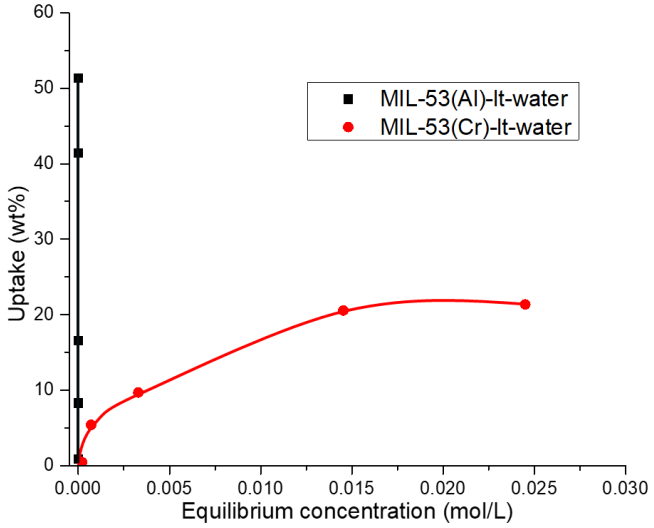

Figure S10 The adsorption isotherms from aqueous solution on MIL-53(Al)-lt, and MIL-53(Cr)-lt. Initially 4-MeG was supplied with concentration of 0.001, 0.002, 0.005, 0.01, 0.02, 0.05 and 0.062M with around 20mg of absorbents.

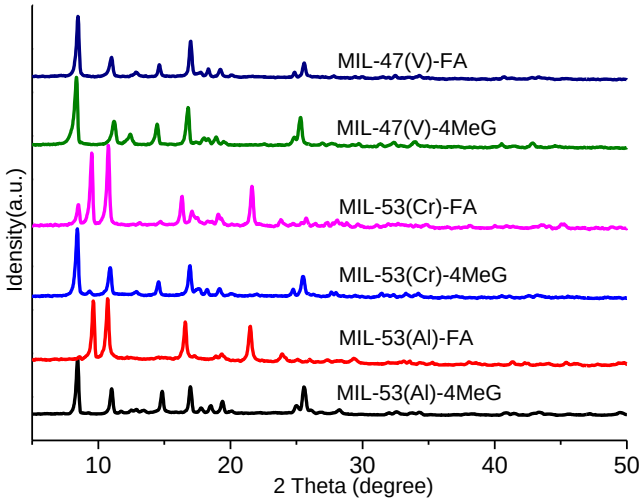

Figure S11 The PXRD patterns for MIL-53(Al)-lt, MIL-53(Cr)-lt, MIL-47(V) after adsorption experiment of 4-MeG /FA from water methanol solution.

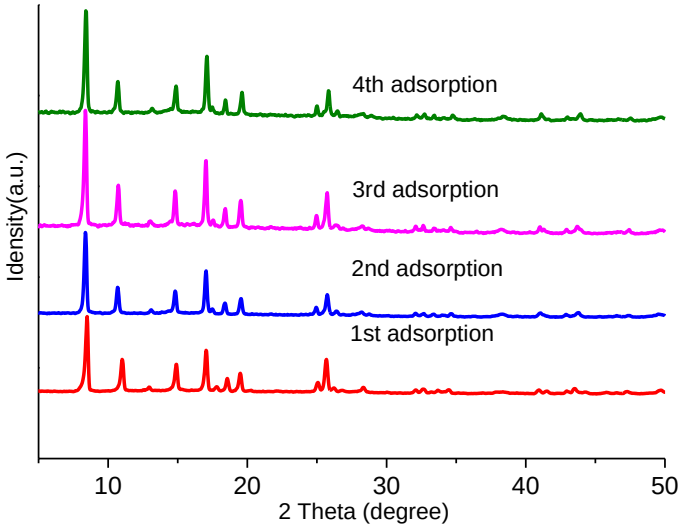

Figure S12 PXRD patterns of MIL-53(Al) after uptake of 4-MeG in each run.

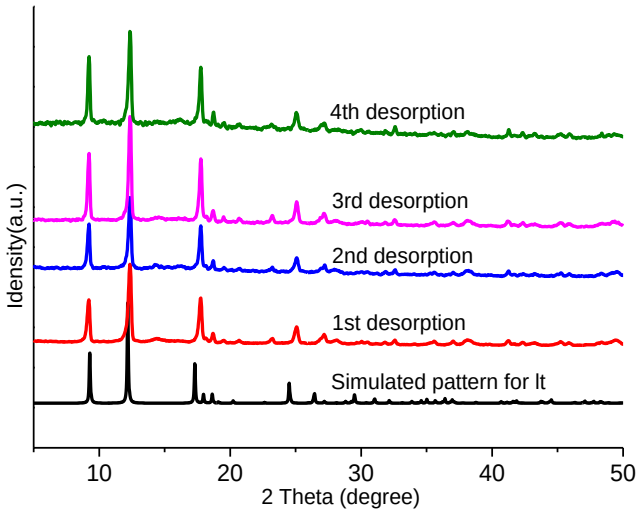

Figure S13 PXRD patterns of MIL-53(Al) after desorption of 4-MeG in each run.

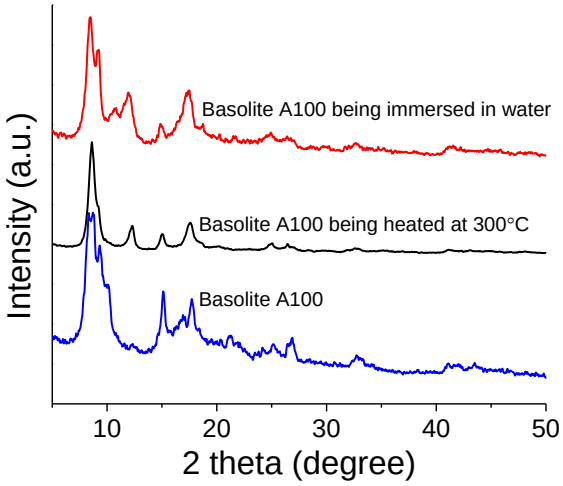

Figure S14 Basolite A100 being heated at 300 °C for 5 hours, and being immersed in water solution for 2 days.

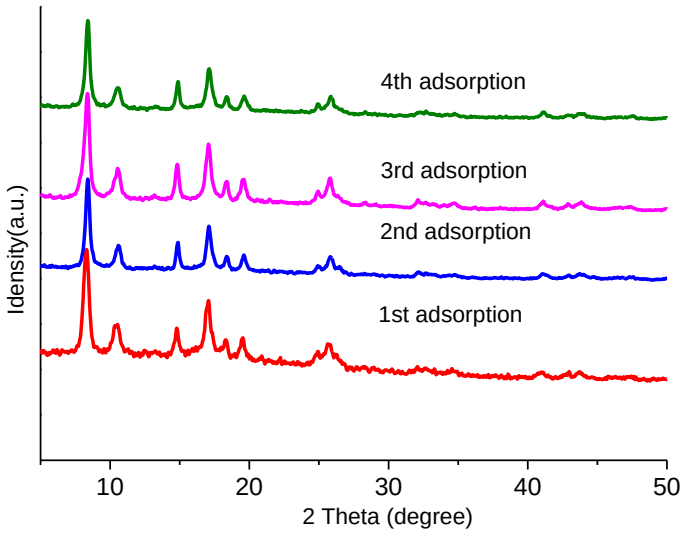

Figure S15 PXRD patterns of Basolite A100 after uptake of 4-MeG in each run.

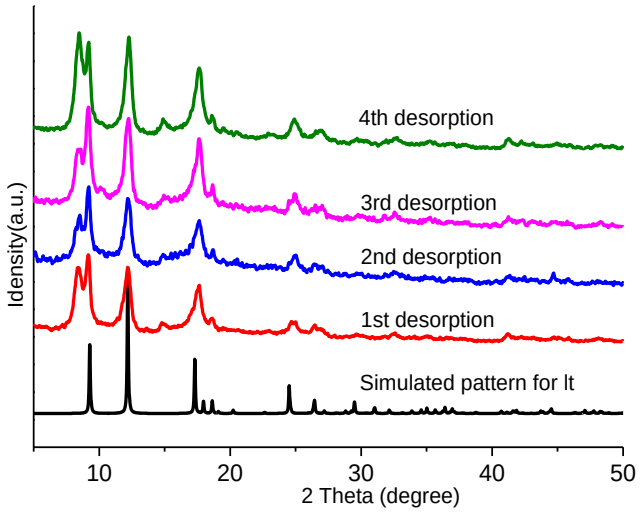

Figure S16 PXRD patterns of Basolite A100 after desorption of 4-MeG in each run.

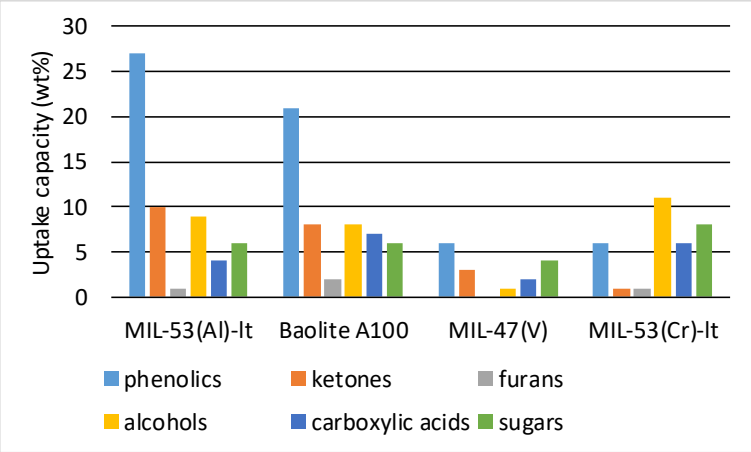

Figure S17 Adsorption experiment from real bio-oil on MIL-53(Al)-lt, Basolite A100, MIL-47(V) and MIL-53(Cr)-lt. Uptake in wt% with respect to the MOFs.

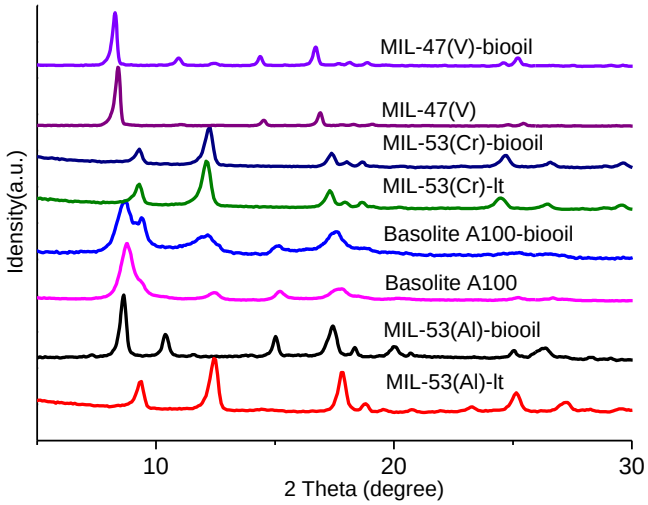

Figure S18 PXRD patterns for MIL-53(Al)-lt, Basolite A100, MIL-47(V) and MIL-53(Cr)-lt as well as their patterns after the adsorption process.

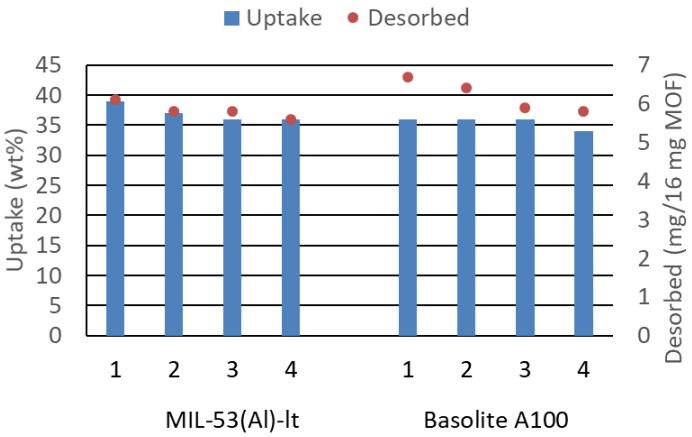

Figure S19 Uptake amount (expressed as wt% 4-MeG) and the desorbed amount (given as mg 4-MeG / 16 mg MOF) using the same sample of MIL-53(Al) and Basolite A100 for four cycles of adsorption from a 0.05 M 4-MeG solution in methanol : water, and desorption by using pure methanol.

The same samples of MIL-53(Al)-*lt* and Basolite A100 were utilized in consecutive adsorption/desorption runs with 4-MeG from a water-methanol solution (v : v 1 : 1) with an initial concentration of 0.05 M (6.9 mg in 1 mL). Both materials show only a small variation in uptake amount, ranging between 35 and 40 wt%, after four cycles (Figure S19; blue bars). Structural degradation of the framework could be ruled out by PXRD, ICP and HPLC measurements, which showed excellent stability of MIL-53(Al) and Basolite A100 during the four cycles (Fig. S12-13 and S15-16). The PXRD indicated the stability of the crystalline metal-organic framework, also confirmed by ICP and HPLC analysis of the 0.05M aqueous solution after adsorption on MIL-53(Al)-lt, indicating a very limited leaching of the Al metal ion (less than 0.1 wt%) or of the bdc linker (< 1 wt%). Furthermore, the quantity of 4-MeG that is recovered in each cycle also shows only small variations, ranging from 5.6 to 6.1 mg / 16 mg MOF for MIL-53(Al)-*lt*, and 5.8 to 6.7 mg / 16 mg MOF for Basolite A100 (Figure S19; red dots).

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