Electronic Supplementary Material (ESI) for CrystEngComm.

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MOF catalysts in biomass upgrading towards value-added fine chemicals

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This Electronic Supplementary Information (ESI) contains the Tables with catalytic conditions, product and by-product yields for MOF and non-MOF catalysts in biomass conversion.

Table S1: Comparison of synthesis conditions for the conversion of sugars.

Catalyst	Substrate	Conditions (solvent, time, temperature, pressure)	Product (%)[a]	Byproducts	Ref.
MIL-101Cr-SO_3H (0.2 g)	cellulose (25 mg)	H_2O (2.0 g), 3 h,. 393 K.	glucose (1%) mono+disaccharides (5%)		1
MIL-101Cr-SO_3H (0.2 g)	glucose (25mg)	H_2O (2.0 g), 24 h, 373 K.	conversion (22 %) fructose (22%)	glucose was recovered (78%)	2
HCl	amylose (25 mg)	HCl aq, (2.0 g), 24 h, 373 K	conversion (99%) glucose (99%) fructose(0%)		2
MIL-101Cr-SO_3H (0.2g)	amylose (25 mg)	water, 2.0 g, 373 K, 24 h;	conversion (n.s) glucose (5%) fructose(1%)	Cellobiose (10%)	2
aqueous solution of HCl (pH 1) + MIL-101Cr-SO_3H (0.2g)	amylose (25 mg)	HCl aq, 2.0 g, 373 K, 24 h;	conversion (100%) glucose (83%) fructose(17%)		2
Ru-PTA/MIL-100Cr (30 mg; Ru (3.2wt%)); PTA (16.7 wt%)	cellulose (50 mg)	H_2O (8.0 mL), 10 h, 190 °C, H_2 (2.0 MPa)	conversion (100%) sorbitol (58%)	mannitol (5%) glycerol +ethylene glycol (1.%)	3
Ru-PTA/MIL-100Cr (30 mg; Ru (3.2wt%)); PTA (16.7 wt%)	cellobiose (50 mg),	H_2O (5.0 mL), 10 h, 150 °C, H_2 (2.0 MPa),	conversion (100%) sorbitol (95%)	mannitol (2%) glycerol +ethylene glycol (1%)	3
Ru/NENU-3 (30 mg; 2.4 wt% Ru, 34.8 wt% PTA	cellulose (50 mg)	H_2O (8.0 mL), 4 h, 245 °C, H_2 (4.0 MPa)	conversion (80%) ethylene glycol (45%)	1,2-propylene glycol (5%) glycerol (6%), glucose (2%),sorbitol +mannitol (2%)	4
other heterogeneous catalysts					
Sn-Beta 1:50 metal:glucose	glucose (10 wt%))	H_2O, 30 min, 383 K	conversion (55%) fructose(32%)	mannose (9%)	5.
Sn-Beta 1:225 metal:glucose	glucose (45 wt%))	H_2O, 1 h, 383 K	conversion (54%) fructose(29%)	mannose (8%)	5
sulfonated activated carbon (50 mg)	cellulose (45 mg)	H_2O (5 mL), 24 h, 423 K	glucose (41%)	water soluble byproducts	6
1%Rh-5%Ni/Mesoporous carbon (0.15 g)	cellulose (0.5 g)	H_2O (50 mL), 30 min, 245 °C, 6 MPa H2	conversion (100%) sorbitol (52%)	various hexitols	7
$H_4SiW_{12}O_{40}$–Ru/C (0.25 g)	cellulose (1 g)	H_2O (50 mL), 1 h, 463 K, 5 MPa H_2	conversion (99%) sorbitol + mannitol (68%)	sorbitan (19%), glucose (1%)	8

If no conversion is stated, the data was not found in the literature

Table S2: Comparison of fructose to 5-HMF synthesis conditions.

Catalyst	Conditions (fructose amount, solvent, time, temperature, pressure)	Product (yield) (Byproduct[a], yield)	Ref.
PTA (3.0)/MIL-101 (20 mg)	fructose (50mg), 1-ethyl-3-methylimidazolium chloride (0.5 g), 1 h, 80 °C	conversion (84%) 5-HMF (63%)	9
PTA (3.0)/MIL-101 (200 mg),	fructose (0.5 g), DMSO (5 mL), 30 min, 130 °C	conversion (82%) 5-HMF (63%)	9
MIL-101Cr	fructose (0.555 mol/L), DMSO (5mL), 1 h, 100 °C	conversion (>99%) 5-HMF (24%)	10
MIL-101Cr-PMAi-Br (250mg)	fructose (0.555 mol/L), DMSO (5mL), 1 h, 100 °C	conversion (>99%) 5-HMF (86%)	10
MIL-101Cr-SO_3H-15% (0.3 g)	fructose (0.5g) DMSO (5mL), 1 h, 120 °C	conversion (>99%) 5-HMF (90%)	11
MIL-101Cr-SO_3H-3% (0.3 g)	fructose (0.5g), DMSO (5mL), 1 h, 120 °C	conversion (83%) 5-HMF (63%)	11
MIL-53Al-SO_3H-8.2% (0.3 g)	fructose (0.5g), DMSO (5mL), 1 h, 120 °C	conversion (>99%) 5-HMF (79%)	11
UiO-66Zr-SO_3H-9.5% (0.3 g)	fructose (0.5g), DMSO (5mL), 1 h, 120 °C	conversion (>99%%) 5-HMF (85%)	11
NUS-6Zr (3.5 mol%, 35 mg)	fructose (50 mg) ,DMSO (1 mL), 1 h, 100 °C	conversion (>99%) 5-HMF (84%)	12
NUS-6Hf (3.5 mol%, 50 mg)	fructose (50 mg), DMSO (1 mL), 1 h, 100 °C	conversion (>99%) 5-HMF (98%)	12
other heterogeneous catalysts			
Amberlyst 15 (20 mg)	fructose (1.7 mmol), DMSO (10 g), 2 h, 120 °C, $1.01 \cdot 10^5$ Pa N_2	conversion (100%) 5-HMF (76%) Levulinic acid (2%)	13
Nafion(15)/MCF (0.1 mmol/L H^+)	fructose (3wt%), DMSO, 2 h, 90 °C	5-HMF (83%)	14
Amberlyst-15 (175 g L^{-1})	fructose (0.5 M), 5:3 (v/v) [BMIM]BF_4–DMSO, 32 h, 80 °C	conversion n.s. 5-HMF (87%)	15

MCF: mesocellular silica foam; n.s.= not stated.

a) If no additional byproducts are given, the difference is attributed to the formation of humins.

Table S3: Comparison of synthesis conditions based on sugar feedstock.

Catalyst	Substrate	Conditions (solvent, time, temperature, pressure)	Product (%)[a]	Byproducts[b]	Ref.
MIL-101Cr-PMAi-Br(250mg)	glucose (0.555 mol/L)	DMSO (5mL), 2 h/6 h,100 °C	5-HMF (7%/ 16%)		10
MIL-101Cr-SO_3H-15%, (0.06 g)	glucose (0.1g)	DMSO (2mL), 2 h, 120 °C	5-HMF (7%)		11
4 mol% (50 mg) MIL-101Cr-SO_3H	glucose (223 mg)	THF:H_2O (v:v 39:1) 5mL, 24 h, 130 °C	5-HMF (29%%)	Levulinic acid (7%)	16,
ZIF-8 (160 mg)	sucrose (225 mg)	methanol (8 g), 24 h, 160 °C	conversion (>99%) methyl lactate (35%)	PADA (2%), TMP (0.4%)	17
ZIF-67 (160 mg)	sucrose (225 mg)	methanol (8 g), 24 h, 160 °C	conversion (66%) methyl lactate (19%)	PADA (0.1%), TMP (0.2%)	17
ZIF-8 (160 mg)	glucose (225 mg)	methanol (8 g), 20 h, 160 °C	conversion (98%) methyl lactate (20%)	PADA (1%), TMP (0.1%)	17
ZIF-8 (160 mg)	fructose (225 mg)	methanol (8 g), 20 h, 160 °C	conversion (98%) methyl lactate (11%)	-	17
other heterogeneous catalysts					
ZrPO (20 wt%)	glucose (6.5 wt%)	H_2O: MIBK 1 : 3 (v/v), 6 h,165 °C	conversion (60%) 5-HMF (24%)		18
Sn-Mont (0.2 g)	glucose (5 wt%)	THF–DMSO (70 : 30 (v/v), 6 mL), 3 h, 160 °C	conversion (98%) 5-HMF (54%)		19
mesoporous $TaOPO_4$ (50 mg) Catalyst:glucose 1:3 (weight ratio)	glucose (150 mg)	H_2O: MIBK 1 h, 170 °C	conversion (56%) 5-HMF (33%)		20
Sn-MCM-41 (150 mg)	sucrose (0.45 g)	methanol (15 g), 16 h, 160 °C	methyl lactate (28%)		21
Sn-MFI(150 mg)	sucrose (0.45 g)	methanol (15 g), 16 h, 160 °C	methyl lactate (24%)		21
Sn-Beta (100 mg)	sucrose (0.3 g)	methanol (10 g), 16 h, 160 °C	conversion (98%) methyl lactate (57%)	MVG (5%)	22,

a) If no conversion is stated, the data was not found in the literature. b) PADA: pyruvaldehyde dimethyl acetal; TMP: 1,1,2,2-tetramethoxypropane; n.i.p.: non-identified products, MVG: methyl vinylglycolate, MIBK: methyl isobutylketone; n.s.: not stated.

Table S4: Feedstock furans

Catalyst	Substrate	Conditions (solvent, time, temperature, pressure)	Product (%)[a]	Byproducts	Ref
Ru/UiO-66Zr (0.1g)	furfural (0.1mL)	H_2O (9.9mL), 4 h, 20 °C, 5 bar H_2	furfuryl alcohol (95%)		23
FeCo/C(500) (20 mol%)	5-HMF (1 mmol, 0.5 mol/L)	toluene (2 mL), 6 h, 100 °C 1.0 MPa O_2, Na_2CO_3 (1mmol)	DFF (>99%)		24
MIL-101Cr-SO_3H(50) (0.1g)	GVL 10 mmol	ethanol (5.8 mL), 10 h, 200 °C, 3 MPa H_2	conversion (39%) ethyl 4-ethoxy pentanoate (66%)	(1) 4-hydroxy-ethylvalerate (20%) (3)ethyl pentenoate (14%)	25
MIL-101Cr-SO_3H(100) (0.1g)	GVL 10 mmol	ethanol (5.8 mL) 10 h 200 °CC, 3 MPa H_2	conversion (44%) ethyl 4-ethoxy pentanoate (70%)	(1) 4-hydroxy-ethylvalerate(14%) (3)ethyl pentenoate (16%)	25
Pd@MIL-101-SO_3H(50), (0.1g)	GVL 10 mmol	ethanol (5.8 mL), 10 h, 200 °C, 3 MPa H_2	conversion (35%) (2) ethyl 4-ethoxy pentanoate (55%)	(1) 4-hydroxy-ethy-lvalerate (19%); (4) ethyl valerate (26%)	25
Pd@MIL-101-SO_3H(100), (0.1g)	GVL 10 mmol	ethanol (5.8 mL), 10 h, 200 °C, 3 MPa H_2	conversion (51%) 2) ethyl 4-ethoxy pentanoate (66%)	(1) 4-hydroxy-ethyl-valerate (8%); (4) ethyl valerate (26%)	25
W/NC3 (W 3.56 μmol), catalyst:reactant 1:320	levulinic acid (1.14mmol)	methanol (20mL), 12 h, 130 °C, 0.1 MPa N_2	conversion (4%) methyl levulinate (42%)		26
W/NC1 (W 3.56 μmol), catalyst:reactant 1:320	levulinic acid (1.14mmol)	methanol (20mL), 12 h, 130 °C, 0.1 MPa N_2	conversion (25%) methyl levulinate (25%)		26
Ru/NC3 (Ru 8.64 μmol), catalyst:reactant 1:160	levulinic acid (1.36 mmol)	H_2O (20mL), 6 h, 130 °C, 2 MPa N_2	conversion (97%) γ-valerolactone (97%)		26
Ru/NC1 (Ru 8.64 μmol), catalyst:reactant 1:160	levulinic acid (1.36 mmol)	H_2O (20mL), 6 h, 130 °C, 2 MPa N_2	conversion (5%) γ-valerolactone (5%)		26
UiO-66 (1.8 mol%Zr with respect to LA)	levulinic acid (1mmol)	ethanol:LA 15:1, 4 h/8 h 78 °C	ethyl levulinate (4h:78%, 8h: 94%)		27
UiO-66-NH_2 (1.8 mol%Zr with respect to LA)	levulinic acid (1mmol)	ethanol:LA 15:1, 4 h/8 h 78 °C	ethyl levulinate (4h:78%, 8h: 95%)		27
UiO-66 (1.8 mol%Zr with respect to LA)	levulinic acid (1mmol)	ethanol:LA 5:1, 4 h 78 °C/100C	ethyl levulinate (78 °C: 49%, 100 °C: 73%)		27
MIL-53Al-NH-NMe_2 (30mg)	glyceryl triacetate (181	methanol (1mL), 4 h, 50 °C	conversion (100%) glycerol (100%)		28

	mg)		methylacetate (100%)		
MIL-53Al-NH-NMe_2 (30mg)	glyceryl butyrate (302 mg)	methanol (1.2mL), 6 h, 60 °C	conversion (95%) glycerol, methylbutyrate		28
other heterogeneous catalysts					
Ag-OMS-2 (Ag 16.7 mol%)	5-HMF (0.063 mol/L)	isopropyl alcohol, 165 °C, 1.5 MPa, air	Conversion (99%) DFF (99%)		29
Ru/HT (0.1g, Ru 4.4 wt%)	5-HMF (1 mmol)	DMF (3 mL) 6 h, 120 °C, 0.1 MPa O_2	DFF (92%)	FFCA (3%)	30
Pd@C (0.1g,Pd 5 wt%)	5-HMF (1 mmol)	DMF (3 mL) 6 h, 120 °C, 0.1 MPa O_2	DFF (21%)	FFCA (2%)	30
Amberlyst (2.5wt%)	levulinic acid	ethanol/acid 5:1, 5h, 70 °C	ethyl levulinate (55%)		31
Sulfated TiO_2 (2.5wt%)	levulinic acid	ethanol/acid 5:1, 5h, 70 °C	ethyl levulinate (40%)		31
HZSM-5 (2.5wt%)	levulinic acid	ethanol/acid 5:1, 5h, 70 °C	ethyl levulinate (4%)		31
DTPA/DHZSM-5 catalyst to LA ratio: 0.25	levulinic acid	ethanol/acid 6:1, 4h, 78 °C	ethyl levulinate (82%)		32
Zn-5 catalyst (5 wt%)	glyceryl triacetate	glyceryl triacetate:methanol (1:29 molar ratio), 3 h, 50 °C	conversion (73%) methylacetate (52%)		33

a) If no conversion is stated, the data was not found in the literature. LA: Levulinic acid, DFF: 2,5-Diformylfuran, FFCA: 5-Formyl-2-furancarboxylic acid

Table S5: Feedstock Lignin

Catalyst	Substrate	Conditions (solvent, time, temperature, pressure)	Product (%)	Byproducts	Ref.
IRMOF-74(I) 45 mg	PPE (n.s)	*p*-xylene (5.0 mL), 16 h, 120 °C, 10bar H_2	conversion (12%) 1 (87%), 4 (91%)	no	34
IRMOF-74(II) 45 mg	PPE(n.s)	*p*-xylene (5.0 mL), 16 h, 120 °C, 10bar H_2	conversion (39%), 1 (83%), 4 (87%)	no	34
Ni@IRMOF-74(II) 45 mg	PPE (n.s)	*p*-xylene (5.0 mL), 16 h, 120 °C, 10bar H_2	conversion (82%), 1 (96%), 4 (98%)	no	34
Raney Ni (n.s.)	PPE (n.s)	*p*-xylene (5.0 mL), 16 h, 120 °C, 10bar H_2	conversion (76%), 1 (81%), 4 (75%)	cyclohexanol	34
Pd@MIL-101Cr (50 mg)	vanillin (2 mmol)	H_2O (20 mL), 1 h 100 °C, H_2 (0.5MPa),	conversion (67%) 2-methoxy-4-methylphenol (58%),	vanillin alcohol(42%)	35
Pd@MIL-101Cr-SO_3H (50 mg)	vanillin (2 mmol)	H_2O (20 mL), 1 h 100 °C, H_2 (0.5MPa),	conversion (96%) 2-methoxy-4-methylphenol (91%),	vanillin alcohol(9%)	35
Pd@UiO-66-NH_2 (50 mg)	vanillin (2 mmol)	H_2O (20 mL), °C, H_2 (0.5MPa),	conversion (100%) 2-methoxy-4-methylphenol (100%)		36
other heterogeneous catalysts					
Pd@C (2 wt%) S/C: 200;	vanillin (2 mmol)	H_2O (20 ml), 60 min, 100 °C; H_2 0.5 MPa.	conversion (55%) 2-methoxy-4-methylphenol(22%)	Vanillin alcohol (78%)	35
Pd@CM170 S/C:100	vanillin (155 mg)	H_2O (30 mL), 1 h, 100 °C, 1 MPa H_2	conversion (>99%) 2-methoxy-4-methylphenol(48%)	Vanillin alcohol (52%)	37

(n.s): not specified. PPE: Phenylethylphenyl ether; BPE: Benzylphenyl ether; DPE: Diphenyl ether.

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