

Supporting Information

Highly Efficient One-pot Conversion of Saccharides to 2,5-Dimethylfuran using P-UiO-66 and Ni-Co@NC Noble Metal-Free Catalyst

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Materials and Methods

Chemicals

Glucose, fructose, cellulose, starch, cellulose, 2,5-dimethylfuran (DMF), 5-hydroxymethylfurfural (HMF), 5-methylfurfural (MFAL), 5-methyl-furanmethanol (MFOL), tetrahydro-2,5-dimethanol (THFDM), tetrahydrofuran (THF), $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, 1,4-benzenedicarboxylic acid, 2-methylimidazole, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, dimethylformamide and acetone were purchased from Sigma-Aldrich and Across without further purification.

Synthesis of Ni@ZIF-67 and derived Ni-Co@NC

Synthesis of Ni@ZIF-67: Ni@ZIF67 was synthesized by in situ synthesis as following procedure. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.0 mmol, 0.291 g) and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.0 mmol, 0.291 g) was dissolved 5 mL methanol. The metal precursor was added into 20 mL methanol solution containing 2-methylimidazole (Hmim, 4.0 mmol, 0.328 g). The mixture stirred at room temperature (RT) for 24 h. Then, the solid was centrifuged at 20000 rpm for 6 minutes, and washed by methanol several times. The purple precipitation was dried under vacuum at RT in 24 h. The obtained materials denoted as Ni@ZIF-67.

Synthesis of Ni-Co@NC: Ni-Co@NC was prepared by pyrolysis of Ni@ZIF-67 at 600 °C for 4 h under N_2 atmosphere, with the ramping temperature of 5 °C/min. The resulting powder was collected and denoted as Ni-Co@NC.

Synthesis of UiO-66 and derived P-UiO-66

Synthesis of UiO-66: UiO-66 was synthesized based on the previous reports with slightly modification [1]. 0.228 g terephthalic acid (BDC, 1.7 mmol) was added into 80 mL dimethylformamide solution containing dissolving 5.026 g benzoic acid (4.1 mol) and 0.442 g $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (1.37 mmol). The mixture was then sealed in an autoclave and heated at 120 °C for 24 h. After 24 h, the white powder was collected by centrifugation (15000 rpm for 5 min) and washing with dimethylformamide and acetone several times. The UiO-66 solid was dried under vacuum at RT in 24 h.

Synthesis of P-UiO-66: 00 mg UiO-66 was mixed with 10 mL Na_2HPO_4 aqueous solution (0.2 M) for 3 hours at 70 °C. The white power was collected by centrifugation and washing with water. The resulted solid was activated under vacuum at RT for 24 h.

Potentiometric titration

Potentiometric titration procedure were conducted similar to the previous report [2]. Commercial pH buffers of pH = 2.00, 4.00, 7.00, and 9.00 (Metrohm) was used for calibration curve. 50 mg of the synthesized samples were dispersed in 50 mL NaNO_3 solution (0.01 M) overnight before titration. NaOH solution (0,1 M) was used for titration process with the injection volume of 0.025 mL and an injection rate of 0.02 mL/min until the pH changes to 10–10.5. Maximum points of the first derivatives was used to determine equivalent points. pKa values were determined as the pH at one-half of the volume of titrant added to reach the equivalence point.

Characterization

Powder X-ray diffraction (XRD) patterns were conducted on a Rigaku-Ultima IV instrument using a Cu K α radiation source. The chemical state of elements present in prepared samples was studied using X-ray photoelectron spectrometer (XPS, Thermo Scientific, Theta Probe). The metal content in the synthesized samples was determined using induced coupled plasma-mass spectrometry (ICP-MS). N₂ adsorption-desorption isotherms were measured at -196 °C on a Microtrac BELSORP MAX II instrument. Fourier-transform infrared spectroscopy (FT-IR) were carried out with Perkin Elmer Spectrum 100.

One-pot conversion of saccharide to DMF over P-UiO-66 and Ni-Co@NC

The reaction was carried out in a Parr reactor connected a mechanical stirring. Typically, 50 mg Ni-Co@NC, 50 mg P-UiO-66, and 1 mmol saccharides were added into a reactor filled with 30 mL THF and 2 mL saturated NaCl aqueous solution. After the reactor was sealed, N₂ was flushed to purge air residue in the reactor (3 times), then filled with hydrogen (0.7 MPa). The reactor was heated to desire temperature at certain reaction time. After completed reaction, the reactor was cooled to room temperature, then the reaction mixture was centrifuged to separate the solids and the liquid phase. The liquid phase was directly analyzed by GC coupling with HP-05 column. The solids were further washed by 10 mL water; the collected aqueous solution was analyzed by HPLC with Shodex SUGAR SP0810 column using water mobile phase. The conversion and product yield were calculated following equation (S1) and (S2), respectively:

$$\text{Conversion (\%)} = \frac{\text{initial mole of saccharide} - \text{mole of saccharide remained}}{\text{Initial mole of saccharide}} \times 100\%$$

(S1)

$$\text{Yield (\%)} = \frac{\text{mole of product generated}}{\text{initial mole of saccharide}} \times 100\% \quad (\text{S2})$$

Table S1: Acidity testing of the synthesized materials using Hemmett indicator method.

Indicators	Color		pK _a	Material	
	Acid form	Based form		UiO-66	P-UiO-66
4-Phenylazoaniline	Red	Orange	+2.8	-	+
2-Nitroaniline	Red	Yellow	-0.2	-	+
4-Nitrodiphenylamine	Red	Yellow	-2.4	-	+
2,4-Dichloro-6-nitroaniline	Red	Yellow	-3.2	-	+

2,4-Dinitroaniline	Red	Yellow	-4.4	-	+
2-Benzoylnaphthalene	Yellow	Colorless	-5.9	-	+
2-Bromo-4,6-dinitroaniline	Red	Yellow	-6.6	-	+
Anthraquinone	Yellow	Colorless	-8.1	-	+
4-Nitotoluene	Yellow	Colorless	-11.4	-	+
4-Nitrofluorobenzene	Yellow	Colorless	-12.4	-	-

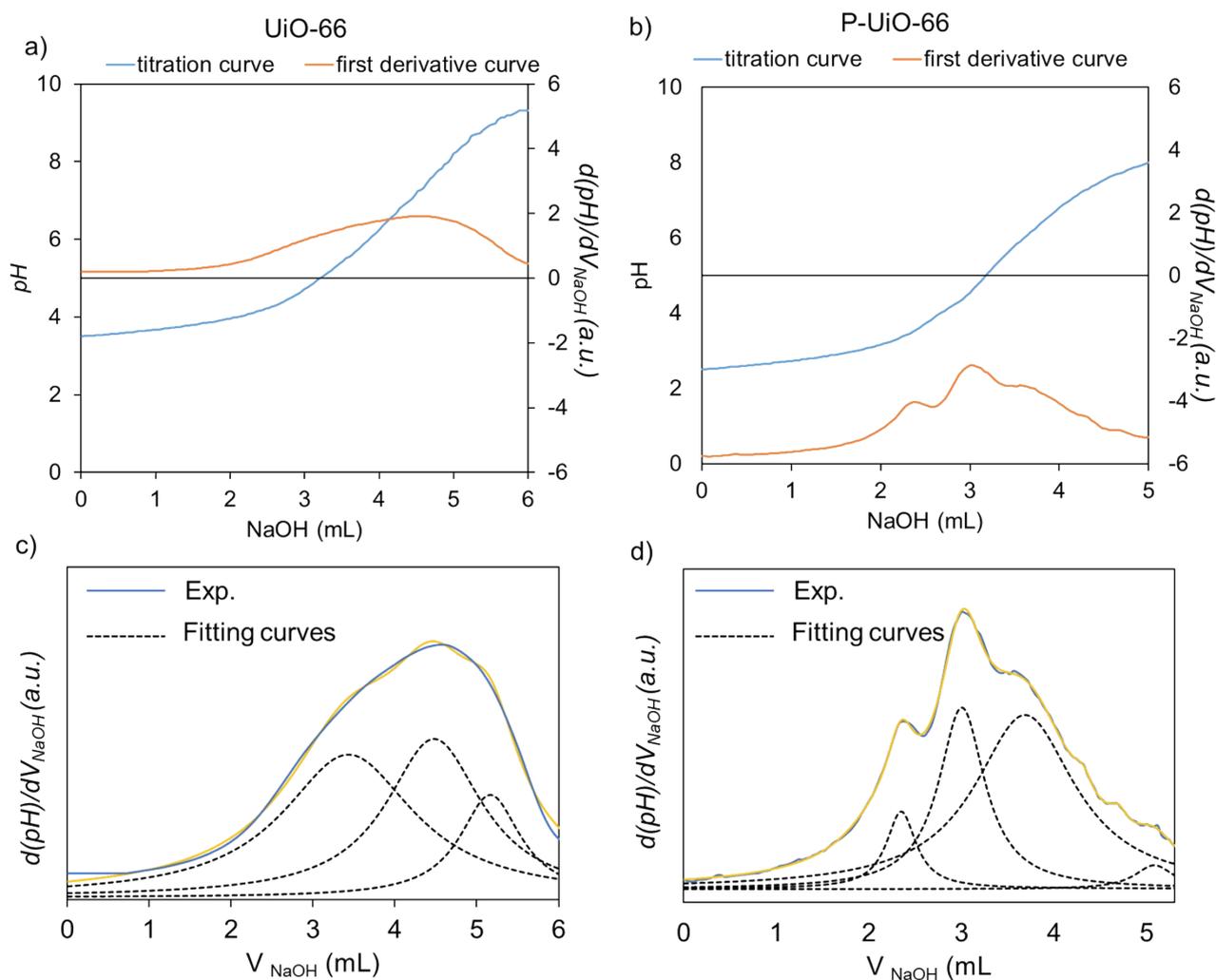


Fig. S1: a-b) potentiometric acid–base titration tests, c-d) first derivative curves of UiO-66 and P-UiO-66, respectively.

The titration curves were analysed using Lorentzian functions, showing that the first derivative curve of UiO-66 is divided into three equivalence points at 3.4, 4.5, and 5.1, contributing to the pKa values of 2.65, 3.55, 4.22, respectively. It was reported that three pKa values of UiO-66 can be attributed to the protons of μ_3 -OH, Zr-OH₂, and Zr-OH groups, to be considered as Brønsted acid sites. Meanwhile, the curve-fitting of the P-UiO-66 displayed four peaks with the central point at 2.3, 3.0, 3. and 5.1, which correspond to pKa values of 1.74, 2.27, 3.08, and 4.03, respectively (Fig. S1). Their first three peak had low pKa values, indicating that the acidity of P-UiO-66 was stronger than that of UiO-66, which consisted with the Hemmett indicator method. Moreover, P-UiO-66 curve-fitting appeared a new equivalence point, which suggested of another Brønsted acid site, resulting from the phosphorylation.

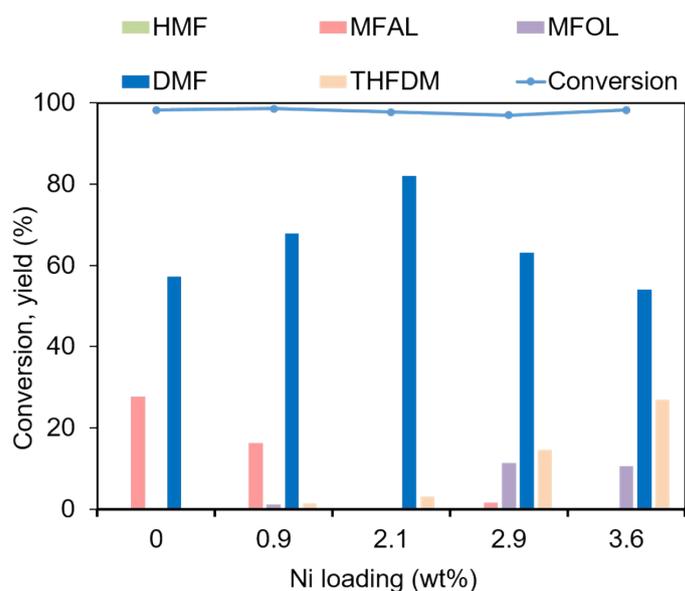


Fig S2. Effect of Ni loading in the Ni-Co@NC catalyst for conversion of glucose to DMF. Reaction condition: glucose (1 mmol, 0.18 g), 0.05/0.05 (g/g) P-UiO-66 and Ni-Co@NC catalyst, THF/H₂O ratio of 30/2 (mL/mL) as solvent, 70 mg NaCl, 0.7 MPa of H₂.

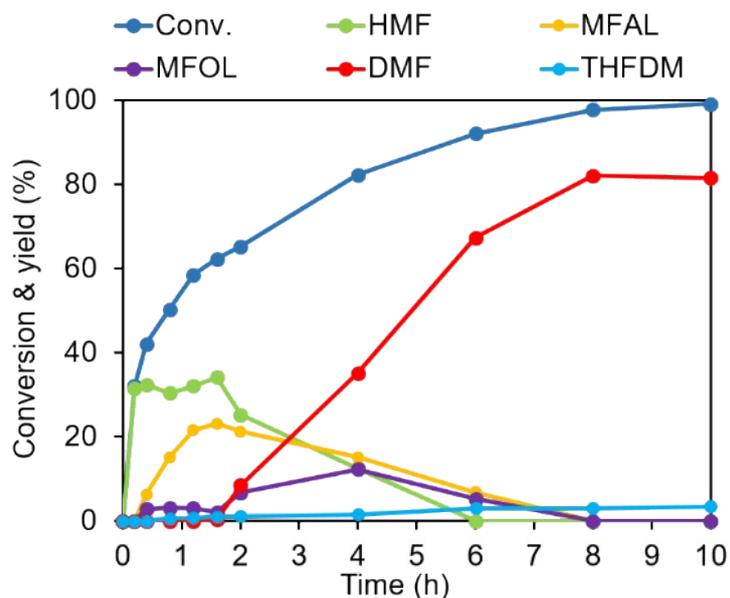


Fig S3. a) Effect of reaction time on the conversion of glucose to DMF. Reaction conditions: Glucose (1 mmol, 0.18 g), P-UiO-66 (0.05 g) and Ni-Co@NC (0.05 g) as catalyst, THF/H₂O ratio of 30/2 (mL/mL) as solvent, 160 °C, 70 mg NaCl, 0.7 MPa of H₂ pressure.

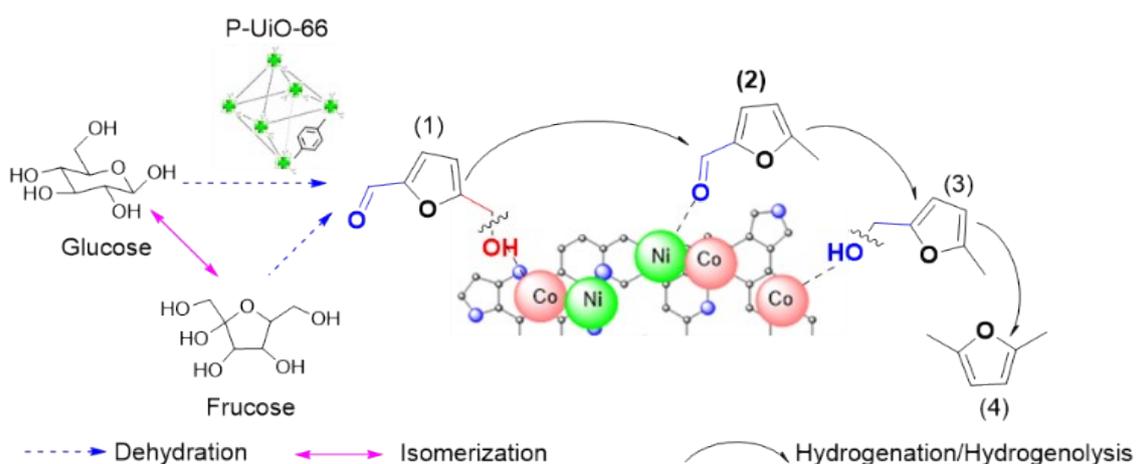


Fig S4. a) Illustration of the proposed reaction pathway for glucose conversion to DMF. (1) 5-hydroxymethylfurfural (HMF); (2) 5-methylfurfural (MFAL); (3) 5-methyl-furanmethanol (MFOL); (4) 2,5-dimethylfuran (DMF)

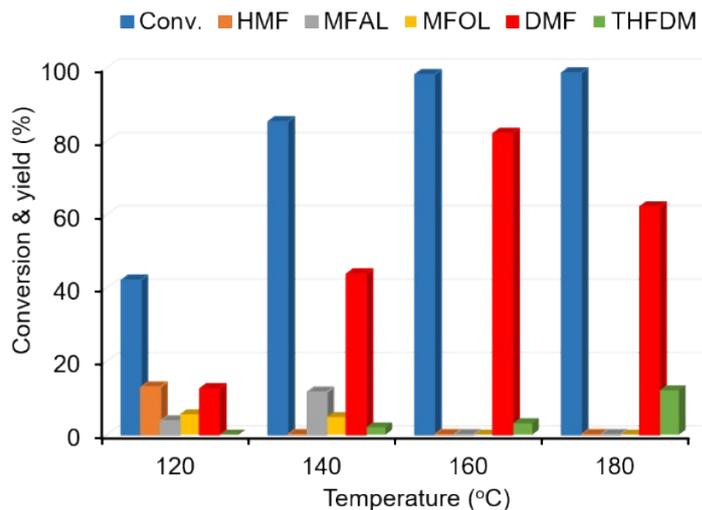


Figure S5: Effect of reaction temperature on the conversion of glucose to DMF. Reaction conditions: Glucose (1 mmol, 0.18 g), P-UiO-66 (0.05 g) and Ni-Co@NC (0.05 g) as catalyst, 8 h reaction time, THF/H₂O ratio of 30/2 mL as solvent, 70 mg NaCl, 0.7 MPa of H₂ pressure.

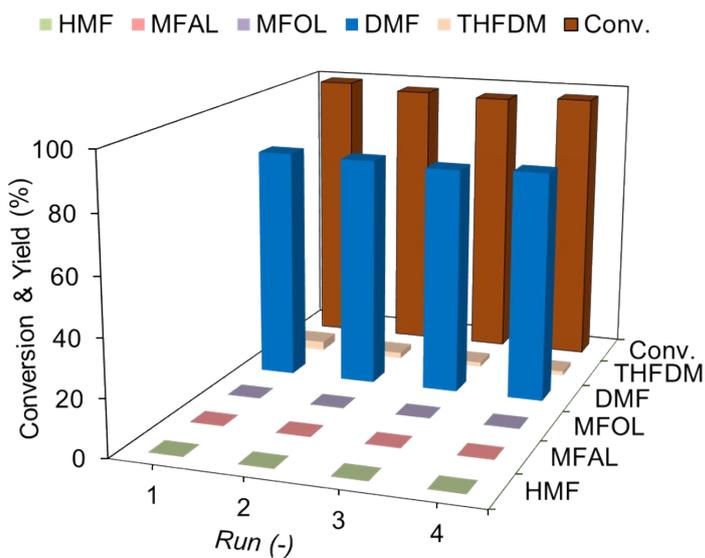


Fig. S6: The reusability of the P-UiO-66 and Ni-Co@NC catalyst for glucose conversion to DMF.

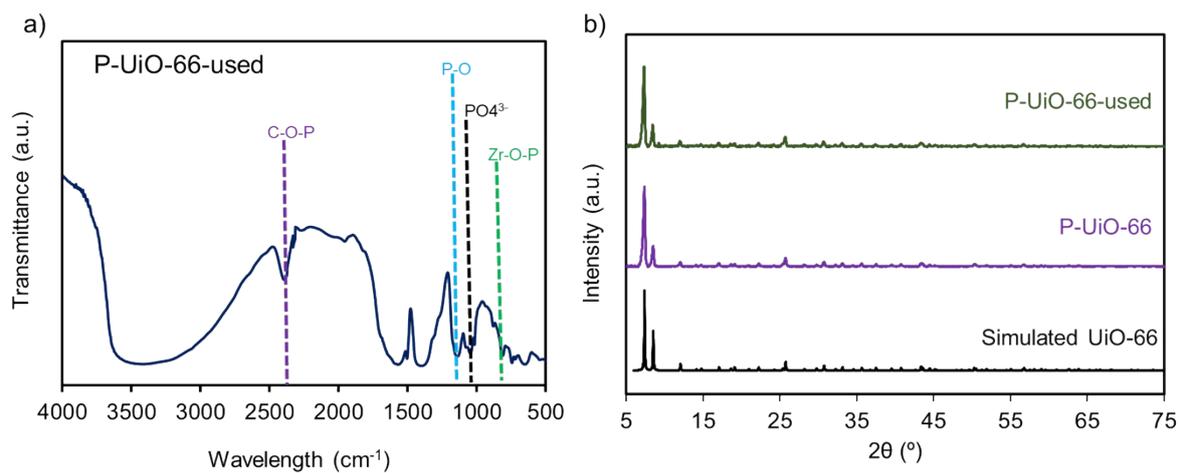


Figure S7: a) FT-IR spectra and b) XRD pattern of reused P-UiO-66 catalyst.

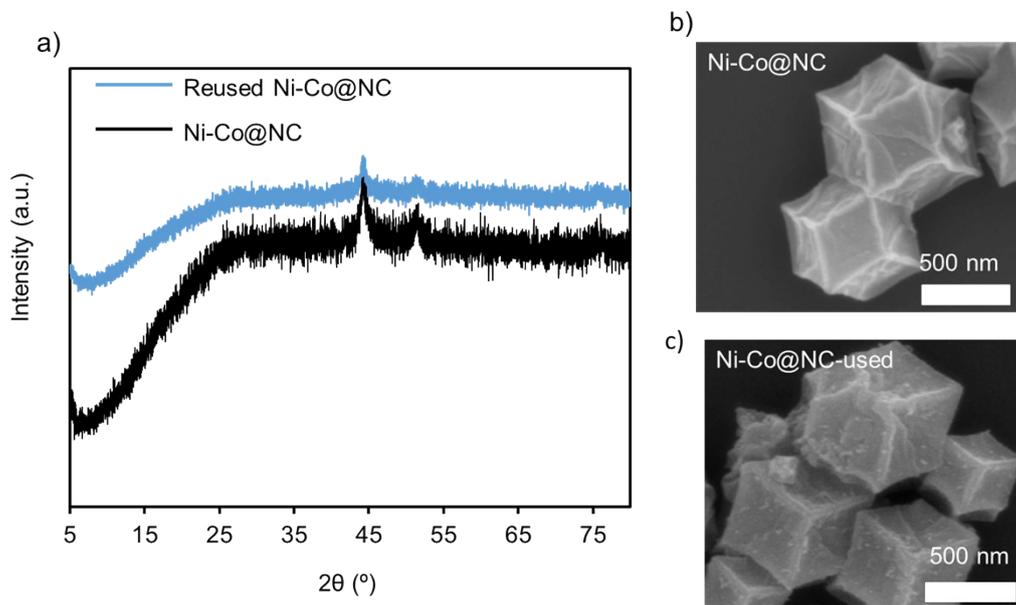


Figure S8: a) XRD pattern and b-d) SEM images

Table S2: The effect of reaction parameters for direct glucose conversion to DMF over the P-UiO-66 and Ni-Co@/NC.

Entry	Reaction parameters			Conversion (%)	Products yield (%)				
	THF/water ratio (mL/mL)	NaCl (mg)	H ₂ pressure (MPa)		HMF	MFAL	MFOL	DMF	THFDM
1	30/0.5	70	0.7	40	n.d.	n.d.	n.d.	10.1	18.6
2	30/2	70	0.7	98.1	Trace	n.d.	n.d.	82.1	3.2
3 ^a	30/10	70	0.7	98.5	n.d.	n.d.	n.d.	23.5	12.5.
4 ^b	30/30	70	0.7	97.4	Trace	n.d.	n.d.	10.5	5.6
5	30/2	0	0.7	45.1	Trace	n.d.	n.d.	37.0	1.4
6	30/2	15	0.7	61.2	Trace	n.d.	n.d.	51.8	2.0
7	30/2	40	0.7	80.1	Trace	n.d.	n.d.	65.0	2.4
8	30/2	90	0.7	98.0	Trace	n.d.	n.d.	83.0	3.6
9	30/2	70	0.1	98.5	Trace	9.8	15.9	31.1	41.5
10	30/2	70	0.3	98.6	Trace	1.2	9.2	52.4	31.2.
11	30/2	70	0.5	99.1	Trace	n.d.	n.d.	70.9	12.3
12	30/2	70	0.9	98.2	Trace	n.d.	10.6	54.0	27.0

Reaction condition: Glucose (1 mmol, 0.18 g), P-UiO-66 (0.05 g) and Ni-Co@/NC (0.05 g) as catalyst, 8 h and 160 °C.

^a sorbitol is the main product with 60% yield.

^b sorbitol is the main product with 81.2% yield.

Table S3: Comparison of catalytic conversion of glucose into DMF over various catalysts

Entry	Feedstock	Catalysts	Solvent	T (°C)	H ₂ pressure (MPa)	t (h)	Conversion (%)	DMF yield (%)	Ref.
Two-step reaction									
1	Fructose	Amberlyst-15 and Ru-Sn/ZnO	n-BuOH	240	1	100	100	99	[3]
2	Fructose	Formic acid and Pd/C, H ₂ SO ₄	THF	150		17	100	46	[]
3	Fructose	NaCl/HCl and CuRu/C	n-BuOH	220	0.68	10	100	72	[45]
4	Glucose	12-molybdophosphoric acid (12-MPA) Pd/C, [EMIM]Cl	Acetonitrile	120	0.62	4	47	0.14	[6]
5	Corn stover	CrCl ₃ , HCl and CuRu/C	DMALiCl [EMIM]Cl n-BuOH	140 /220		12	-	9	[7]
One-step reaction									
6	Fructose	ZnCl ₂ -Pd/C	THF	150	0.8	8	-	19	[8]
7	Fructose	H-Zeolite-Y and Cu/ZnO/Al ₂ O ₃	GVL/H ₂ O	240	2	10	100	40.6	[9]

8	Fructose	AlCl ₃ /H ₂ SO ₄ /H ₃ PO ₄ /Ru/C	<i>N,N</i> -DMF	200	1.5	12	99	66.3	[10]
9	Fructose	4.8Pd/UiO-66@SGO	THF	160	1	3	92	70.5	[11]
10	Fructose	10Cu-1Pd/U50S50	THF	200	1	3	98	85.1	[12]
11	Fructose	PMHS and Pd/C-SO ₃ H-TMS	<i>n</i> -Butanol	120	-	2	>95	~80	[13]
12	Glucose	4.8Pd/UiO-66@SGO	THF	160	1	3	87	45.3	[11]
13	Glucose	10Cu-1Pd/U50S50	THF	200	1	3	97	79.9	[12]
14	Glucose	PMHS and Pd/C-SO ₃ H-TMS	<i>n</i> -Butanol	120	-	4	80	~60	[13]
15	Cellobiose	PMHS and Pd/C-SO ₃ H-TMS	<i>n</i> -Butanol	120	-	5	60	~50	
16	Starch	4.8Pd/UiO-66@SGO	THF	200	1	6	53	19.5	[12]
17	Cellulose	4.8Pd/UiO-66@SGO+HCl	THF	200	1	6	26	10.3	
18	Fructose						98.5	82.1	
19	Glucose						98.1	85..2	
20	Cellubiose	P-UiO-66 and Ni-Co/NC	THF/Water	160	0.7	8	83.6	63.3	This work
21	Starch						70.2	35.0	
22	Cellulose						65.3	20.0	

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