

Supporting information

One-pot tandem dehydration-hydrogenation of xylose with formic acid over Co catalysts

Authors:

Ling Xu ^a, Renfeng Nie ^{b*}, Haifeng Xu ^a, Xujie Chen ^a, Yanchen Li ^a, Xiuyang Lu^{a*}

Address:

^a Key Laboratory of Biomass Chemical Engineering of Ministry of Education, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, PR China

^b Hubei Collaborative Innovation Center for Advanced Organic Chemical Materials, & Ministry-of-Education Key Laboratory for the Synthesis and Application of Organic Functional Molecules, School of Chemistry and Chemical Engineering, Hubei University, Wuhan 430062, P.R. China

* Corresponding authors

Renfeng Nie, Tel/Fax: 86-27-88662747

Email: refinenie@163.com

Xiuyang Lu

Email: luxiuyang@zju.edu.cn

Experimental Procedures

Maierials

1,10-phenanthroline (99 %) was purchased from Innochem, China. FAL (99 %), FOL (98 %), D-xylose (98 %), D-glucose (99.5 %), D-fructose (99 %), D-xylulose (95 %), sucrose (AR), lactose(98 %), Co(OAc)₂·4H₂O (99.9 %), Ni(OAc)₂·4H₂O (99.9 %), Cu(OAc)₂·H₂O (99 %), Fe(OAc)₂ (99 %), Pt/C (5 wt%), Pd/C (5 wt%),

Ru/C (5 wt%) were purchased from Aladdin Chemicals. Nano MgO (99.9 %, 50 nm), FA (98 %) were purchased from Macklin, China. HNO₃ (65-68 %), 1,4-dioxane (≥ 99.5 %), methanol (≥ 99.5 %) were purchased from Sinopharm Chemical Reagent Co. Ltd, China. All chemicals were used without any further treatment.

Catalyst preparation

Co-N-C catalysts were prepared via pyrolysis of the mixture of Co(phen)_x(OAc)₂ and nano-MgO in nitrogen atmosphere. Typically, Co(OAc)₂·4H₂O (147 mg) and 1,10-phenanthroline monohydrate (330 mg) were added into 50 mL ethanol to form a transparent solution. After that, nano-MgO (3.16 g) was added and the suspension was sonicated for 10 min. The mixture was stirred at 60 °C overnight. After ethanol was removed by rotary evaporation, the solid was dried, and heated to a 700 °C in N₂ atmosphere at a heating rate of 2 °C /min and kept for 2 h. The calcinated solid was treated by HNO₃ solution (100 mL, 1 mol/L) in order to completely remove MgO and soluble cobalt species. The resulting sample was thoroughly washed with DI water until free of Mg²⁺ and Co²⁺, dried and named as Co-N-C. Replacing cobalt acetate with nickel acetate, ferric acetate or copper acetate gave rise to Ni-N-C, Fe-N-C or Cu-N-C, respectively.

Characterizations

Powder X-ray diffraction (XRD) was carried out with Ni-filtered Cu K α ($\lambda=0.154$ nm) operating at 40 kV and 30 mA on a Bruker D8 diffractometer. Raman spectra were collected at room temperature from 100 to 3000 cm⁻¹ with 532 nm argon ion laser (LabRAM HR Evolution). Transmission electron microscope (TEM) images were obtained using an accelerating voltage of 200 kV on a JEOL 2100F Transmission Electron Microscope. X-ray photoelectron spectra (XPS) were recorded on a Thermo Scientific ESCALab 250Xi employing a 200 W monochromatic Al K α radiation ($h\nu=1486.6$ eV). C1s at 284.6 eV was used for calibrating the XPS spectra.

One-pot synthesis of FOL from xylose

The reactions were carried out in an autoclave (8 mL) purchased from Zhengxin, China. In a typical run, 0.20 mmol xylose, 30 mg catalyst, a certain amount of FA and 3.5 mL mixture of 1,4-dioxane and water were added into the autoclave. The sealed autoclave was purged, pressurized with N₂ to 0.5 MPa and heated to 160 °C under magnetic stirring (500 rpm). After the completion of reaction, the autoclave was quickly soaked within cold water. The liquid was diluted with methanol. The xylose was analyzed by HPLC/RID (Agilent 1100). The FOL and FAL were analyzed by GC/FID (Agilent 7890A) and were confirmed by GC-MS (Agilent 5977A MSD). A quantitative analysis was performed using calibration curves for every compound in the mixture. All data were calculated by the average of three replicate experiments. After the reaction, the catalyst was successively washed by methanol for 3 times and then dried at 80 °C for 12 h. The recovered catalyst was submitted to the next batch of reaction.

Analysis method

The FAL and FOL were quantitatively analyzed via gas chromatography (GC, Agilent 7890A) with a capillary column (HP-5, 30 m×0.32 mm×0.25 μm) using a flame ionization detector (FID). The carrier gas was nitrogen, and the temperature of the injector and detector were 250 °C and 320 °C, respectively. A quantitative analysis was performed using calibration curves for every compound in the mixture. The FAL and FOL were qualitatively identified via gas chromatography-mass spectrometry (GC-MS, Agilent 5977A MSD) system, and the retention times of the unknown products with known standards were matched on the gas chromatograph. The xylose was quantitatively analyzed via high performance liquid chromatography (HPLC, Agilent 1100) with a column (Aminex HPX-87H, 300 mm×7.8 mm I.D., Bio-Rad Laboratories, Inc.). The flow rate of mobile phase (5 mmol/L H₂SO₄) was 0.4 mL/min. The temperature of the column and the RID were 60 °C and 35 °C, respectively. Reactant mole conversions were obtained as the number of moles of reactant consumed divided by the initial number of moles of reactant added to the reactor. Selectivity was calculated by the number of moles of product recovered

divided by the number of moles of reactant reacted. All data were calculated by the average of three replicate experiments.

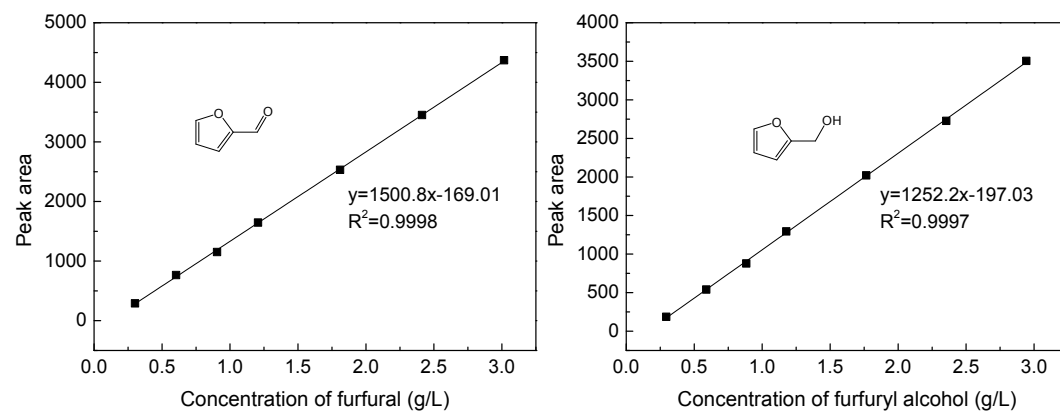


Fig. S1 Standard curves of furfural (left) and furfuryl alcohol (right) for GC analysis.

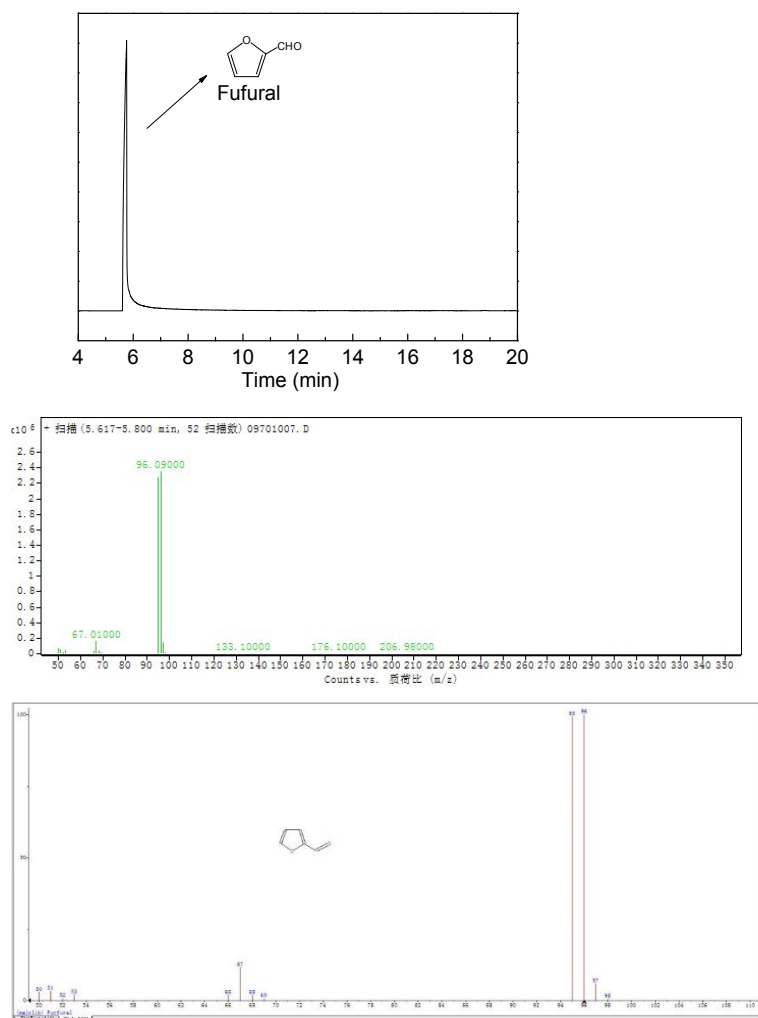


Fig. S2 GC-MS profiles of FAL. Reaction conditions: xylose (0.2 mmol), FA/xylose=20 (mole ratio), solvent (water+1,4-dioxane, 3.5 mL), water content (22%,

v/v), 0.5 MPa N₂, 160 °C, 3 h, 500 rpm.

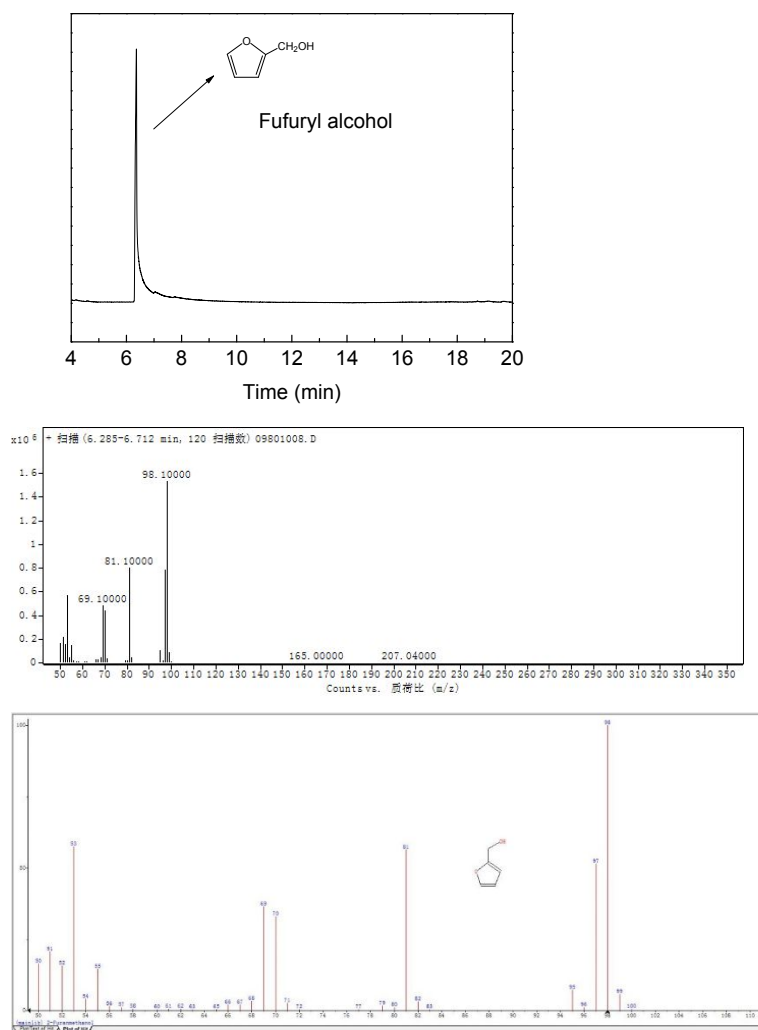


Fig. S3 GC-MS profiles of FOL. Reaction conditions: xylose (0.2 mmol), Co-N-C (30 mg), FA/xylose=20 (mole ratio), solvent (water+1,4-dioxane, 3.5 mL), water content (22%, v/v), 0.5 MPa N₂, 160 °C, 3 h, 500 rpm.

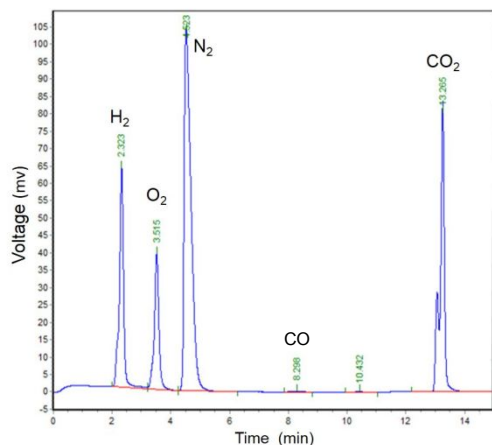


Fig. S4 GC spectrum of FA dehydrogenation over Co-N-C. (The observed O₂ and N₂ were extraneous gases due to the gas analysis)

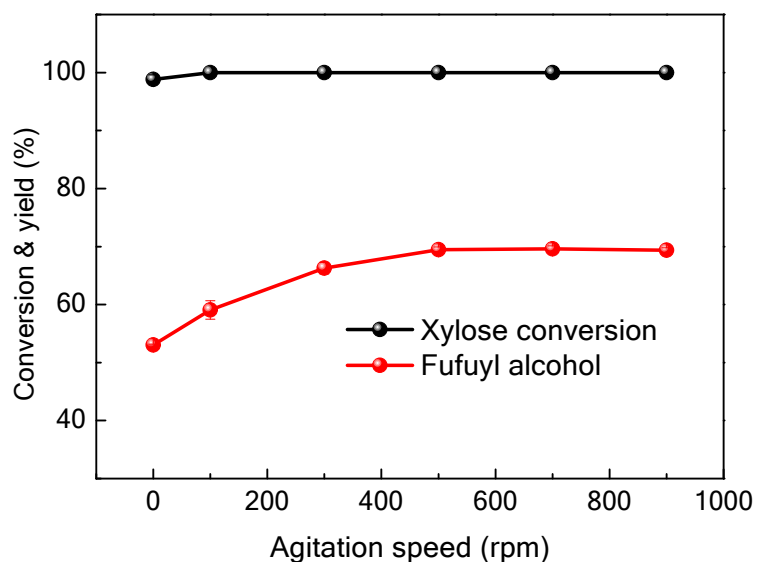


Fig. S5 Effect of agitation speed on one-pot conversion of xylose over Co-N-C. Reaction conditions: xylose (0.2 mmol), Co-N-C (30 mg), FA/xylose=20 (mole ratio), solvent (water+1,4-dioxane, 3.5 mL), water content (22%, v/v), 0.5 MPa N₂, 160 °C, 3 h.

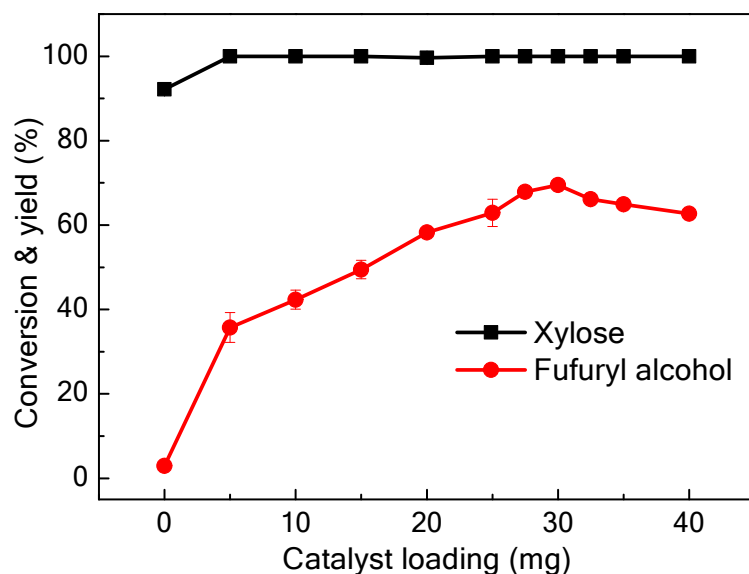


Fig. S6 Effect of catalyst loading on one-pot conversion of xylose over Co-N-C. Reaction conditions: xylose (0.2 mmol), FA/xylose=20 (mole ratio), solvent (water+1,4-dioxane, 3.5 mL), water content (22%, v/v), 0.5 MPa N₂, 160 °C, 3 h, 500 rpm.

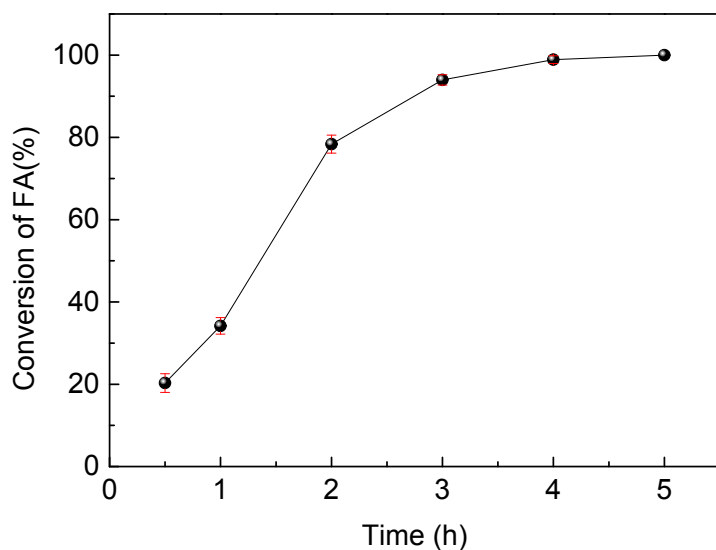


Fig. S7 FA decomposition over the Co-N-C catalyst. Reaction conditions: xylose (0.2 mmol), Co-N-C (30 mg), FA/xylose=20 (mole ratio), solvent (water+1,4-dioxane, 3.5 mL), water content (22%, v/v), 0.5 MPa N₂, 160 °C, 500 rpm.

Table S1 The reaction rate constants (k) of one-pot xylose transformation under different temperature.

T/K	k/h ⁻¹	R ²
403	0.2978	0.9960
413	0.5476	0.9869
423	1.2714	0.9945

433	1.5896	0.9901
443	4.9037	0.9743

Reaction conditions: xylose (0.2 mmol), FA/xylose=20 (mole ratio), solvent (water+1,4-dioxane, 3.5 mL), water content (22%, v/v), 0.5 MPa N₂, 500 rpm.

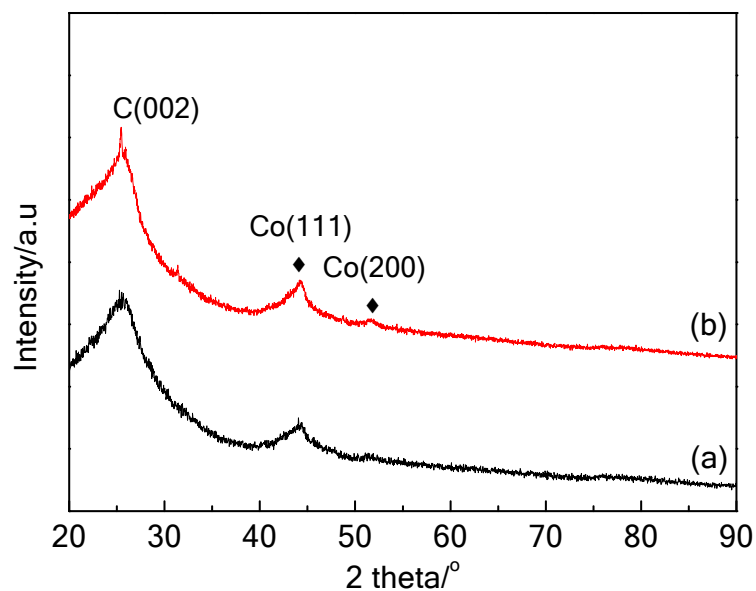
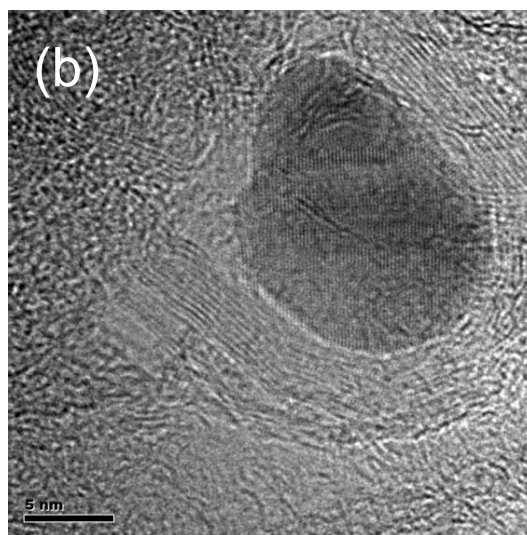
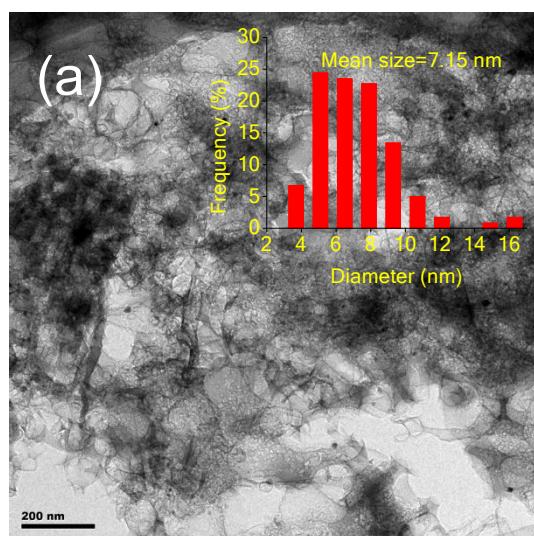


Fig. S8 XRD patterns of (a) fresh Co-N-C and (b) 5 times reused Co-N-C.



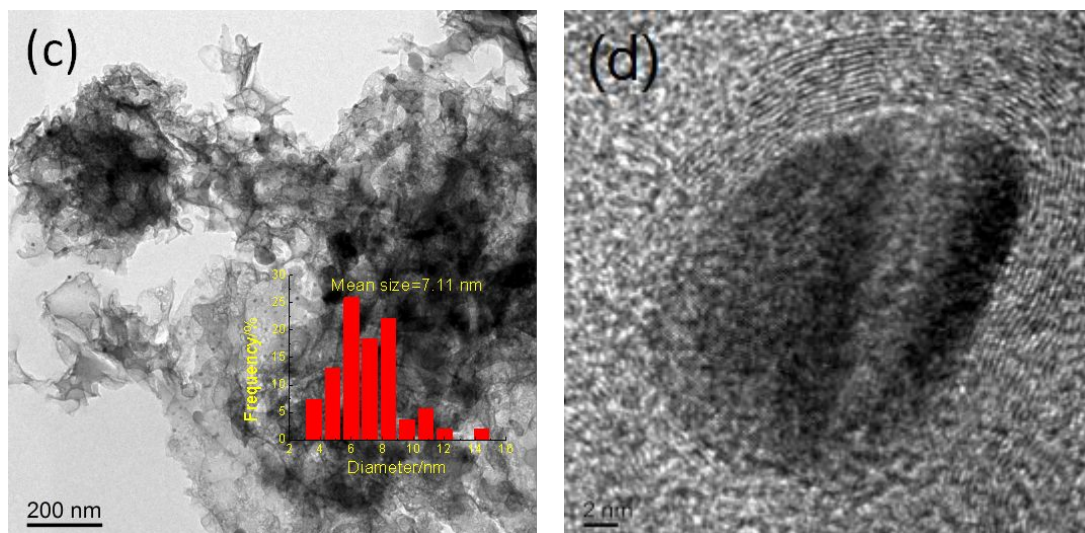


Fig. S9 TEM images of (a, b) fresh Co-N-C and (c, d) 5 times reused Co-N-C. The inserts in (a) and (c) are corresponding histograms of Co particle size distribution.

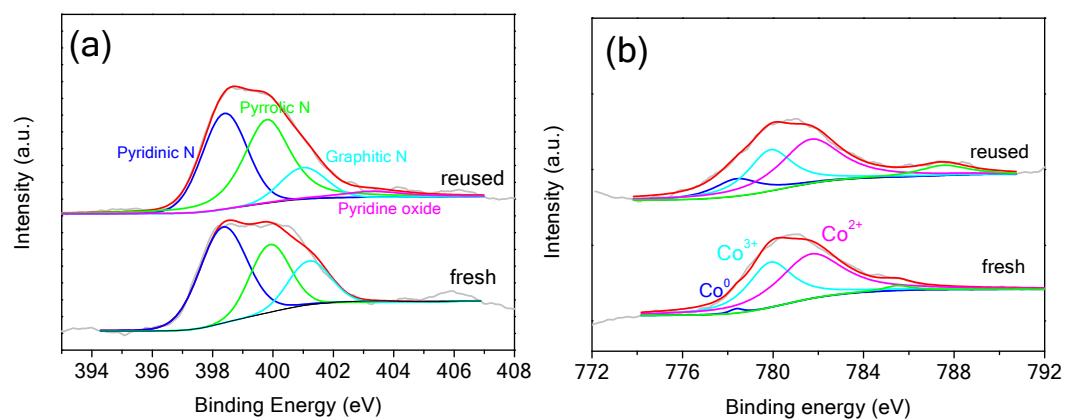


Fig. S10 (a) N1s and (b) Co2p spectra of fresh and reused Co-N-C catalysts.

Table S2 Representative works for FOL production from sugars.

catalysts	hydrogen donor	reaction conditions	yield (%)	ref.
Homogeneous Ir catalyst	Formic acid	1: 20 mmol D-xylose, 1 ml DMSO+10 ml THF, 2 mol formic acid, 150 °C, 7 h; 2: 2 mmol Et ₃ N+0.1 mmol Ir +20 mmol formic acid, 40 °C, 5 min.	FOL yield= 63%	1
ZrO ₂ -SO ₄ + Pt/SiO ₂	Isopropanol	SO ₄ /Pt molar ratio = 8, H ₂ O-Isopropanol (1:3), 130 °C, 6 h.	xylose conv.=65%, FOL selec.= 51%	2
β zeolite	Isopropanol	H ₂ O-Isopropanol (0.0026:1), 30 bar N ₂ , 130 °C, 1 h.	FOL yield=75%	3
SO ₄ ²⁻ /SnO ₂ -KL+ CCTU-T15	biocatalysis	1: SO ₄ ²⁻ /SnO ₂ -KL, toluene- H ₂ O (1:2), 170 °C, 30 min; 2: CCTU-T15, glucose, toluene- H ₂ O (1:3), 30 °C, 6 h.	FOL yield=74.3%	4
SO ₄ ²⁻ /SnO ₂ -MMT+ CCTU-T14	biocatalysis	1: SO ₄ ²⁻ /SnO ₂ -MMT, pH 6.5, 170 °C, 20 min; 2: CCTU-T14, glucose, pH 6.5, 30 °C, 24 h.	FOL yield=41.9%	5
Pt/ZrO ₂ -SO ₄	H ₂	Acid/metal ratio=142, H ₂ O-Isopropanol(1:1), 3 MPa H ₂ , 130 °C.	xylose conv.=32%, FOL selec.=27%	6
Amberlyst-15+ Ru/C	H ₂	Ru/C (0.4 g), Amberlyst-15 (10 g), xylose (10 g), 2.5 MPa H ₂ , H ₂ O (300 mL), cyclohexane (300 mL), 135 °C.	xylose conv.=32%, tetrahydrofurfuryl alcohol selec.=50%	7
Pt/SBA-15- SO ₃ H	H ₂	H ₂ O-Isopropanol (1:1), 30 bar H ₂ , 130 °C, 6 h.	xylose conv.=65% FOL selec.=83%	8
Hβ+Cu/ZnO/Al ₂ O ₃	H ₂	γ- butyrolactone- H ₂ O, WHSV=0.023 h ⁻¹ , H ₂ feed= 25 mLmin ⁻¹ , 0.1 MPa H ₂ , 150 °C.	FOL yield=87.2%	9

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