Supporting information

Highly selective one-pot production of 2, 5-furandimethanol from saccharides

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Experimental Procedures

Materials

1,10-phenanthroline (99%) was purchased from Innochem, China. Poly(enthylene glycol)-block-poly(propylene glycol)-block-poly(enthylene glycol) (P123, Mn~5800) and $SnCl_4$ (98%) were purchased from Sigma-Aldrich. Glucose (≥99.5%), Fructose (99%), $Co(OAc)_2 \cdot 4H_2O$ (99.9%), $CoCl_2 \cdot 6H_2O$ (99.99%), $MgCl_2 \cdot 6H_2O$ (99%), $CeCl_3$ (99.9%), $LuCl_3$ (99.9%), $AlCl_3$ (99%), glucan (MW~20000), cellobiose (AR) and sucrose (AR) were purchased from Aladdin Chemicals. Formic acid (98%), $CrCl_3$ (98%), $NiCl_2$ (99%), $ZnCl_2$ (98%), $MoCl_5$ (99.5%), $PrCl_3$ (99.9%), lactose (70%β+30%α), maltose (95%), 5-hydroxymethylfurfural (97%), 2,5-furandimethanol

(98%) and 5-methyl-2-furranmethanol (97%) were purchased from Macklin, China. Tetraethyl orthosilicate (AR), HCl (36.0-38.0%), HF (≥40%), 1,4-dioxane (≥99.5%), methanol (≥99.5%)and ethanol (≥99.5%) were purchased from Sinopharm Chemical Reagent Co. Ltd, China. HFCS-42, HFCS-55 and HFCS-90 were purchased from Hubei qianfengxiang food Co. Ltd, China. All chemicals were used without any further treatment.

Catalyst preparation

Preparation of SBA-15: Pluronic polymer surfactant P123 was used as structure-directing agent. First, 6 g P123 was dissolved in the 200 g 1.6 M HCl aqueous solution, the resulting solution was stirred at 40^{o}C until the solution became clear. Then, 12.75 g TEOS was added dropwise into this solution under stirring. The mixture was kept under stirring at 40 ^{o}C for 12 h. This mixed solution was then transferred into a Teflon-lined autoclave and heated to and kept at 100 ^{o}C for 24 h. Finally, white precipitates were collected, filtered and washed with water, dried, and calcined at 550 ^{o}C for 6 h at a heating rate of 4^{o}C/min in a tube furnace to remove the organic template.

Co-NC catalyst was prepared *via* pyrolysis of the mixture of $Co(phen)_2(OAc)_2$ and SBA-15 in nitrogen atmosphere. Typically, $Co(OAc)_2{\cdot}4H_2O$ (124 mg) and 1,10-phenanthroline monohydrate (198 mg) were added into 25 mL ethanol to form a transparent solution. After that, SBA-15 (0.2495 g) was added and the suspension was sonicated for 10 min. The mixture was stirred at 60 ^{o}C overnight. After ethanol was removed by rotary evaporation, the solid was dried, and heated to a 700 ^{o}C in N_2 atmosphere at a heating rate of 2 ^{o}C /min and kept for 2 h. The calcinated solid was treated by HF and HCl solution in order to completely remove SBA-15 and soluble cobalt species. The resulting sample was thoroughly washed with DI water until free of Co^{2+}, dried and named as Co-NC. Replacing cobalt acetate with nickel acetate, ferric acetate or copper acetate gave rise to Ni-NC, Fe-NC or Cu-NC, respectively.

Characterizations

Powder X-ray diffraction (XRD) was carried out with Ni-filtered Cu Kα (λ=0.154

nm) operating at 40 kV and 30 mA on a Bruker D8 diffractometer. Transmission electron microscope (TEM) images were obtained using an accelerating voltage of 200 kV on a JEOL 2100F Transmission Electron Microscope. Small angle X-ray diffraction (SAXRD) was carried out on the Japanese Rigaku Ultima IV diffractometer, scanning in the range of 0.5-10° and the scanning speed is 0.5°/min. N_2 adsorption was carried out at 77 K using an auto-adsorption analyzer (Micromeritics, 3Flex). The thermal stabilities of Co-NC were obtained by thermogravimetry (TG) and differential scanning calorimetry (TGA55) in an N_2 atmosphere. X-ray photoelectron spectra (XPS) were recorded on a Thermo Scientific ESCALab 250Xi employing a 200 W monochromatic Al Kα radiation (hv=1486.6 eV). C1s at 284.6 eV was used for calibrating the XPS spectra.

Catalytic reactions

The reactions were carried out in an autoclave (8 mL) purchased from Binhai County Zhengxin Instrument Factory, China. In a typical run, 30 mg glucose, 20 mg Co-NC, 5 mg metal chloride, a certain amount of FA and 3.5 mL solvent were added into the autoclave. The sealed autoclave was purged, pressurized with N_2 to 0.5 MPa and heated to the treatment temperature under magnetic stirring (500 rpm). After the completion of reaction, the autoclave was quickly soaked within cold water. The spent Co-NC was separated via centrifugation, washed by methanol for 3 times and then dried at 60 ^{o}C for 12 h. While the liquid (containing chlorate) was diluted with methanol, in which the products and substrate were analyzed by high performance liquid chromatography (HPLC). Each experiment was repeated three times, and each data point represented the mean result from three replicate experiments.

Analysis method

Glucose, fructose, HMF, FDM, FA and other by-products were quantitatively analyzed *via* high performance liquid chromatography (HPLC, Agilent 1100) with a colum (Aminex HPX-87H, 300 mm × 7.8 mm I.D., Bio-Rad Laboratories, Inc.). The flow rate of mobile phase (5 mmol/L H_2SO_4) 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. 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. The conversion of sugars, yield and selectivity of products were defined as follows:

$$Conversion/\% = \frac{n_{sugar} - n'_{sugar}}{n_{sugar}} \times 100\%$$

$$Yield/\% = \frac{n_{product}}{n_{sugar}} \times 100\%$$

$$Selectivity/\% = \frac{Yield}{Conversion} \times 100\%$$

Here n_{sugar} is the initial mol of sugar, n'_{sugar} is the residual mol of sugar after reaction and $n_{product}$ is the generated mol of product after reaction. If sugars are di/polysaccharides, n_{sugar} is the mole of its corresponding monosaccharide.

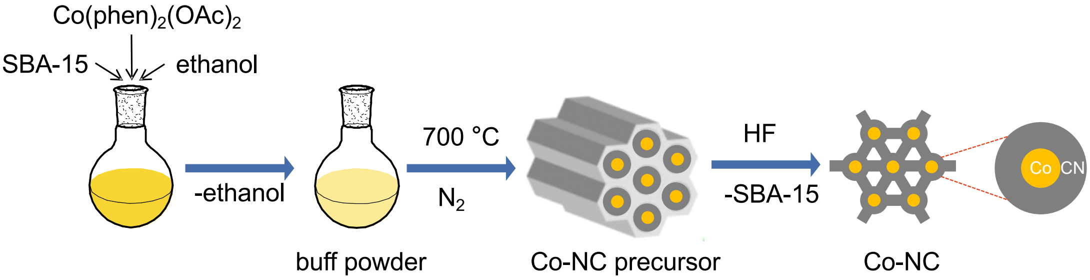


Fig. S1 Schematic illustration of synthesis of Co-NC catalyst.

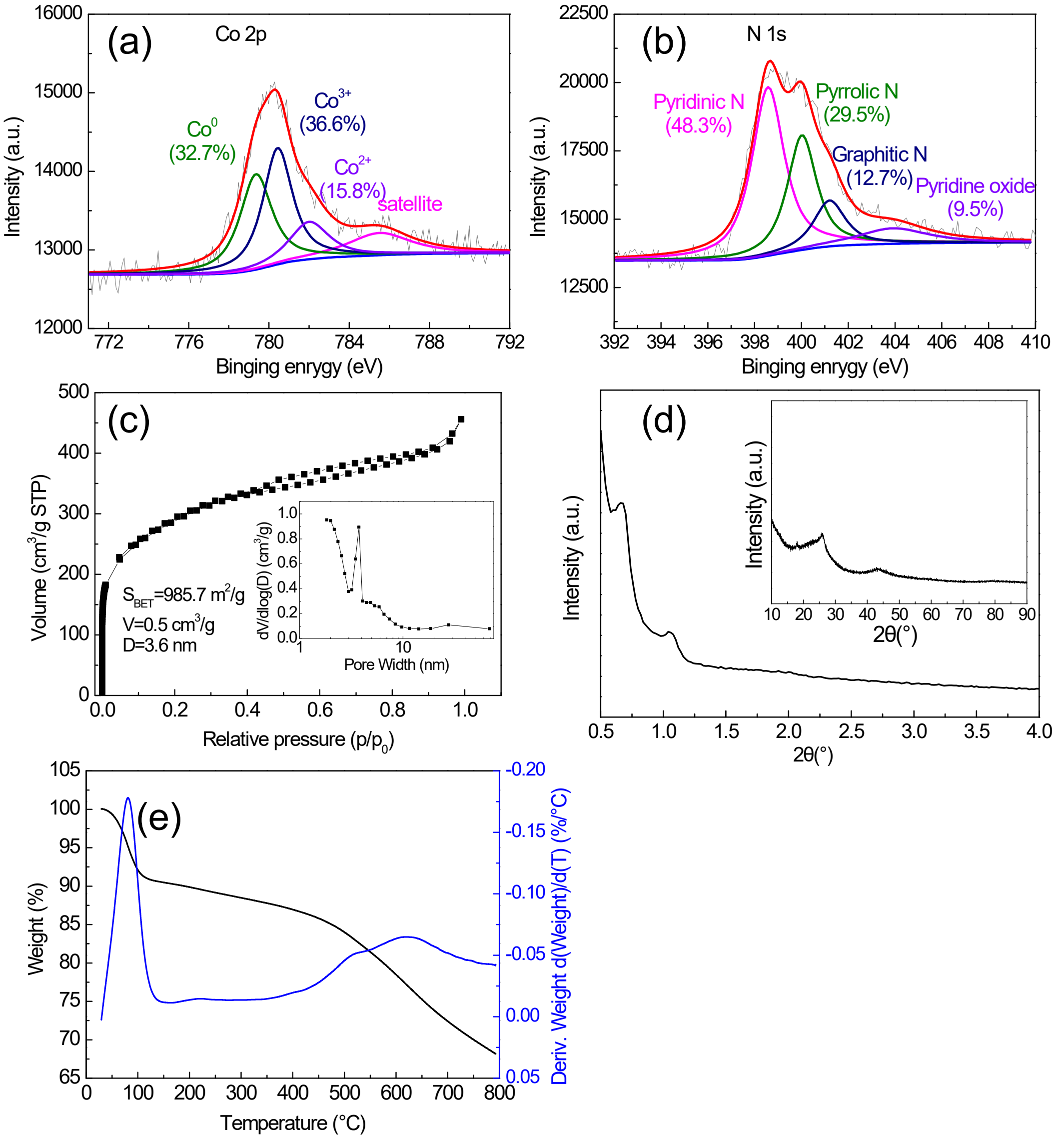


Fig. S2 (a) N1s spectra, (b) Co2p spectra, (c) N_2 adsorption/desorption isotherm, (d) XRD and SAXRD patterns and (e) TGA analysis of Co-NC.

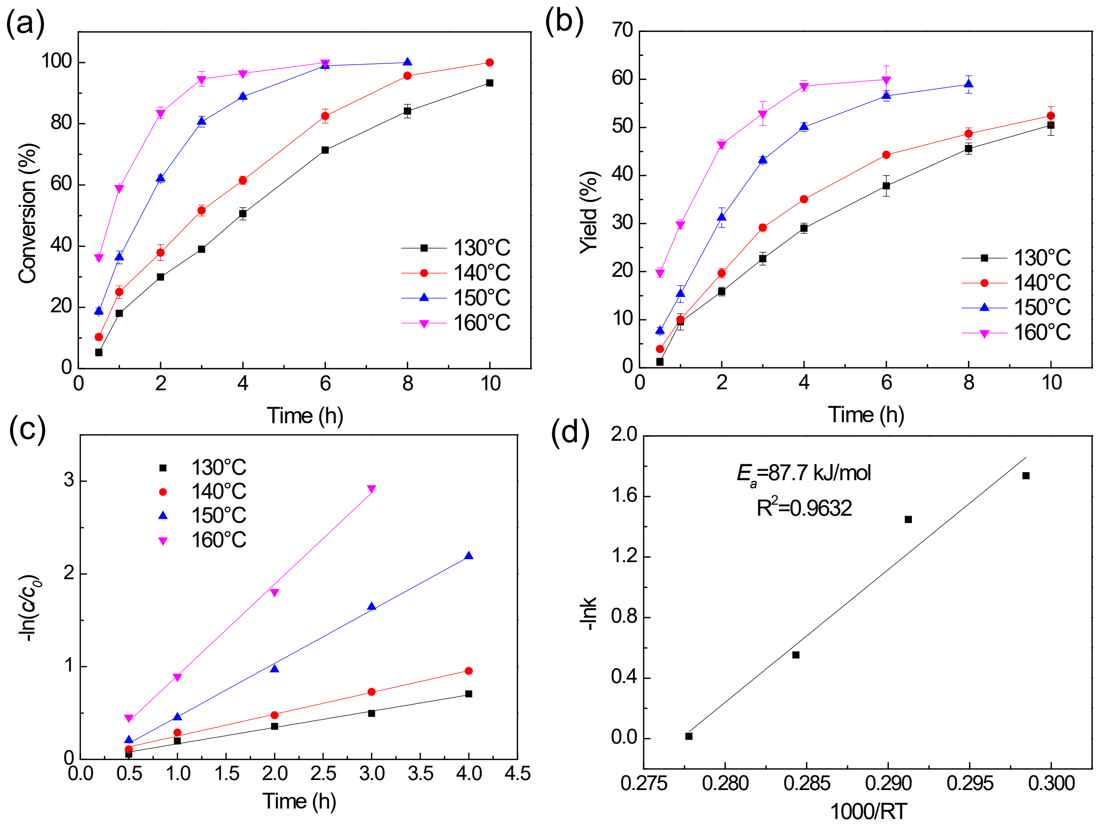


Fig. S3 (a, b) One-pot conversion of glucose at different temperatures. (c) Pseudo-first-order plot of ln(c/c_0) against reaction time for one-pot conversion of glucose. (d) Plot of ln k against 1/T for one-pot conversion of fructose. Reaction conditions: glucose (30 mg), NiCl$_2$ (5 mg), FA/glucose=20 (mole ratio), Co-NC (20 mg), solvent (water+1,4-dioxane, 3.5 mL), water content (30%, v/v), 0.5 MPa N$_2$, and 500 rpm.

Table S1 Reaction rate constants (*k*) of one-pot transformation of glucose at different temperature.

T/K	k/h^{-1}	R^2
403	0.1761	0.9904
413	0.2352	0.9954
423	0.5752	0.9975
433	0.9856	0.9968

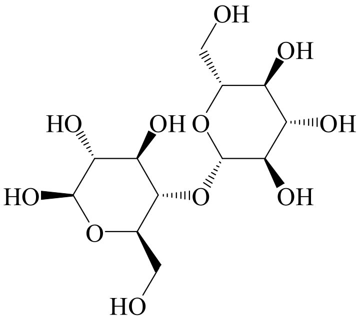
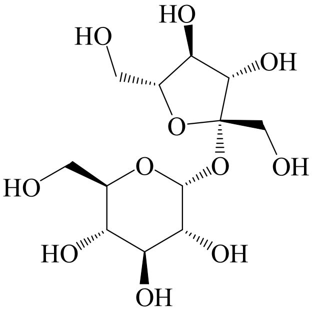
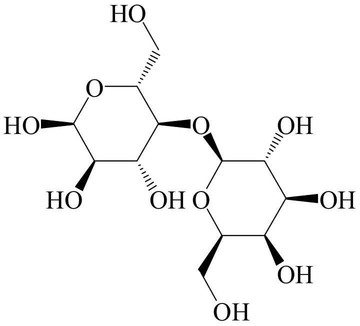
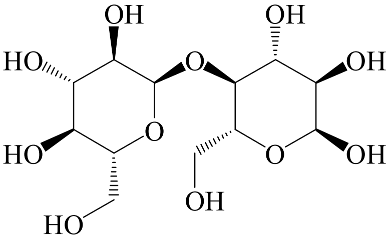
Table S2 Constituent of different types of high fructose corn syrup.

Entry	Type	Content (wt.%)		
		Fructose (solid content)[a]	Glucose (solid content)[a]	H_2O[b]
1	F42	42	53	29
2	F55	55	40	23
3	F90	90	7	25

[a] Fructose/glucose (solid content) means the mass fraction of fructose/glucose in solid.

[b] H_2O content means the mass fraction of H_2O in high fructose corn syrup.

Table S3 Structure and market price of cellobiose, sucrose, lactose and maltose.

Sugars	Market price (USD/ton)	Structure
Cellobise	~2400	
Sucrose	~440	
Lactose	~1800	
Maltose	~1800	

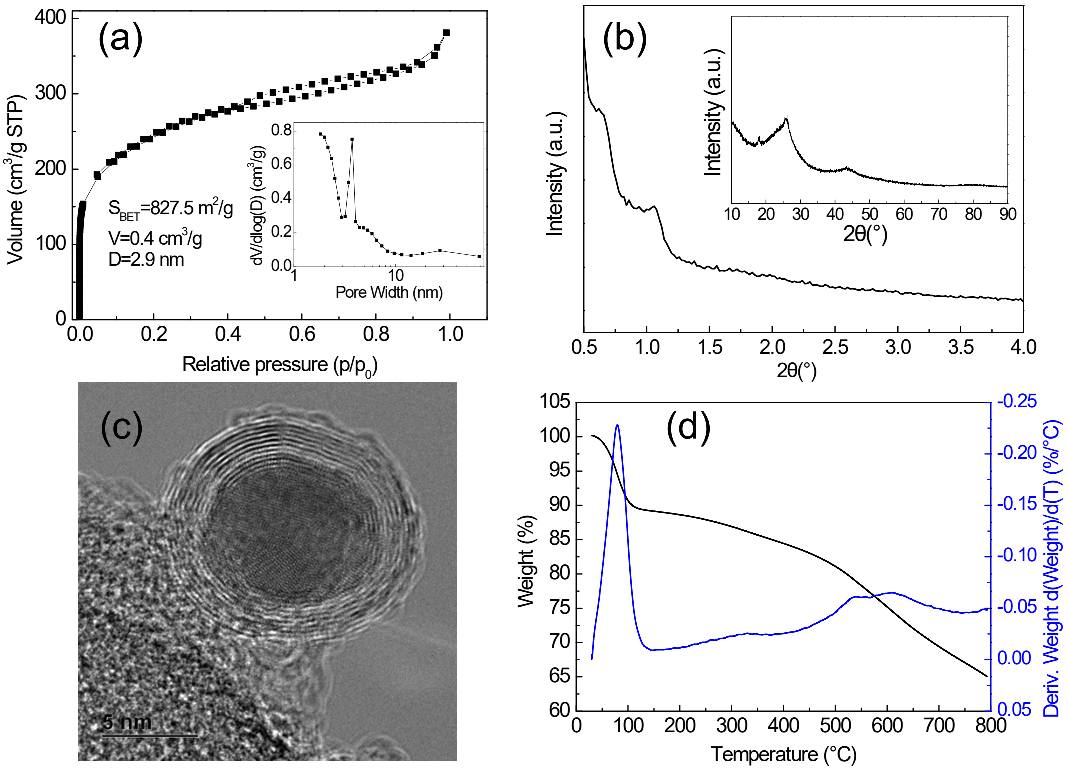


Fig. S4 (a) N_2 adsorption/desorption isotherms, (b)XRD and SAXRD patterns, (c) TEM image and (d) TGA analysis of recycled Co-NC.