Single-step catalytic conversion of furfural to 2-pentanols over bimetallic Co-Cu catalysts

Bhogeswararao Seemala,[†,‡,#] *Rajeev Kumar,* [†] *Charles E Wyman,*[†,‡] *Charles M. Cai,*[†,‡,] *and Phillip Christopher,*[‡,#,] *
[†]Bourns College of Engineering - Center for Environmental and Research Technology (CE-CERT), University of California, Riverside, California 92507, USA.
[‡]Department of Chemical and Environmental Engineering, Bourns College of Engineering, University of California, Riverside, California 92521, USA.
[#] Department of Chemical Engineering, University of California, Santa Barbara, Santa Barbara, CA 93106, USA.

*Corresponding Author Email: pchristopher@ucsb.edu

Materials and Methods

Catalysts synthesis

(a) In a typical synthesis, the required amounts of copper (II) nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$, purity 99%, CAS: 10031-43-3, Aldrich, New Jersey, USA) was dissolved in 50 mL deionized (DI)-water and added to 5 g of θ-Al_2O_3 contained in a round bottom flask to obtain a 5 wt% loading of Cu. The solution was mixed thoroughly, and dried at 80 °C in a rotary evaporator. The resulting solids were dried at 100 °C for 12 hours in an oven and calcined at 450 °C for 5 hours in air. Supported Ni and Co catalysts on Al_2O_3 catalysts were prepared in the similar manner by using $Ni(NO_3)_2 \cdot 6H_2O$, (Aldrich, purity 99.99%, Louis, MO 63103, USA) and $Co(NO_3)_2.6H_2O$, (Acros Organics, purity 99+%, Louis, MO 63103, USA), as precursors, respectively. Prior to reactivity experiments, all catalysts were reduced with pure H_2 gas (flow rate of 50 mL min^{-1}) at 450 °C for 3 hours and cooled to 25 °C under the same environment.

(b) To synthesize bimetallic Cu(5%)-Ni(5%) (or) Co(5%)-Cu(5%) (or) Co(5%)-Ni(5%) supported catalysts, required amounts of corresponding precursors (details mentioned above) were simultaneously added to 50 mL DI-water. This solution was added to 5 g of θ-Al_2O_3 in a round bottom flask, thoroughly mixed and then dried at 80 °C using rotary evaporator. The obtained material was dried in a vacuum oven at 100 °C for 12 hours followed by calcination at 450 °C for 5 hours. Prior to reactivity studies, catalysts were reduced by pure H_2 (flow rate of 50 mL min^{-1}) at 150°C, 300°C and 450 °C for 3 hours and cooled to 25 °C under the same environment.

Reactivity measurements

0.3 g of reduced catalyst was transferred into a 100 mL stainless-steel Parr micro bench-top reactor (4590 Series, Parr instruments Co., Moline, IL) containing 1 g of FF (or) MF (99.9% pure, Sigma Aldrich) with 25 ml of 1,4-dioxane (HPLC Grade, Fisher Chemicals) as a solvent.

The reactor was initially flushed with H_2 and then pressurized with H_2 gas. Then, the reactor temperature was raised to desirable (180 °C to 240 °C) and reactions were conducted for 0.5-12 hours. After the reaction, liquid samples were separated by vacuum filtration, and analyzed by gas chromatography.

Liquid products were analyzed on an Agilent gas chromatograph (7890A, Agilent Technologies). A DB-WAX Ultra Inert column (Agilent Technologies) that was 30 m long x 0.320 mm internal diameter x 0.5 micron was used to quantify FF, FOL, THFOL, MF, furan, and 2-POL using a flame ionization detector (FID) using the following program: hold for 1 min at 30 °C, increase from 30 to 100 °C at a ramp rate of 10 °C min^{-1}, hold for 2 min at 100 °C, increase from 100 to 250 °C at a ramp rate of 10 °C min^{-1}. MF and MTHF yields were further quantified by using Hp-5 column that was 30 m long × 0.320 mm internal diameter × 0.25 micron via FID using the following program: 1 min hold at 30 °C, increase from 30–100 °C at a ramp rate of 10 °C/min, 2 min hold, increase from 100–325 °C at a ramp rate of 25 °C/min and hold for 1 min. Final product in molar yields were quantified by using calibration curves of standard samples in the gas chromatograph. Reactant conversion and product yield were calculated as follows:

$$FF\ conversion, \% = \left(1 - \frac{Moles\ of\ unreacted\ FF}{Moles\ of\ FF\ before\ reaction}\right) \times 100 \quad \text{------> (1)}$$

$$Yields\ (mol\ \%) = \frac{Moles\ of\ the\ product\ formed}{Initial\ mole\ of\ FF} \times 100 \quad \text{---------> (2)}$$

Catalyst Characterizations

XRD spectra of reduced catalysts were recorded in the 2θ range of 20 to 90° using an X'pert Pro PANalytical diffractometer equipped with a Nickel filtered Cu Kα radiation source.

H_2-TPR experiments were carried out on a Micromeritics AutoChem 2920 instrument. In each experiment, 0.05 g of catalyst was placed in a quartz tube, and treated with O_2 gas (50 mL min^{-1} flow rate) followed by raising the temperature to 350 °C by 10 °C/min ramp rate. Reactor was held at 350 °C for 1 hour and then cooled it to 35 °C. A gas mixture of H_2 (10%)−Ar (90%) was passed through the quartz reactor at same temperature for 1 h with a 50 mL min^{-1} flow rate. The temperature was raised to 700 °C at a linear heating rate of 5 °C min^{-1}. A standard CuO powder was used to calibrate H_2 consumption.

Table S1: Temperature effect on FF conversions over monometallic Cu, Ni and bimetallic Cu-Ni catalysts

Al_2O_3 support catalyst	**At 200 °C, 25 bar H_2 pressure**				**At 240 °C, 35 bar H_2 pressure**			
	Product yields (mol %)				Product yields (mol %)			
	THFOL/FOL	MF	MTHF	2-POL	THFOL	MF	MTHF	2-POL
Cu	0.0/18.2[a]	74.9[a]	0.0	0.0	0.0	92.5	0.0	0.0
Ni	54.5/0.0	2.5	30.5	0.0	13.1	0.0	63.0	2.1
Co	0.0/0.0	50.3	5.0	26.1	0.0	15	23.1	45.5

Reaction conditions: Reactions were run at a FF loading of 1 g, catalyst loading of 0.3 g, 25 mL of 1,4 Dioxane as solvent after 2 hours reaction time. [a]8 hours reaction. FF conversions were 100% in all the above cases.

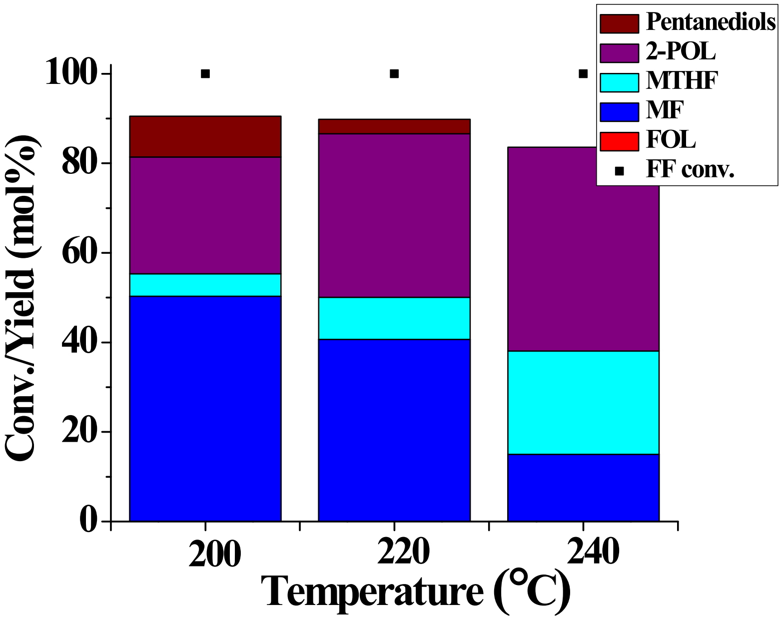

Figure S2. FF conversions and products yield on monometallic Co (5%) on Al_2O_3 catalysts. All reactions were run with a FF loading of 1 g, a catalyst loading of 0.3 g, 25 mL of 1,4-dioxane as a solvent, and an H_2 pressure of 35 bar.

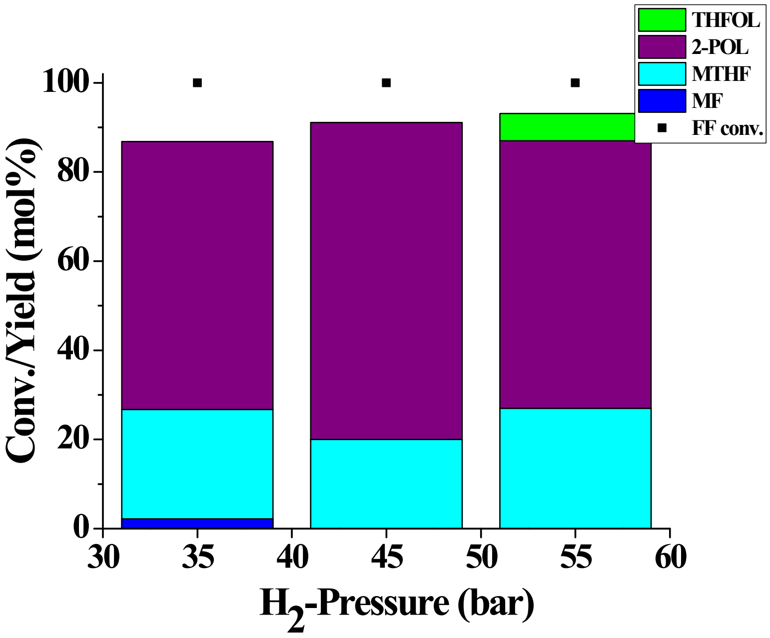

Figure S3. FF conversion and products yield over Cu-Co/Al_2O_3 catalysts as function of H_2 pressure. Reaction conditions were a FF loading of 1 g, catalyst loading of 0.3 g, 25 mL of 1,4-dioxane as a solvent, a temperature of 240 °C, and 12 h run time.

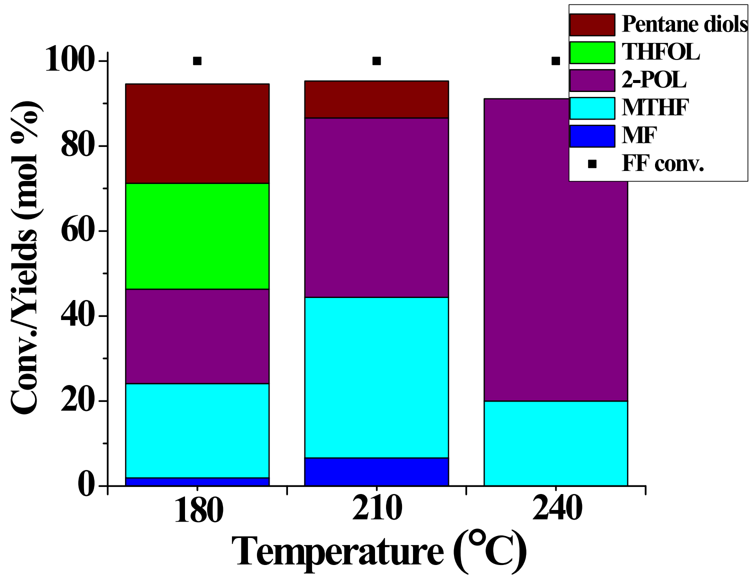

Figure S4. FF conversion and products yield over Cu-Co/Al_2O_3 catalysts as function of reaction temperature. Reaction conditions were a FF loading of 1 g, catalyst loading of 0.3 g, 25 mL of 1,4-dioxane as a solvent, H_2 pressure of 45 bar, and 12 h run time.

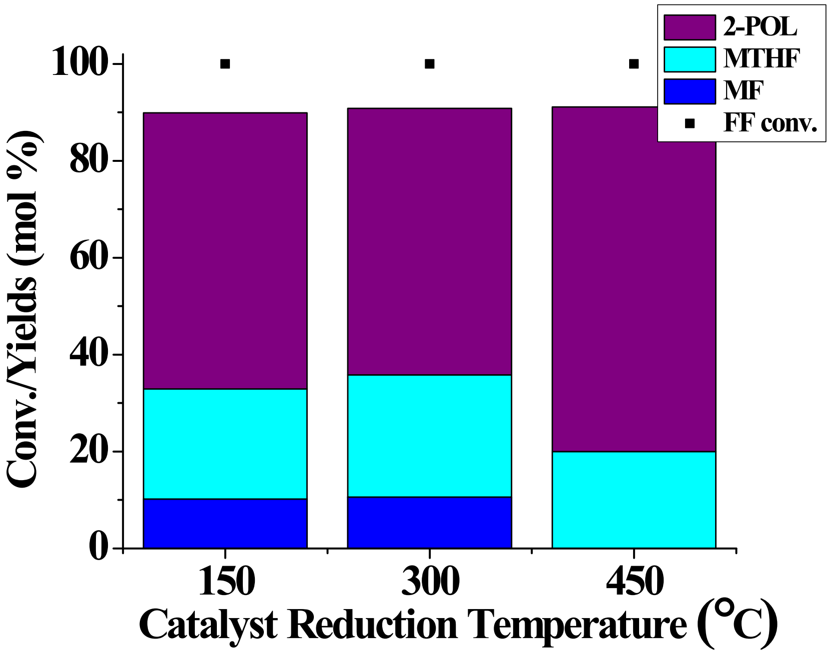

Figure S5. Effect of catalyst reduction temperature over FF conversion and products yield. Reaction conditions were a FF loading of 1 g, catalyst loading of 0.3 g, 25 mL of 1,4-dioxane as a solvent, reaction temperature of 240 °C, H_2 pressure of 45 bar, and 12 h run time