New catalytic strategies for α,ω-diols production from lignocellulosic biomass

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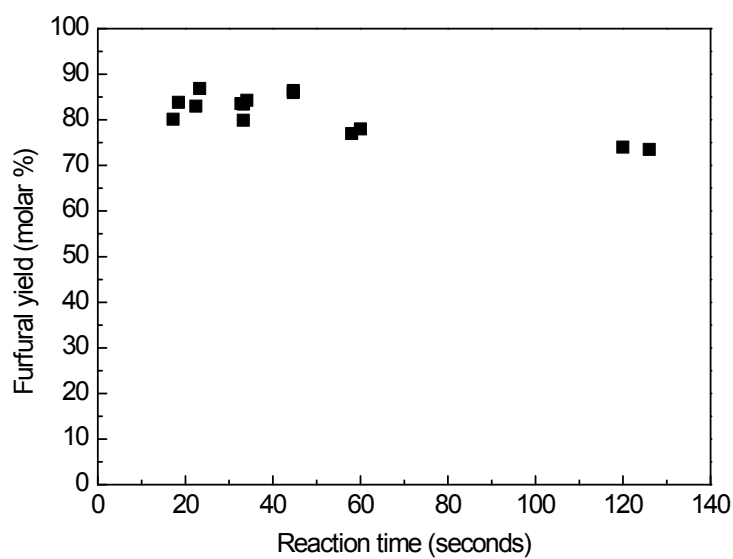
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Figure S1. Production of furfural from solubilized hemicellulose derived from white birch at 225 °C.

Table S1 Reaction time (minutes) for maximum yields of LGO and HMF at various water content at 210 °C.

Time (min.) Cellulose Loading (wt%)	Water content (wt.%)						
	0	0.19	0.5	1	2.5	5	10
3	55	48	47	51	48	42	45

Reaction conditions: THF (60 mL), H_2SO_4 (64 μL Conc., 20 mM), 6.9 MPa He, 700 rpm.

Chemicals

The following chemicals were used as received: LGO (98%, Apollo Scientific), HMF (99%, Sigma Aldrich), Levoglucosan (TCI, purity 99%) cellulose (Avicel® PH-101, moisture content ca. 3 wt%), THFDM (98%, Alfa Chemicals), and THF stabilized with butylated hydroxytoluene (99.9%, Acros Organics), 2-hydroxytetrahydropyran (Acros organics, 90%), tetrahydrofurfuryl alcohol (Aldrich, 99%), Ni/SiO$_2$ (64 wt%, Strem Chemcials), SiO$_2$ support (Sigma, Davisil 646), Gamma-valerolactone (>98% purity, Shenzhen Nexconn Pharmatechs Ltd.), Pd(NO)$_3$ (10% in 10% HNO$_3$, Sigma Aldrich), Ruthenium nitrosyl nitrate (Aldrich), chloroplatinic acid hexahydrate (Sigma), nickel nitrate hexahydrate (Sigma, 99.999%), cobalt nitrate hexahydrate (Sigma), rhodium chloride (Mitsubishi Chemical Company, 40% Rh), Grade 135 amorphous SiO$_2$-Al$_2$O$_3$ (Sigma Aldrich), TiO$_2$ (Aldrich, > 99.5%), Sulfuric acid (Sigma, >96%), glucose (Sigma, >99%), xylose (Sigma, >99%), mannose (Sigma, >99%), galactose (Sigma, >99%), fructose (Sigma, >99), arabinose (Sigma, >99%). furfural (Sigma, >98%), levulinic acid (Sigma, >97%), formic acid (Sigma, >99%), acetic acid (Sigma, >99%), white birch (Flambeau River Paper, Park Falls, WI), 50% Cu/Al$_2$O$_3$ (BASF), deionized water (Millipore Milli-Q grade, 18 MΩ), H$_2$ (Airgas, 99.999%), He , Airgas, Industrial grade), Air (Airgas, Industrial grade), 1 wt.% O$_2$/Ar mixture(Airgas), γ-Al$_2$O$_3$ (Strem, low soda), granular silicon dioxide (Sigma, 99.9%, 4-20 mesh), quartz wool (Grace), and carbon support (Cabot, Vulcan XC-72)

Tetrahydrofuran-dimethanol (THFDM) synthesis

HMF (Hefei leaf biotech, 12.0 g), the solvent (120 mL ethanol, Decon Laboratories, INC.) and Ni/SiO$_2$ (64 wt.%, Strem #28-1900, 1.20 g) were added to a 300 mL Hastalloy Parr autoclave. The reactor was flushed three times with H$_2$ and pressurized to 8.0 MPa. Then the reaction mixture was stirred at 700 rpm and heated to 80 ºC for 6 hrs. The autoclave was then allowed to cool to ambient temperature and the pressure was released. The obtained mixture was first filtered with 0.22 μm PTFE (polytetrafluoroethylene) syringe filter to remove Ni/SiO$_2$. The solvent ethanol was then evaporated with rotary evaporation using an oil bath of 80 ºC under vacuum. The obtained liquid (THFDM) was analyzed by GC.

Catalyst preparation

The 3 wt% Ni/SiO$_2$ catalyst used in hydrogenation reactions was synthesized by incipient wetness impregnation. The appropriate mass of nickel nitrate hexahydrate was added to deionized water. The

resulting solution was added dropwise and mixed with the SiO_2 support. The catalyst was dried in an oven at 110 °C overnight. Once dry, the catalyst was reduced in flowing hydrogen for 4 hours at 400 °C, with a 1.5 °C min^{-1} ramp. The catalyst was passivated at room temperature for 1 hour in a 1% O_2/Ar mixture.

The 5 wt% Co/SiO_2 catalyst used in hydrogenation reactions was synthesized by incipient wetness impregnation. The appropriate mass of cobalt nitrate hexahydrate was added to deionized water. The resulting solution was added dropwise and mixed with the SiO_2 support. The catalyst was dried in a vacuum oven at 45°C overnight. Once dry, the catalyst was reduced in flowing hydrogen. The temperature was ramped (5 °C min^{-1}) to 100 °C and held for 20 minutes, ramped to 200 °C and held for 20 minutes, ramped to 400 °C and held for 15 hours. The catalyst was passivated at room temperature for 1 hour in a 1% O_2/Ar mixture.

The 5 wt% Rh/C catalyst used in hydrogenation reactions was synthesized by incipient wetness impregnation. The appropriate mass of rhodium chloride was added to deionized water. The resulting solution was added dropwise and mixed with the carbon support. The catalyst was dried in an oven at 100 °C for 3 hours. Once dry, the catalyst was reduced in flowing hydrogen at 450 °C, with a 0.5 °C min^{-1} ramp. The catalyst was passivated at room temperature for 1 hour in a 1% O_2/Ar mixture.

The 5 wt% Pt/C catalyst used in hydrogenation reactions was synthesized by incipient wetness impregnation. The appropriate mass of chloroplatinic acid hexahydrate was added to deionized water. The resulting solution was added dropwise and mixed with the carbon support. The catalyst was dried in an oven at 100 °C for 3 hours. Once dry, the catalyst was reduced in flowing hydrogen at 260 °C, with a 0.5 °C min^{-1} ramp. The catalyst was passivated at room temperature for 1 hour in a 1% O_2/Ar mixture.

The 1 wt% Ru/TiO_2 catalyst used in hydrogenation reactions was synthesized by incipient wetness impregnation. The TiO_2 was calcined in air for 12 hours at 750 °C, with a 4 °C min^{-1} ramp, to change the phase to rutile. Ruthenium nitrosyl nitrate was mixed with deionized water to give the proper concentration of Ru. The Ru was added to TiO_2 in three separate additions. Between each addition, the catalyst was dried in static air at 110 °C for 10 hours. The Ru salt solution was added dropwise and mixed with TiO_2 until the color was homogeneous. After the final addition, the catalyst was reduced in flowing hydrogen for 2 hours at 300 °C, with a 1 °C min^{-1} ramp. The catalyst was passivated at room temperature for 1 hour in a 5% air and 95% He mixture.

The Pd/Si-Al catalyst was synthesized by incipient wetness impregnation of a $Pd(NO)_3$ precursor onto SiO_2-Al_2O_3. After impregnation, the catalyst was dried overnight in an oven at 110°C, calcined in flowing air at 400°C, reduced in flowing H_2 at 260°C, and passivated in 1% O_2/He at room temperature.

Pt-based catalyst was synthesized according to the method in literatures[1].

Batch Reaction Studies of 2-HY-THP

Catalysts were loaded into Hastelloy autoclaves (Parr Instrument, Multi Reactor System 5000). The autoclaves were seated in their housing and purged 3 times with 2 MPa of Ar (Airgas, industrial grade) and then 3 times with 2.0 MPa of H_2 (Airgas, industrial grade). The catalysts were reduced at 200°C for 15 minutes, with a 4 K/min ramp. 1 wt% 2-hydroxytetrahydropyran (Acros organics, 90%) feeds in deionized water (Millipore Milli-Q grade, 18 MΩ) were prepared and pumped into each autoclave once cooled to 25 °C. The autoclaves were stirred with magnetic stir bars at 500 rpm. The autoclaves were then pressurized to 6.5 MPa with H_2. The autoclaves were heated to 100 °C (6 °C min^{-1}). The autoclaves were held at 100°C K for 1 to 3 hours. After cooling, the samples were analyzed by both gas chromatography (Shimadzu GC2010 equipped with a flame ionization detector (FID) and a RTX-VMS column) and high-performance liquid chromatography (HPLC) (Waters Alliance 2695 system equipped with a Waters 410 differential refractometer and Aminex HPX-87H ion exchange column) using a 5 mM H_2SO_4 mobile phase.

Hydrogenolysis of THFDM in a batch reactor

Reactions were carried out in 50 mL HEL high-pressure batch reactors. Prior to the reactions, the catalysts were first reduced under flowing H_2 at 250 °C for two hours (1 °C min^{-1}). Then the feedstock was added to the reactor. The reactor was purged three times with H_2 prior to reaction, pressurized to the desired H_2 pressure, stirred at 700 rpm, and heated to the reaction temperature. After the reaction, the reactor was cooled in ice water and depressurized. Products were quantified using a Shimadzu Gas Chromatograph using a Flame Ionization Detector (FID) with liquid injection. A Restek RTX-VMS capillary column (Length: 30 m, ID: 0.25 mm, film thickness: 1.4 μm) was used.

Catalyst Characterizations

CO (Airgas, 99.99 %) uptake for Ni/SiO_2, Rh/C, and Pt/C catalysts was measured using a Micromeritics ASAP 2020 following reduction in flowing H_2 (Airgas, UHP). All three catalysts were reduced at 200 °C (held for 0.25, 1, and 1 hour for Ni/SiO_2, Rh/C, and Pt/C, respectively). The Co/SiO_2 catalyst was reduced for 5 hours at 300 °C prior to chemisorption. The site density for Co/SiO_2 was measured using an apparatus and procedure previously described [2]. Turnover frequencies were calculated based on the CO uptake measured for each catalyst.

Reference:

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