Supplementary Information

Dual-bed catalyst system for C-C coupling of biomass-derived oxygenated hydrocarbons to fuel-grade compounds

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Catalyst Preparation

The Pt-Re/C catalyst was prepared by incipient wetness impregnation of carbon black (Norit-SX1G) with an aqueous solution of H₂PtCl₆·6H₂O and HReO₄ to yield a catalyst with loadings of 5.1 wt% Pt and 4.9 wt% Re. The Ce₁Zr₁Oₓ support with a 1:1 Ce:Zr molar ratio was prepared via co-precipitation of Ce(NO₃)₃ and ZrO(NO₃)₂ with NH₄OH (Aldrich), and the ZrO₂ support was prepared via precipitation of ZrO(NO₃)₂ with NH₄OH (Aldrich) according to Serrano-Ruiz, et al.² The Pd/ZrO₂ catalyst was prepared via incipient wetness impregnation of ZrO₂ with an amount of aqueous solution of Pd(NO₃)₂ (Aldrich) necessary to obtain a nominal metal loading of 0.25 wt%. The catalyst was dried in air at 373 K overnight and calcined in air at 623 K for 2 h. The Pt/SiO₂-Al₂O₃ catalyst was prepared by incipient wetness impregnation of SiO₂-Al₂O₃ (Grace Davision, MS-25 FCC Catalyst Sample) with an amount of aqueous solution of Pt(NH₃)₄(NO₃)₂ required to obtain a nominal metal loading of 2 wt%. The catalyst was dried in air at 373 K overnight and calcined in air at 533 K for 2 h.

Reaction kinetics studies

The conversion of 60 wt% sorbitol solution over Pt-Re/C was carried out at 18 bar and at 503 K with a flow rate of 0.04 mL/min.¹ The ketonization of the organic liquid obtained from sorbitol feed was carried out over Ce₁Zr₁Oₓ at 623 K, a pressure of 5 bar, and a liquid flow rate of 0.02 mL/min with 4 g catalyst. The aldol condensation reaction was carried out over Pd/ZrO₂ at 623 K and 5 bar with 0.02 mL/min liquid flow (2 g catalyst). The molar ratio of the gas flow rate to the
liquid flow rate was maintained at 5.5 for both reactions. The hydrodeoxygenation reactions were carried out over 2 wt% Pt/SiO$_2$-Al$_2$O$_3$ at 573 K, 28.5 bar and a liquid flow rate of 0.02 mL/min with 2 g catalyst and 50 cm$^3$(STP)/min of H$_2$ flow.

A fixed bed, down-flow reactor consisting of a half-inch stainless steel tube was used for all experiments. Quartz wool was used in the lower end of the reactor to keep the catalyst bed in place. The Pt-Re/C catalyst was mixed with an equal volume of whole fused SiO$_2$ granules, whereas Ce$_x$Zr$_{1-x}$O$_y$, Pd/ZrO$_2$ and Pt/ SiO$_2$-Al$_2$O$_3$ catalysts were mixed with crushed fused SiO$_2$ granules (Aldrich) in a 2:1 volumetric ratio to maintain bed height. The reactor was heated with an aluminum block that was heated externally by a well-insulated furnace (Applied Test Systems). Type-K thermocouples (Omega) were used to measure the reaction temperature, which was controlled by a PID controller (Love controls) connected to a variable transformer (Tesco). Mass flow controllers (Brooks 5850E) were used to regulate the flow of H$_2$ during the C-C coupling and hydrodeoxygenation experiments. The liquid feed was pumped from a graduated cylinder by an HPLC pump (Lab Alliance series 1) to a needle located at the entrance of the catalyst bed. A back-pressure regulator (GO model BP-60) was used to control the total pressure, which was measured by two gauges at the entrance and the exit of the bed. A gas-liquid separator at room temperature was used to collect the liquid effluent phase for analysis. The Pt-Re/C catalyst was reduced in situ at 723 K (ramp rate of 0.5 K min$^{-1}$) for 2 h. The Ce$_x$Zr$_{1-x}$ and Pd/ZrO$_2$ catalysts were reduced in-situ at 623 K (ramp rate of 0.5 K min$^{-1}$) for 2 h, and the Pt/SiO$_2$-Al$_2$O$_3$ catalyst was reduced in situ at 573 K (ramp rate of 0.5 K min$^{-1}$) for 2 h in flowing H$_2$ (200 cm$^3$(STP) min$^{-1}$). After the reduction was completed, the temperature and pressure were adjusted and the feed flow was started without flowing H$_2$ for Pt-Re/C and with flowing H$_2$ for the C-C coupling and hydrodeoxygenation reactions. The weight hourly space velocity (WHSV) was calculated for experiments using the mass flow rate of the liquid flow into the reactor and the mass of the catalyst used.

Experiments employing a double bed, single reactor configuration were performed in a fixed bed, down-flow reactor system consisting of a half-inch stainless steel tube. In contrast to the single bed experiments, two different catalysts were loaded in the same reactor, separated by whole fused SiO$_2$ granules. Pd/ZrO$_2$ catalyst (2 g) was placed on the quartz wool, and fused SiO$_2$ granules were placed on top of this bed. Ce$_x$Zr$_{1-x}$O$_y$ catalyst (4 g) was then placed on the silica chips, so that the feed could pass through the ketonization catalyst first and the aldol condensation/hydrogenation
catalyst second. Both catalysts were mixed with crushed fused SiO₂ granules (Aldrich) in a 1:1 volumetric ratio.

For all experiments, the rate of gas production was measured with a bubble flow meter. An HP GC5890 gas chromatograph, equipped with a Haysep DB 100/120 column (Alltech) and thermal conductivity detector (TCD), was used to quantify CO and CO₂, and an Agilent GC6890, equipped with an Rtx column (Agilent) and a flame ionization detector (FID), was used to quantify gas-phase alkanes. Liquid phase analysis was performed with a Shimadzu GC 2060, equipped with a DB-5 column (Restek) and an FID detector and a Shimadzu 2060 GC/MS with a NIST library of spectra. Liquid and gas analysis points were collected every 2-3 h, and steady state was usually achieved after 6 h time-on-stream.

Acknowledgements

This work was supported in part by the U.S. Department of Energy Office of Basic Energy Sciences, and by the DOE Great Lakes Bioenergy Research Center (www.greatlakesbioenergy.org), which is supported by the U.S. Department of Energy, Office of Science, Office of Biological and Environmental Research, through Cooperative Agreement DE-FC02-07ER64494 between The Board of Regents of the University of Wisconsin System and the U.S. Department of Energy.

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