

Supplementary Information

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

Elif I. Gürbüz, Edward L. Kunkes and James A. Dumesic*

*University of Wisconsin, Madison, 1415 Engineering Drive, Madison, Wisconsin, 53706, USA
Fax: 1 608 262 5434; Tel: 1 608 262 1095; E-mail: dumesic@engr.wisc.edu*

Catalyst Preparation

The Pt-Re/C catalyst was prepared by incipient wetness impregnation of carbon black (Norit-SX1G) with an aqueous solution of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and HReO_4 to yield a catalyst with loadings of 5.1 wt% Pt and 4.9 wt% Re.¹ The $\text{Ce}_1\text{Zr}_1\text{O}_x$ support with a 1:1 Ce:Zr molar ratio was prepared via co-precipitation of $\text{Ce}(\text{NO}_3)_3$ and $\text{ZrO}(\text{NO}_3)_2$ with NH_4OH (Aldrich), and the ZrO_2 support was prepared via precipitation of $\text{ZrO}(\text{NO}_3)_2$ with NH_4OH (Aldrich) according to Serrano-Ruiz, et al.² The Pd/ ZrO_2 catalyst was prepared via incipient wetness impregnation of ZrO_2 with an amount of aqueous solution of $\text{Pd}(\text{NO}_3)_2$ (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/ $\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyst was prepared by incipient wetness impregnation of $\text{SiO}_2\text{-Al}_2\text{O}_3$ (Grace Davison, MS-25 FCC Catalyst Sample) with an amount of aqueous solution of $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ 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 $\text{Ce}_1\text{Zr}_1\text{O}_x$ 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/ ZrO_2 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/SiO₂-Al₂O₃ at 573 K, 28.5 bar and a liquid flow rate of 0.02 mL/min with 2 g catalyst and 50 cm³(STP)/min of H₂ 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 SiO₂ granules, whereas Ce₁Zr₁O_x, Pd/ZrO₂ and Pt/ SiO₂-Al₂O₃ catalysts were mixed with crushed fused SiO₂ 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 H₂ 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 Ce₁Zr₁O_x and Pd/ZrO₂ catalysts were reduced in-situ at 623 K (ramp rate of 0.5 K min⁻¹) for 2 h, and the Pt/SiO₂-Al₂O₃ catalyst was reduced in situ at 573 K (ramp rate of 0.5 K min⁻¹) for 2 h in flowing H₂ (200 cm³(STP) min⁻¹). After the reduction was completed, the temperature and pressure were adjusted and the feed flow was started without flowing H₂ for Pt-Re/C and with flowing H₂ 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 SiO₂ granules. Pd/ZrO₂ catalyst (2 g) was placed on the quartz wool, and fused SiO₂ granules were placed on top of this bed. Ce₁Zr₁O_x 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.

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References

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