Supplementary Information

Catalytic Upgrading of Levulinic Acid to Fuels and Chemicals

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Catalyst Preparation

Pd/Nb2O5 was prepared by incipient wetness impregnation of a commercial niobium oxide (HY-340 from CBMM-Brazil) using an aqueous solution of Pd(NO3)2·xH2O (Aldrich) with the concentration adjusted to load 1 and 0.1 wt% of palladium. The catalyst was dried at 380 K overnight, followed by calcination at 538 K in flowing air (250 cm³(STP) min⁻¹, 1 K·min⁻¹ ramp) for 2 h. The ceria-zirconia catalyst with Ce:Zr molar ratio of 1:1 was prepared according to Serrano-Ruiz, et al. [1]. Commercial Ru(5%)/C used for levulinic acid reduction to GVL was purchased from Sigma-Aldrich.

Reaction Kinetics Studies

Catalysts (1g of Ru/C, 2.5 g of Pd/Nb2O5 or ceria-zirconia) were loaded into a 1/4” tubular stainless steel reactor between two end-plugs of quartz wool (Grace). The reactor was mounted in an upflow configuration and surrounded by aluminum blocks heated externally by a well-insulated furnace (Applied Test Systems Inc.). A K-type thermocouple (Omega) was attached to the outside of the reactor to measure temperature, controlled with a 1600 series type temperature controller (Dwyer Instruments). Prior to reaction kinetics studies, Ru/C was reduced in flowing H2 (100 cm³(STP) min⁻¹) at 673 K for 2 h with a ramp of 2 K min⁻¹, and the reactor was then cooled to the reaction temperature (423 K) under flowing hydrogen. The Pd/Nb2O5 catalysts were reduced in flowing H2 (100 cm³(STP) min⁻¹ at 538 K (1 K·min⁻¹ ramp) for 3 h, and then heated to the reaction temperature under flowing H2. Before reaction the ceria-zirconia catalyst was heated under flowing He (20 cm³(STP) min⁻¹) to the reaction temperature (698 K, 5 K·min⁻¹ ramp). The flow-rates of H2 and He were fixed with Brooks Model 5850 mass-flow controllers. The system pressure was controlled by a backpressure regulator (GO Regulator, Model BP-60). Solutions of levulinic acid
and GVL (Sigma-Aldrich) in deionized water, or pure pentanoic acid (Sigma-Aldrich) were introduced into the upflow reactor using an HPLC pump (Lab Alliance Series 1) along with a co-feed of H₂ (80 cm³(STP) min⁻¹ for levulinic acid reduction to GVL, and varying flows for the GVL conversion to pentanoic acid over Pd/Nb₂O₅). The effluent liquids (organic and aqueous) were collected at room temperature in a gas-liquid separator and drained for gas chromatography (GC) analysis (Shimadzu GC-2010 with a FID detector and Rtx-5 column) and identification (Shimadzu GC-2010 with a mass spectrometer and DB-5ms column). The effluent gas stream passed through a back-pressure regulator and was then analyzed by gas chromatography: CO and CO₂ with a Shimadzu GC-8A (equipped with TCD detector and an Alltech packed column model HayeSep DB 100/120) and gaseous alkanes with a Varian GC (Saturn 3) using a FID detector and a GS-Q capillary column (J&W Scientific). The overall carbon balance gave recoveries ranging from 85-104%.

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References