Supplementary Material (ESI) for Green Chemistry

Supplementary Information

Catalytic Upgrading of Levulinic Acid to Fuels and Chemicals

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Catalyst Preparation

Pd/Nb_2O_5 was prepared by incipient wetness impregnation of a commercial niobium oxide (HY-340 from CBMM-Brazil) using an aqueous solution of $Pd(NO_3)_2 \cdot xH_2O$ (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 $cm^3(STP) \cdot min^{-1}$, 1 $K \cdot min^{-1}$ 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/Nb_2O_5 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 H_2 (100 $cm^3(STP)\ min^{-1}$) 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/Nb_2O_5 catalysts were reduced in flowing H_2 (100 $cm^3(STP) \cdot min^{-1}$ at 538 K (1 $K \cdot min^{-1}$ ramp) for 3 h, and then heated to the reaction temperature under flowing H_2. Before reaction the ceria-zirconia catalyst was heated under flowing He (20 $cm^3(STP) \cdot min^{-1}$) to the reaction temperature (698 K, 5 $K \cdot min^{-1}$ ramp). The flow-rates of H_2 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 H_2 (80 cm^3(STP) min^{-1} for levulinic acid reduction to GVL, and varying flows for the GVL conversion to pentanoic acid over Pd/Nb_2O_5) 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 CO_2 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

[1]. J.C. Serrano-Ruiz, J. Luettich, A. Sepulveda-Escribano, F.J. Rodriguez-Reinoso, J.Catal. 241 45 (2006).