



Supporting Information

for

Angew. Chem. Int. Ed. Z53050

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69451 Weinheim, Germany

Renewable Alkanes by Aqueous-Phase Reforming of Biomass-Derived Oxygenates

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Materials and Methods

Catalyst Preparation and Characterization

Catalysts were prepared by incipient wetness impregnation of alumina (Catapal B, Sasol) and SiO₂-Al₂O₃ (MS-25, Al₂O₃ content 25 wt%, Grace Davison), using tetra-amine platinum (IV) nitrate (Strem Chemicals) and tetra-amine palladium(II) nitrate (Strem Chemicals) as the precursor salts. Following impregnation, the catalysts were dried in air at 393 K for 12 h and then calcined in flowing 10 % O₂/He mixture (GHSV ~ 1000 h⁻¹) to 533 K (at 1.3 K/min) and held at this temperature for 2 h. Prior to collecting reaction kinetics data and CO chemisorption measurements, each catalyst was reduced in flowing H₂ (GHSV ~ 250 - 1000 h⁻¹) at a temperature of 723 K for Pt/SiO₂-Al₂O₃ and Pd/SiO₂-Al₂O₃, and at a temperature of 533 K for the Pt/Al₂O₃ catalyst and the physical mixtures. The temperature was ramped from room temperature to the desired reduction temperature over a period of 8 h and held at the final temperature for 2 h. The irreversible CO uptake at 300 K of each reduced catalyst (measured on a standard gas adsorption apparatus described elsewhere ^[1]) was 101, 141 and 40 micromoles per gram of catalyst for the 3 wt% Pt-Al₂O₃, 4 wt% Pt-SiO₂-Al₂O₃ and 3 wt% Pd-SiO₂-Al₂O₃ catalysts, respectively.

Reaction Kinetics Studies

Figure 1 shows the apparatus used to conduct reaction kinetics studies. The catalysts were loaded into a 1/2 or 1/4" outside diameter tubular stainless steel reactor. Catalysts were pelletized to ensure that the pressure drop across the catalyst bed was less than 0.7 bar. The catalyst bed was contained in the tubular reactor between two end-plugs of quartz wool (Alltech). The temperature of the reactor was measured using type-K thermocouples (Omega) attached to the outside of the reactor, and controlled with a series 16A type temperature controller (Dwyer Instruments). Prior to reaction kinetics studies, the calcined catalyst was reduced in flowing H₂ as outlined above in the catalyst preparation section. The flow-rates of H₂ and N₂ were controlled with mass-flow meters (5850 Brooks Instruments). A liquid solution of 5 wt% sorbitol (Aldrich, >99%) in deionized water was introduced into the upflow reactor using an HPLC pump (Model 301, Alltech). Once liquid was observed in the separator, the reactor was heated to the desired temperature, and the liquid from the pump was set at the desired flow rate (0.02 to 0.06 cm³/min). The effluent from the reactor was water-cooled in a double-pipe heat exchanger to liquefy the condensable vapors. The fluid from this cooler was combined with nitrogen (at a flowrate of ~ 75 cm³(STP)/min), which bubbled through the

effluent and swept out the gaseous products, while the liquid effluent collected in the separator. When hydrogen was co-fed with the aqueous sorbitol, nitrogen was not used as a sweep gas (since the H₂-feed served this purpose). The effluent liquid was drained periodically for total organic carbon (TOC) analysis (Shimadzu TOC-6001 with autosampler) and for detection of the primary carbonaceous species with high precision liquid chromatography (Waters 2695 separations module in series with 410 Differential Refractometer and 996 Photodiode Array detectors and a BIO-RAD Aminex HPX-87H Ion Exclusion Column with 5 mM H₂SO₄ as the carrier solvent).

The effluent gas stream passed through a back-pressure regulator (GO Regulator, Model BP-60) which controlled the system pressure. This off-gas stream was analyzed with two different gas chromatographs: a) the H₂ and CH₄ with a Carle GC (Series 400 AGC) with a TCD detector and a Porapak Q packed column (Alltech) and b) the CO₂ and alkanes heavier than methane in a Varian GC-MS (Saturn 3) with a mass spectrometer detector and a GS-Q capillary column (J&W Scientific).

- [1] B.E. Spiewak, J. Shen, J. A. Dumesic, *J. Phys. Chem.* **1995**, *99*, 17640.

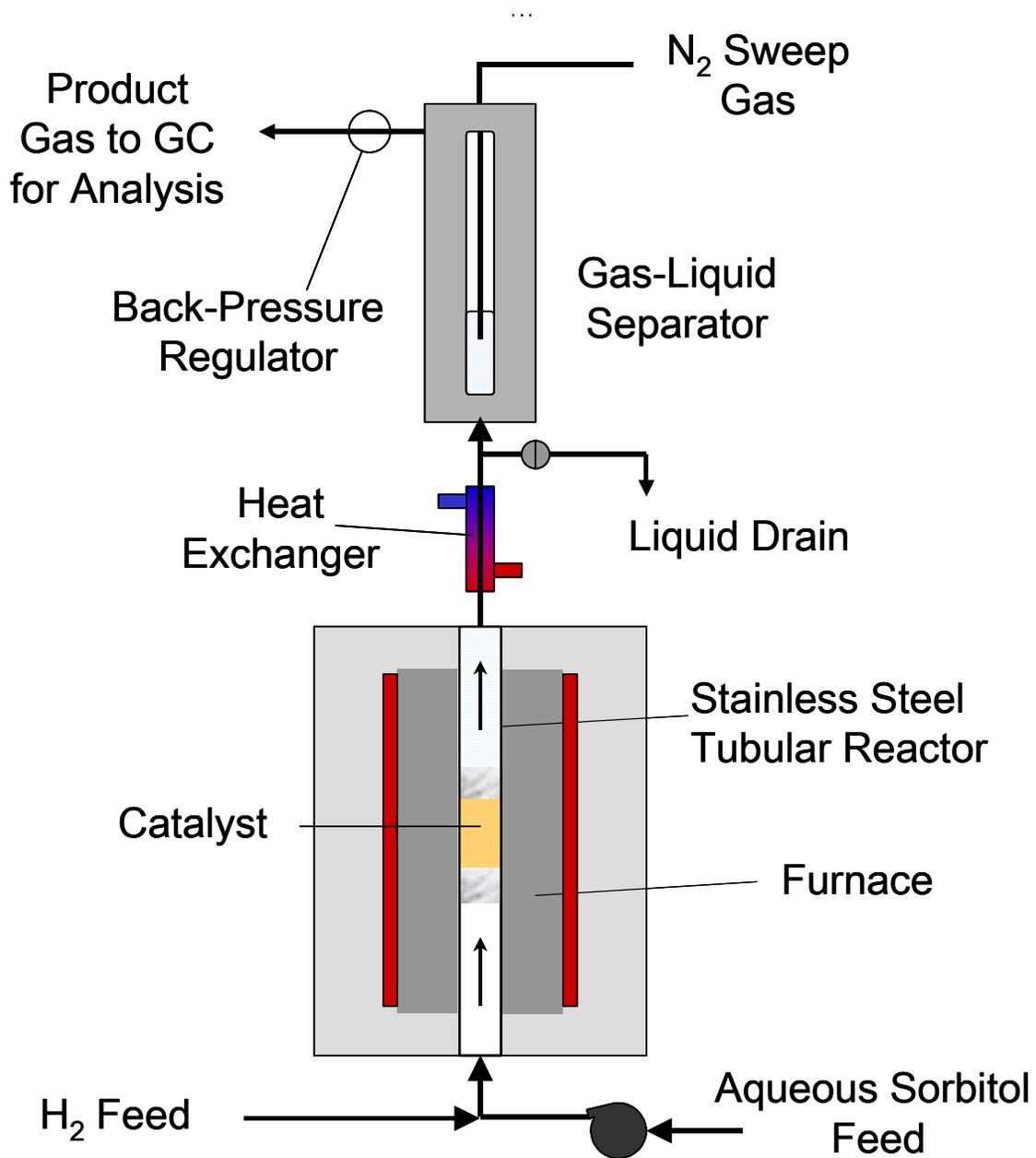


Figure 1: Schematic diagram of aqueous-phase reforming flow reactor.