Supporting Information

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Catalytic Reforming of Oxygenated Hydrocarbons for Hydrogen with Low Levels of Carbon Monoxide

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Catalyst Preparation and Characterization

The catalyst used in this study was 3 wt% Pt supported on nanofibers of \( \gamma \)-alumina (500 m\(^2\) g\(^{-1}\), Argonide Corporation). The catalyst was prepared by incipient wetness impregnation of alumina, using tetraamine platinum (IV) nitrate as the precursor salt. The catalyst was dried at 380 K for 3 h, followed by calcination at 533 K in flowing 10% O\(_2\) in N\(_2\). The metal composition of the catalyst was measured by an inductively coupled plasma emission technique (ICPE) with a Perkin Elmer Plasma 400 ICP Emission Spectrometer. Adsorption experiments using carbon monoxide at 300 K showed a CO uptake of 105 micromoles per gram of catalyst. The irreversible CO uptake was measured on a standard gas adsorption apparatus described elsewhere.\(^1\)

Reaction Kinetics Studies

Figure 1 shows the apparatus used to conduct reaction kinetics studies of the aqueous-phase reforming of EG. The catalyst was loaded into a ½” tubular stainless steel reactor. To avoid a large pressure drop across the reactor using large amounts of catalyst, the ½” tube was filled with inert crystals of fused aluminum oxide (6-10 mesh size, Aldrich). The void spaces between the fused alumina crystals were then filled with 22 g of Pt/\( \gamma \)-alumina fibers (void space ~ 50% of empty tube volume). The bed of crystals and catalyst was contained in the tubular reactor between two end-plugs of quartz wool. The reactor, mounted in an upflow
configuration, was divided into two separately-heated zones: the bottom section was the reforming-zone and the top section was the shift-zone. The temperatures of each zone were measured using Chromomega®-Alomega® K-type thermocouple (Omega) attached to the outside of the reactor, and each temperature was controlled separately. Prior to reaction kinetics studies, the fresh catalyst was reduced in flowing H_2 (100 cm\(^3\) (STP) min\(^{-1}\)). The catalyst was heated, using a linear temperature ramp (1.25 K min\(^{-1}\)) to the final reduction temperature of 523 K, held at this temperature for 2 h and then cooled to room temperature, all in flowing H_2. Hydrogen (>99.99%) was purified by flowing through a bed of activated molecular sieves at room temperature. The flow-rate of H_2 (and other gases) was fixed using calibrated mass-flow meters (Brooks Instruments). After reduction, the system was purged with flowing nitrogen and pressurized to the desired pressure with nitrogen. Nitrogen was purified by flowing through an OxyTrap (Alltech) followed by a bed of activated molecular sieves at room temperature. The system pressure was controlled by a backpressure regulator (GO Regulator, Model BP-60). A liquid solution of the desired concentration EG (Aldrich, >99%) in deionized water was introduced into the upflow reactor using an HPLC pump (Alltech, Model 301). Once liquid was observed in the separator, the reactor was heated to the desired temperature over 1 h. The liquid from the pump was set at the desired flow rate (0.1 cm\(^3\) min\(^{-1}\) for most runs). 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, which bubbled through the effluent and swept out the gaseous products, while the liquid effluent collected in the separator. The effluent liquid was drained periodically for detection of the primary carbonaceous species using gas chromatography (a HP 6890 GC with a FID detector and an HP Innowax capillary column).

The effluent gas stream passed through a back-pressure regulator. This off-gas stream was analyzed with several different gas chromatographs; a) the H₂ concentration using a Carle GC with a TCD detector and a Porapak Q column in series with a Hayesep T column, b) CO₂, methane, and ethane concentrations in a HP 5890 GC with a TCD detector and a Porapak QS column, and c) the total hydrocarbon and other volatile oxygenates using a HP 6890 GC with a FID detector and an HP Innowax capillary column.

The CO concentration of the effluent gas stream was obtained using a Siemens Ultramat 5E gas analyzer, specially calibrated for low concentrations of CO, ranging from 0 to 1000 ppm. The analyzer was calibrated periodically, using pure N₂ as the zero gas and 1000 ppm CO in N₂ (Scott Specialty Gases) as the span gas. An intermediate calibration gas of 50.4 ppm CO in N₂ (Scott Specialty Gases) was used to check the linearity of the calibration.

*Figure 1:* Apparatus for reaction kinetics studies of the aqueous-phase reforming of ethylene glycol.