

492a Stability of Silica-Supported Ru Catalysts for Glucose Hydrogenation to Sorbitol

Erin P. McKoon, William C. Ketchie, Vladimir P. Oleshko, and Robert J. Davis

The production of chemicals and fuels relies heavily upon petroleum-derived precursors that are finite in supply. Efforts to find alternatives to these fossil-based resources have focused on species derived from renewable biomass, such as carbohydrates. Carbohydrates have been shown to be useful for the production of fuels, oxygenated chemicals and other industrially important molecules [1-4]. As a first step, a sugar such as glucose can be hydrogenated to form sorbitol. Sorbitol is used in the production of vitamin C and is a precursor for lower molecular weight oxygenated chemicals. Although supported Ru catalysts are known to be effective in the hydrogenation of glucose to sorbitol, the stability of these catalysts under hydrogenation conditions is still an open question. This work investigates the stability of silica-supported Ru catalysts in the aqueous phase conversion of glucose to sorbitol.

Silica-supported Ru catalysts (0.5 - 4.47 wt.% Ru) were prepared by an incipient wetness impregnation method. Results from H₂-chemisorption confirmed that the Ru was highly dispersed (53 – 91%) on the as-prepared catalysts. Hydrogenation reactions were conducted in a 30 mL batch reactor at 373 K and 80 bar H₂ for 3 h. Over a Ru/SiO₂ (4.47 wt.%) catalyst, glucose hydrogenation was nearly 100% selective to sorbitol with an average turnover frequency of $0.32 \pm 0.13 \text{ s}^{-1}$. The hydrogenation reaction was not mass transfer limited according to the Koros-Nowak criterion, evaluated with the various Ru-loaded silica catalysts. In-situ x-ray absorption spectroscopy (XAS) revealed the silica-supported Ru to be in an oxidized state initially that was subsequently reduced in aqueous solutions saturated with high pressure H₂ at 373 K. Furthermore, in-situ XAS indicated that Ru particles agglomerated on the silica surface following exposure to liquid water at 373 K. In the presence of aqueous-phase glucose, pre-reduced Ru particles also agglomerated, but at a slower rate. Glucose appeared to have a stabilizing effect on the oxidized Ru particles of the as-prepared catalyst. This observation suggests there was little growth of Ru particles during the standard hydrogenation reaction. Transmission electron microscopy of the catalysts before and after reaction supports this conclusion. The electron micrographs show that Ru particles migrated to regions of higher particle density but did not necessarily coalesce into larger particles. This phenomenon of Ru agglomeration under aqueous conditions was related to silica supports; during complementary experiments conducted on carbon-supported catalysts, there was negligible agglomeration of Ru particles.

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