Catalytic Production of Renewable Fuels by Aqueous-phase Reforming of Biomass-Derived Oxygenated Hydrocarbons

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Research is being conducted worldwide to develop hydrogen fuel cells for environmentally benign generation of energy, since these devices operate at high efficiencies and water is the only by-product formed during operation. However, production of hydrogen fuel for these devices is currently limited to energy-intensive processing of non-renewable hydrocarbons, such as steam reforming of natural gas. The full environmental benefits of using hydrogen as a fuel are realized when hydrogen is derived from renewable sources, such as biomass. We have recently reported a process to generate hydrogen by aqueous-phase reforming (APR) at temperatures near 500 K of oxygenated hydrocarbons derived from biomass, such as sorbitol, glycerol, and ethylene glycol (1-4). The APR process is greenhouse-gas neutral, because the CO_2 by-product that accompanies the H_2 is consumed by biomass growth. In addition to utilizing renewable feed-stocks, the APR process eliminates the need to vaporize water and the oxygenated hydrocarbon, which reduces the energy requirements for producing hydrogen. Furthermore, the APR process can lead to low levels of CO (100 ppm) in a single-step catalytic process (5), because the reforming of oxygenated hydrocarbons and the water-gas shift reaction are both thermodynamically favorable at the same low temperatures.

In the present contribution, we report results from catalyst characterization studies and reaction kinetics measurements for aqueous-phase reforming over Pt, Ni, and NiSn-based catalysts. The results from these studies allow us to document the role of Sn in controlling the selectivity of Ni-based catalysts and to determine the reaction conditions under which NiSn-based catalysts perform as well or better than Pt catalysts for aqueous-phase reforming reactions. Aqueous-phase reforming of sorbitol, glycerol, and ethylene glycol solutions produces an effluent gas stream composed of 50-70 mol% H_2, 30-40 mol% CO_2, and 2-11 mol% alkanes (dry basis) at high conversion. Addition of Sn to Ni improves the selectivity for production of H_2 by ethylene glycol reforming from 35 to 51 % at a Ni:Sn ratio of 270:1, while the alkane selectivity is reduced from 44 to 33%. At a Ni:Sn ratio of 14:1, the hydrogen selectivity increases to 90 %, while alkane production is nearly eliminated. As the system pressure decreases to the bubble-point of the feed (25.1 bar at 498 K), production of alkanes decreases and the hydrogen selectivity increases accordingly. Hydrogen selectivity is also maximized by operation at higher reactor space velocities. The addition of Sn to Ni significantly decreases the rate of methane formation from C-O bond cleavage, while maintaining sufficiently high rates of C-C bond cleavage required for hydrogen formation. Turnover frequencies for hydrogen production at 498 K over Raney-Ni-based catalysts are several times lower than that over 3 wt% Pt/Al_2O_3 based on CO chemisorption. However, the high CO uptakes and high densities of Raney-Ni-based catalysts lead to comparable rates of hydrogen production per unit reactor volume as 3 wt% Pt/Al_2O_3 at 498 K. Results from XRD, SEM, and [119]Sn Mössbauer spectroscopy suggest that Raney-NiSn catalysts are comprised of alumina and nickel particles surrounded by a Ni-Sn alloy. After exposure to reaction conditions, Sn is present primarily as Ni_3Sn alloy with small amounts of Sn(IV) probably associated with alumina.

We also report how the selectivity for production of hydrogen can be increased for liquid-phase reforming of glucose. Glucose is a particularly important reactant for the

generation of hydrogen from renewable resources, because this sugar makes up the major energy reserves in plants and animals. While the selectivity for hydrogen production is insensitive to the liquid-phase concentration of sugar-alcohols such as sorbitol, the hydrogen selectivity from reforming of glucose decreases as the liquid concentration increases from 1 to 10 wt% because of undesired hydrogen-consuming side reactions that occur in the liquid phase. This decrease in selectivity is an important limitation, because processing dilute aqueous solutions involves the processing of excessive amounts of water. We show in this contribution how high selectivities can be achieved for hydrogen production from high liquid-phase concentrations of glucose by combining a hydrogenation reactor with an APR reactor and employing hydrogen recycle between reactors.

Another approach for utilization of biomass resources for energy applications is the production of clean-burning liquid fuels. In this respect, current technologies to produce liquid fuels from biomass are typically multi-step and energy-intensive processes. We show how aqueous-phase reforming of sorbitol can be tailored to selectively produce a clean stream of heavier alkanes consisting primarily of butane, pentane and hexane. The conversion of sorbitol to alkanes plus CO_2 and water is an exothermic process that retains approximately 95 % of the heating value and only 30 % of the mass of the biomass-derived reactant. Production of alkanes by aqueous-phase reforming of sorbitol takes place by a bi-functional reaction pathway involving first the formation of hydrogen and CO_2 on the appropriate metal catalyst (such as Pt) and the dehydration of sorbitol on a solid acid catalyst (such as silica-alumina). These initial steps are followed by hydrogenation of the dehydrated reaction intermediates on the metal catalyst. When these steps are balanced properly, the hydrogen produced in the first step is fully consumed by hydrogenation of dehydrated reaction intermediates, leading to the overall conversion of sorbitol to alkanes plus CO_2 and water. The selectivities for production of alkanes can be varied by changing the catalyst composition, the reaction conditions, and by modifying the reactor design. In addition, these selectivities can be modified by co-feeding hydrogen with the aqueous sorbitol feed, leading to a process in which sorbitol can be converted to alkanes and water without the formation of CO_2. As another variation, the production of alkanes can be accomplished by replacing the solid acid with a mineral acid (such as HCl) that is co-fed with the aqueous sorbitol reactant. In general, the selectivities to heavier alkanes increase as more solid acid sites are added to a non-acidic Pt/alumina catalyst by making physical mixtures of Pt/alumina and silica-alumina. The alkane selectivities are similar for an acidic Pt/silica-alumina catalyst and a physical mixture of Pt/alumina and silica-alumina components, both having the same ratio of Pt to acid sites, indicating that the acid and metal sites need not be mixed at the atomic level. The alkane distribution also shifts to heavier alkanes for the non-acidic Pt/alumina catalyst when the pH of the aqueous sorbitol feed is lowered by addition of HCl. The advantages of using a solid acid are that the liquid products do not need to be neutralized, and the reactor does not need to be constructed from special corrosion-resistant materials. On the other hand, acids may already be present in liquid streams following hydrolysis of biomass feeds, thereby promoting the formation of heavier alkanes during aqueous-phase reforming.

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