492g Gas Phase Esterification on Solid Acid Catalysts

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Esterification reactions of carboxylic acids with alcohols play a central role in the manufacture of different products that range from perfumes to fuels. The latter is of particular importance given our society's current level of energy consumption and the perspective of near-future shortages in oil reserves. Present processes to synthesize fuels from vegetable oils and animal fats using esterification are inefficient and expensive, employing batch processes with homogeneous acids. The application of heterogeneous catalysis for the synthesis of biofuel (biodiesel) offers significant advantages over homogeneous catalysis because it can reduce catalyst usage cost, decrease costly separation steps, and permit the use of continuous processing. Many active solid acid catalysts have site activities close to concentrated sulfuric acid and could replace it in most processes. Heterogeneous catalysts, however, have been less studied for esterification and there is no systematic fundamental reaction study measuring and comparing the different performances of solid catalysts over a range of temperatures.

This presentation reports on an investigation of different solid acids [sulfated zirconia (SZ), tungstated zirconia (WZ), Amberlyst-15 (A-15), supported Nafion on silica (SAC-13) and zeolite Hb (Hb)] for the gas phase esterification of acetic acid (HAc) [a model compound for free fatty acids (FFAs)] with methanol as a reaction probe of catalyst activity for biodiesel fuel synthesis applications. Our interest here has been to identify the main catalyst characteristics key to high catalyst activity and the behavior of the catalysts at relatively high reaction temperatures (for biodiesel synthesis). Reaction temperatures above 100oC are desired due to the lower concentration of active sites per weight of catalyst for solid catalysts and a need to remove water during reaction. The use of three phase reaction is likely to greatly improve biodiesel synthesis economics in the future.

X-ray diffraction patterns have been obtained for all the inorganic catalysts studied to elucidate their structural characteristics. Catalyst surface areas were obtained using BET analysis. Temperature-programmed desorption of ammonia was used to obtain surface acidity and an estimate of the strength of the acid sites. IR spectroscopy was used to characterize the concentration of Bronsted vs. Lewis acid sites. Esterification of HAc with methanol was carried out in a stainless steel fixed-bed reactor (I.D. = 2.5 in.) at 90-140°C and 1.5 atm pressure under differential reaction conditions. A-15 was not studied about 100oC due to its lack of thermal stability. Gas samples were analyzed by gas chromatography using an Alltech CP WAX 52 CB column (60 m x 0.53 mm x 1 ìm) with He as the carrier gas.

Esterification activity plots showed Hb and the organic resins to be the most active catalysts on a per weight basis, followed by SZ and WZ. However, when TOF numbers were compared, Hb was by far the most active catalyst with the other catalysts showing similar TOF values. Reasons for the heighten activity of Hb sites point to a combination of preferential acetic acid absorption over methanol and less deactivation by reaction byproducts of esterification like water. This latter observation was supported by experiments using controlled amounts of water added with the reactants. In summary, this work suggests that it is not only acid strength what determines catalyst activity in solid catalysts; characteristics which favor the absorption of the carboxylic acid and lessen the deactivating effect of water are probably more important determinants of catalyst activity. The application of the results of this study to the design of future biodiesel processes will be discussed.