

Kinetic and Spectroscopic Studies of Catalytic Mechanisms: Hydrodeoxygenation of Biomass Feedstocks on Transition Metal Phosphides

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Abstract

The study of mechanisms of reaction is an active area of chemical kinetics, even though it is generally held that mechanisms cannot be proven on the basis of kinetics alone. This work shows that reactivity, spectroscopic, and transient data can be combined to give a unified picture of a reaction mechanism. The reaction studied is the hydrodeoxygenation of a pyrolysis liquid model compound, gamma-valerolactone (GVL). Use is made of in situ Fourier transform infrared spectroscopy and in situ x-ray absorption spectroscopy to probe adsorbed species and the nature of the catalyst surface at reaction conditions. A new method, called Analysis of Coverage Transients (ACT) is used to prove that an adsorbed species is an actual reaction intermediate. The ACT method is general and can be used with any spectroscopic technique.

The application of the work is in the conversion of pyrolysis liquids derived from biomass, whose high oxygen content (~40 wt.%) results in low heating value (about half that of petroleum liquids), high acid content (leading to corrosion problems), and low stability (resulting in increasing viscosity with storage). The catalyst studied is a member of a new family of catalysts, the transition metal phosphides, which have outstanding activity for removal of heteroatoms such as sulfur, nitrogen, and oxygen, from hydrocarbon feedstreams.

A contact time study allowed the determination of a reaction sequence for GVL HDO on Ni₂P/SiO₂ and it was found that C-O bond cleavage of the lactone ring to generate n-pentanoic acid was the rate-determining step. This was followed by hydrogen transfer steps to produce oxygen free compounds, n-pentane or n-butane. Fitting of the results using a rate mechanism that considers adsorbed intermediates indicates that the surface species from the adsorbed GVL are majority species. In situ x-ray absorption near-edge spectroscopy measurements using the ACT method give strong evidence to support this reaction mechanism.

Biography



S. Ted Oyama earned his bachelor's degree in chemistry and chemical engineering at Yale University in 1976 working with Gary Haller and his doctorate in chemical engineering at Stanford University in 1981 with Michel Boudart. He currently holds dual appointments in the Chemical Systems Engineering Dept. at the University of Tokyo and the Chemical Engineering Dept. at Virginia Tech. His research interests are in the areas of catalytic fuel processing, biomass conversion, steam reforming, gas separation membranes, and membrane reactors. He carries out research on the development of new materials, including novel catalytic materials such as phosphides and advanced inorganic membranes. He concentrates on studying the mechanisms of reaction and permeance using kinetic tools coupled with in situ spectroscopy. He is a recipient a 2009 Humboldt Senior Researcher Prize, 2012 Fellow of the American Chemical Society (ACS), the 2014 ACS Distinguished Researcher Award, the 2014 ACS Storch Award, and 2016 Fellow of the American Association for the Advancement of Science. He served as 2009 Chair of the Division of Petroleum Chemistry of the American Chemical Society, and currently is editor of the Journal of Catalysis, a highly-ranked chemical engineering journal. He has published over 240 refereed papers, 7 edited books, and 1 monograph.

Curriculum Vitae

Education:

1976.05 B.S., Yale University, New Haven, Connecticut, USA
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Professional career:

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