

EXPERIMENTAL CONSIDERATION OF CATALYTIC KINETICS IN THE AQUEOUS PHASE: LEVULINIC ACID HYDROGENATION OVER SUPPORTED RU

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Abstract

This study attempts to extract rigorous kinetic data from the hydrogenation of levulinic acid over supported Ru in aqueous solutions. In this system, rapid and profound catalyst deactivation is observed under reaction conditions, which has to date impeded development of meaningful structure-activity relations. Here, this challenge is addressed to the extent possible, permitting conclusions regarding the source of apparent differences in hydrogenation kinetics over a range of catalysts and media.

Keywords

Aqueous Phase, Ketone Hydrogenation, Levulinic Acid, γ -valerolactone, Ru

Introduction

Within the biomass processing community, many catalytic technologies seek to upgrade reactive, low-vapor pressure poly-oxygenated hydrocarbons. Their physical and chemical characteristics tend to imply relatively low-temperature processing in condensed media, which contrasts with traditional hydrocarbon processing. Frequently, water is employed as a solvent, and depending on the chemistries of interest, one may frequently operate at low pH. Experimental kinetic analysis of these systems can be challenging, and a portion of this presentation considers the set of purpose-built reactors employed for acquisition of reliable kinetic data in our laboratory. With respect to reaction kinetics, the presence of a condensed phase and its chemical makeup are generally shown to have a profound impact on catalyst performance; however, the complexity

of the media frequently impedes a rigorous analysis. In particular, we highlight the confounding effects of catalyst instability and active site dynamics, which are often profound and may underlie much of the variability in published kinetic data within the community.

Abstract Body

Supported Ru catalysts are often cited as being extremely active and selective during ketone hydrogenation in water. A specific example of this chemistry that is commonly studied in the biomass community is levulinic acid hydrogenation, which generally occurs in aqueous, acidic media to form γ -valerolactone. Ru has demonstrated pronounced instability in these systems; here, we probe the

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source of this instability, examine its variation across multiple Ru-Support systems, and delineate differences in catalyst stability from those in catalyst activity. Mass transfer restrictions are extremely constraining in this system; however, kinetic data can be obtained at low temperatures and active metal surface areas. Broadly, we observe that intrinsic turnover frequencies of levulinic acid hydrogenation are insensitive to the nature of the support and the size of the Ru cluster; however, each system exhibits unique deactivation profiles that lead to an entirely different set of conclusions as steady states are approached. Thus, the critical need in anticipating the performance of the working catalyst in these systems is likely the evolution of active metal surface area with time on stream, and we attempt to correlate stability with both the nature of the media and the catalyst-support combination.

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