

Theoretical Investigation of the Catalytic Hydrodeoxygenation of Levulinic Acid over Ru Catalysts

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Abstract

Due to the rapidly declining fossil fuel reserves and the onset of global climate change, the development of active, selective, and stable catalytic materials for the efficient production of biomass derived platform chemicals, i.e., levulinic acid (LA), succinic acid (SA), γ -valerolactone (GVL) etc., is receiving considerable attention in order to produce renewable second generation biofuels and commodity chemicals. Though solid lignocellulosic biomass is significantly cheaper than petroleum; the available technology for its conversion is a significant barrier for large scale utilization of biomass for the production of biofuels and chemicals. A prerequisite for the development of biomass conversion technology requires: 1) identification of potential biomass chemicals that can selectively be transformed into targeted molecules, 2) understanding fundamental bond breaking/formation mechanisms (i.e. C-H, O-H, C-C bond cleavage and formation) at solid/gas and solid/liquid interfaces, and 3) identification of the active site in the catalysts.

Among the 'top 10' platform biomass chemicals identified by the Department of Energy (DOE), GVL is of particular interest because of its widespread application as a gasoline blender and in the production of bio based polymers. Understanding the reaction kinetics governing the aqueous phase hydrodeoxygenation (HDO) of levulinic acid (LA) to γ -Valerolactone (GVL) over Ru surfaces will expedite the design of better catalysts for this conversion process considering that Ru/C catalyst is the most used catalysts for the HDO of LA. In this dissertation, we report a computational investigation of the reaction mechanism of LA to GVL using DFT calculations and mean-field microkinetic modeling in both vapor and liquid phase reaction conditions. In vapor phase calculations, our model predicts a dominant reaction route that propagates through the alkoxy formation step leading to the formation of a five member ring structure which is subsequently followed by a C-OH cleavage to form GVL. This pathway deviates from the previously proposed mechanism that involves formation of 4-hydroxypentanoic acid (HPA). In the low temperature region ($T < 373$ K), our model identifies that at a vapor phase condition Ru(0001) is not the experimentally observed active sites, while at high reaction temperatures ($T > 423$ K), Ru(0001) constitutes the majority of the active site. Next, our liquid phase results indicate that polar solvents (i.e. water) have a beneficial effect on the reaction kinetics of the hydrodeoxygenation of LA. Specifically, in an aqueous phase environment and a reaction temperature of 323 K, the reaction rate is 4-5 orders of magnitude higher than the rate under gaseous phase condition which explains the low temperature activity found in experimental studies. In contrast, non-polar solvents (1,4-dioxane) have a detrimental effect on the reaction kinetics, as also confirmed by several experimental studies, due to the high solvent coverage on the Ru surface.

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