

Catalytic upgrading of biomass-derived acids by dehydration/hydrogenation and C-C coupling reactions

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Introduction

The utilization of renewable feedstocks for the chemical industry is becoming more important in view of decreasing fossil resources and increased pressure on our environment [1]. In this respect, biomass is a promising candidate to serve as a sustainable source of organic carbon and to help establish a renewable chemical industry that is cost-competitive with the current petrochemical-based industry. In this respect, the production of organic acids (such as lactic acid, 2-hydroxypropanoic acid) from biomass by low cost and high-efficiency fermentation processes is a good example. Lactic acid, containing adjacent hydroxyl and carboxylic groups, may undergo a variety of reactions leading to useful products [2]. However, this high functionality (typical of biomass-derived molecules) also leads to high reactivity and makes necessary the development of strategies to decrease the degree of functionality and, with it, to control the reactivity of the final products and avoid undesired reactions. In the present contribution, we address a number of routes (e.g., dehydration/hydrogenation and C-C coupling reactions) that can be used to upgrade the lactic acid into valuable chemicals and, how, by changing the support properties, is possible to more selectively convert lactic acid to desired products.

Materials and Methods

Two catalysts were tested in conversions of lactic acid and propanoic acid by dehydration/hydrogenation reactions: Pt(0.1%)/Vulcan (from a commercial Pt(5%)/Vulcan XC-72 catalyst, BASF) and Pt(0.1%)/Nb₂O₅ (prepared by incipient wetness impregnation of a commercial niobium oxide, HY-340 CBMM-Brazil, using [Pt(NH₃)₄](NO₃)₂ precursor). Catalysts were pre-reduced at 523 K for 4 h under flowing H₂ before reaction kinetics studies. These studies were conducted in a upflow fixed-bed reactor, loaded with 2.5 g of catalysts (1.0 g in the case of Pt/Vulcan) feeding with a concentrated acid solution (60 wt% lactic acid or 40 wt% propanoic acid) and employing a co-feed of H₂ (80 cm³(STP)/min) at temperatures from 523 to 623 K and a constant pressure of 825 psi. Detection and quantification of the different products were carried out by means of GC and GC-MS analyses.

Results and Discussion

Various reaction pathways that we have studied for lactic acid conversion (accounting for 90 % of the total reacted carbon) over Pt(0.1%)/Vulcan and Pt(0.1%)/Nb₂O₅ are shown in Figure 1. The primary reaction products (those detected at high space velocities) are: acetaldehyde (produced by decarboxylation/decarbonylation with the release of CO and CO₂) and propanoic acid. These two products were detected in significant amounts for both catalysts, although Pt(0.1%)/Nb₂O₅ showed higher activity than the Pt(0.1%)/Vulcan catalyst. To study further the reactivity of propanoic acid over both catalysts, independent reaction kinetic studies were carried out with this acid as feed at the same conditions used with lactic

acid. Interestingly, while propanoic acid reacted over Pt(0.1%)/Vulcan to form almost exclusively ethane (with equimolar amounts of CO_x) and 1-propanol, the reactivity of propanoic acid over Pt(0.1%)/Nb₂O₅ favored the conversion of propanol to propane (by a dehydration/hydrogenation mechanism) and, more importantly, induced the onset of C₅ species (3-Pentanone and Pentane) by ketonization. The evolution of the other primary product, acetaldehyde, was studied by investigating lactic acid reactions at low space velocities. Again, Pt(0.1%)/Nb₂O₅ favored the production of C₄ species by aldol-condensation reactions (2-butenal, butanal and 2-butanone), while the Pt(0.1%)/Vulcan catalyst led to the formation of ethanol, which is a lower-value direct hydrogenation product. Consequently, the use of a bifunctional Pt(0.1%)/Nb₂O₅ catalyst allows us to maximize the yield of the desired products (pentanones and C₄ carbonyls) by adding two new C-C coupling reaction routes.

Significance

This study provides new insight into the reaction pathways of an important biomass-derived molecule, lactic acid, over Pt catalysts and addresses the upgrading of this resource into valuable chemicals (pentanones and C₄ carbonyls).

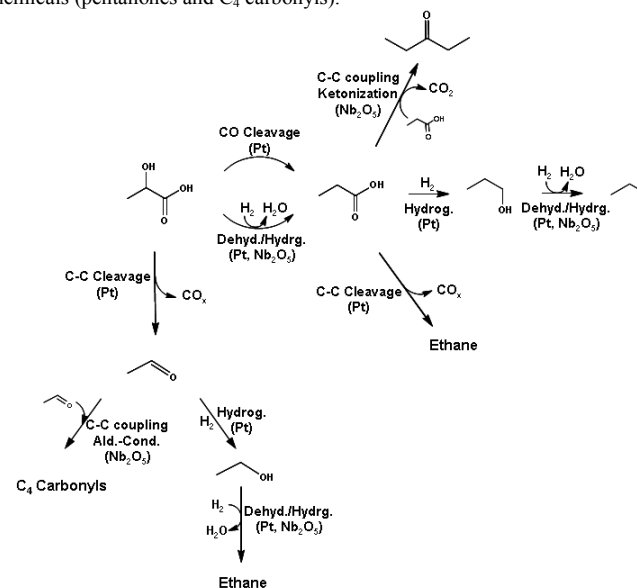


Figure 1. Reaction pathways for lactic acid dehydration/hydrogenation and C-C coupling over Pt/Vulcan and Pt/Nb₂O₅ catalysts.

References

1. C. H. Christensen et al, *ChemSusChem* 1, 283 (2008).
2. R. Datta et al., *FEMS Microbiology Reviews* 16, 221 (1995).