

Lactic acid hydrogenation over copper-containing catalysts

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Introduction

Lactic acid (LA) can be produced through the fermentation of a number of renewable resources such as refined carbohydrates (sugars and starches) derived from agricultural crops. Furthermore, LA can be produced from carbohydrates derived from waste biomass streams (i.e. cheese whey and wood molasses). Well known carbohydrate-derived organic acids could produce important chemical commodities. The combination of fermentation process and selective catalytic process provides green route for the production of these chemical commodities from renewable carbohydrate feed stocks instead of from non-renewable petroleum. There is a considerable interest in the conversion of LA to produce 1,2-propanediol by direct hydrogenation of lactic acid [1-3] which is otherwise produced by the hydration of propylene oxide starting from petroleum derivatives in an environmentally unfriendly way [4].

According to literature survey this reaction could occur both in gas and liquid phase over heterogeneous catalysts. However high pressure up to 350 bar and temperature till 350°C is necessary for reasonable lactic acid conversion over Re, Ni Reney and Ru catalysts [5-7], showing silica-supported copper is a high selective catalyst to convert LA carboxylic group to 1,2-propanediol hydroxyl one at less hydrogen pressure [8].

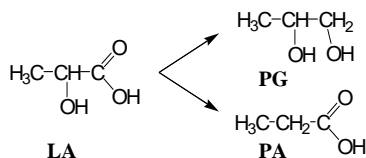
The goal of the present work is to study gas phase LA hydrogenation over various copper-containing catalysts in order to develop high selective catalytic process of 1,2-propanediol synthesis in mild reaction conditions.

Materials and Methods

Four samples of copper-containing samples were tested: copper chromite with a tetragonally distorted spinel structure (Cu-Cr), copper-zinc oxide (Cu-Zn), copper hydroxysilicate with Chrysocolla mineral structure (Cu-Si), copper-zinc hydroxysilicate with Zincsilite mineral structure (Cu-Zn-Si) [9]. Besides a sample of porous copper was tested for comparison. The main liquid products (Fig.1) were analyzed by GLC analysis (FID, glass column 2m x2mm, Carbowax, 5% FPPT).

Catalytic runs were performed in glass downflow reactor with substrate supplying by syringe. Before activity test sample placed between quartz wool was activated in hydrogen stream with temperature ramp 2K/min up to 523K.

Figure 1. The scheme of LA hydrogenation to propylene glycol (PG) and propionic acid (PA).



Results and Discussion

Catalytic activity and selectivity obtained for different catalyst samples are presented on Fig. 2. Sample Cu-Cr with copper loading 33 % exhibited very low conversion of LA and was deactivated rapidly. Despite the fact that copper content in Cu-Zn-Si and Cu-Si catalyst samples is quite the same (13 and 14%), LA conversion of the latter is essentially higher. It was not observed any catalytic activity of Cu-Zn catalyst sample. The different activities indicate the different Cu state and environment as well support influence.

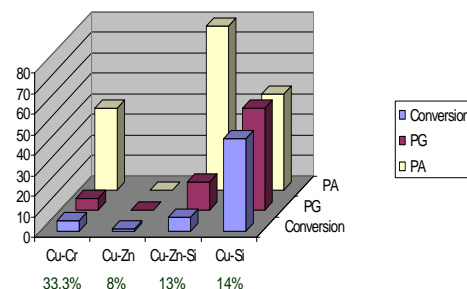


Figure 2. Comparison of catalytic activity and selectivity of catalyst samples in lactic acid hydrogenation. Reaction conditions: T=473K, P_{H₂}= 1 bar, WHSV=0,08 h⁻¹

Significance

This work manifests a promising route for the production of chemical commodities from renewable carbohydrate feed stocks instead of from non-renewable petroleum.

Acknowledgement

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The most active catalyst precursor was found to provide 95% LA conversion and 65% PG selectivity in mild reaction conditions. To compare the known copper-silica catalyst provides 7% LA conversion and 75% PG selectivity in the same reaction conditions [3]. The long term stability of the most active sample was studied and discussed in details. It was found that in spite of catalytic activity gradual decrease the LA selectivity does not change notably during 110 hours on stream.