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A study of the catalytic hydroconversion of biocarboxylic acids to bioalcohols using octanoic acid as model reactant

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ABSTRACT

The catalytic hydrodeoxygenation (HDO) of octanoic acid (C₇COOH) to octene and octane was found to proceed in consecutive reaction through octyl aldehyde and octyl alcohol intermediates. Aluminosilicate and γ -alumina supported Cu and Cu,In catalysts were applied in a fixed bed flow-through reactor at 21 bar total pressure in the temperature range of 330–380 °C. The feed was 7.1% C₇COOH/84.3% H₂/He. The WHSV of the acid was 1.82 h⁻¹. The results suggested that at lower temperatures the rate of acid hydrogenation/dehydration determined the rate of the consecutive hydroconversion process and alcohol selectivity. The reduction of aldehyde was facile, thus, the aldehyde selectivity was low under most conditions. At lower temperatures and conversions the acid coverage was high hindering the catalytic dehydration of the product alcohol. At higher temperatures and acid conversions the alcohol dehydration activity of the catalyst determined the alcohol selectivity. The favorable effects of indium were attributed to the formation of new catalytically active Cu₂In alloy phase.

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1. Introduction

Because of the tightening supply of fossil carbon sources and the increasing environmental and the social concerns related to their extensive use the biomass, being renewable carbon source, becomes more and more important as raw material for the chemical industry. Nowadays a rapidly increasing amount of triglycerides, mainly vegetable oils, are converted to fuel. Biodiesel is made by the catalytic transesterification of the oil. Also, the oil is converted to diesel substitute "green diesel" or to fatty alcohol by catalytic hydrodeoxygenation (HDO) [1-3]. Lower alcohols, such as ethanol, can partially or fully substitute gasoline. Ethanol is usually obtained by microbial fermentation of sugar or starch. The fermentation to fuel ethanol involves the conversion of potential food materials, causing distressing increase of food prices. However, lower acids mainly acetic acid, are generated by pyrolysis or by anerobic fermentation of non-food lignocellulose and organic wastes, Thus, an alternative route to get lower alcohols is the selective HDO of the carboxylic acids from renewable resources. The growing importance of biomass conversion to chemicals and transportation fuels explains the increasing interest in the selective catalytic HDO reaction of esters and carboxylic acids.

The catalytic hydroprocessing of triglycerides, mainly vegetable oils, was started about 130 years ago by the food industry. Liquid phase catalytic hydrogenation of vegetable oil over metal catalysts, such as nickel or palladium, under mild conditions ($120-280 \degree C$, 1-5 bar), was applied to obtain butter substitutes of various softness by partial saturation of the oil double bonds.

The increasing demand for fuels and detergents from renewable resources made the vegetable oil important raw material of the chemical industry [4]. For the production of alkanes ("green diesel") it was plausible to adopt the catalysts routinely used for heteroatom removal from crude oil fractions. The most important and difficult is to-reduce the sulfur content of the crude oil. Hydrodesulfurization (HDS) catalysts typically consist of γ -alumina-supported small clusters of MoS2 with low concentrations of cobalt or nickel promoters. In the virtual absence of sulfur in vegetable oil the sulfide form of the catalyst could not be maintained during HDO reaction without co-feeding sulfur precursor compound. Therefore, it was a rational decision to study the oxide precursor of the HDS catalyst in the HDO reaction, namely the alumina supported nickel molybdate or cobalt molybdate [5]. Alternatively, supported Ni or Pd catalysts were tested in the HDO reaction under conditions, which were more severe than those used for oil hardening. The removal of oxygen was shown to be consecutive reaction introduced by the facile triglyceride hydrogenolysis giving carboxylic acid and propane, followed by oxygen removal from the acid [5,6]. Over the supported metal catalyst decarboxylation/decarbonylation was the dominant reaction of carboxylic

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