



Effect of Pt/HZSM-5 dealumination by high temperature reduction on glycerol oxidation

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Abstract

Glycerol oxidation was investigated using as catalyst an acid zeolite (H-ZSM-5) impregnated with different contents of Pt (1 and 3 wt%), and H₂O₂ and air as oxidants. Catalysts were characterized by XRD, XRF, FT-IR, ²⁷Al MAS NMR, N₂ adsorption, NH₃-TPD, XPS and TEM. After calcination, catalysts were reduced at 1000 °C under H₂ and this treatment lead to some dealumination that influenced catalyst acidity. The influence of acidity was evaluated in glycerol oxidation. All tested catalysts were able to oxidize glycerol, and the main products were 1,3-dihydroxyacetone, glyceric acid and glyceraldehyde.

Keywords Glycerol oxidation · Pt/HZSM-5 · Glyceric acid · Dihydroxyacetone

Abbreviations

GLY	Glycerol
GLYA	Glyceric acid
DHA	Dihydroxyacetone
TART	Tartronic acid
GLYCA	Glycolic acid
GLYOX	Glyoxylic acid
OXA	Oxalic acid
βPY	β-Hydroxypyruvic acid
GLYALD	Glyceraldehyde

1 Introduction

The finitude and instability of oil reserves, associated with the environmental impacts, have motivated researches around the world to develop fuels and chemicals from biomass. Biomass can be used as a source to produce fuels and valuable chemicals, and can replace, at least in part, fossil fuels. Biodiesel is a renewable biofuel, that has been used mixed with diesel, or not, aiming decreasing fossil

fuel dependence. However, biodiesel production, via transesterification reaction of oils and fats, generates a surplus of glycerol: each ton of produced biodiesel produces 100 kg of glycerin. The possible use for this glycerin is a matter of concern; nowadays, great part of this surplus is incinerated [1]. The search for alternatives to incineration would be of great value both economically and environmentally.

An interesting option for a noble use of glycerol is its selective oxidation. Glycerol oxidation may produce dihydroxyacetone (DHA), glyceric acid (GLYA), glyceraldehyde (GLYALD), tartronic acid (TART), among others. However, it is still a challenge, since these rich functionalized glycerol derivatives are either produced by using costly and polluting stoichiometric oxidation processes (e.g. potassium permanganate, nitric acid or chromic acid) [2] or low productivity fermentation processes [3, 4]. Regarding to glycerol oxidation products, the oxidation at terminal carbon leads to the formation of glyceraldehyde/glyceric acid, which can undergo further oxidation to tartronic acid and C–C bond cleavage reactions to form glycolic, oxalic and formic acids. Oxidation at the central carbon leads to the formation of dihydroxyacetone and further oxidation of this material may lead to hydroxypyruvic and mesoxalic acids [5].

These oxidation products have several roles in the chemical industry, Dihydroxyacetone (DHA) is one of the most high-valued product derived from glycerol. It is frequently used in cosmetic industry, as an active ingredient in sunless tanners, and as building block for the organic synthesis of a variety of fine chemicals [6, 7]. Particularly relevant is its potential use for a green and sustainable

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