

Glycerol Conversion as Side Product of Biodiesel Production to Propylene Glycol

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Abstract

In recent years, characterized by increasing production of the first generation of biofuels, glycerol, which is the main side product from the biodiesel production, stopped to be viewed as specialty chemical or the raw material for specialties production only. Its increasing availability as well as its decreasing price have created conditions for its utilization as a substitute for some petrochemical intermediates, mainly for propylene, in medium scale or even large scale chemical production processes, like epichlorohydrine or propylene glycol (1,2-propanediol). Propylene glycol is commonly produced prevalably from fossil sources. It is used in many application, as monomer for polyester resins, deicing liquid, coolant, humectant, solvent or stabilizer. The yearly production is about 700 000 tun/year in European union. Hydrogenolyses of glycerol is an alternative way for the production of propylene glycol. Glycerol can be converted to 1,2-propanediol by a catalytic reaction with hydrogen, following the dehydration-hydrogenation mechanism in which hydroxyacetone (acetol) takes part of the key intermediate, ethyleneglycol, ethanol, isopropanol being the main byproducts. Maximizing of the catalyst selectivity is the main assumption for the competitive production process development, therefore main attention is paid to the catalyst research. The catalyst should have the redox and acid-based properties, which influenced the catalytic activity. Currently, the catalysts with noble metals, mainly Ru, Rh or Pt, impregnated on different types of carriers, and Cu based catalyst are most frequently used in the selective hydrogenolysis of glycerol. The Cu based catalysts are usually prepared in the form of mixed oxides prepared by different methods, mainly by coprecipitation. The composition, as well as the preparation method can influence very substantially the properties of the Cu based catalysts.

Our research was focused on the CuZnAl mixed oxides, prepared from hydrotalcites, which were used as precursors of the catalysts for selective hydrogenolysis of glycerol to propylene glycol. The redox and acid-based properties were modified by the change of Cu/Zn/Al molar ration. It was found, that the selectivity to propylene glycol was influenced by acidity of the catalysts. The high amount of Zn in the catalyst positively influenced the catalysts acidity. On the other hand, the conversion of glycerol was strongly influenced by the amount of copper. The hydrogenolysis over all the catalysts was carried out at the same conditions, namely at 230 °C, 7 MPa H₂, 30 dm³/h H₂, the catalyst load of 5 wt% to glycerol and 5 hours of the reaction time. The best catalyst exhibited 99 % conversion of glycerol the selectivity to propylene glycol being of 90 %.