

Liquid Phase Glycerol Hydrogenolysis using Commercial and Laboratory prepared Copper Chromite Catalysts: Characterisation and effect of Cu-Cr ratio.

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1 Introduction

Biodiesel is a non-petroleum based fuel that consist of alkyl esters derived from either the transesterification of triglycerides or the esterification of free fatty acids (FFAs) with low molecular weight alcohols [1]. The use of vegetable oil as an alternative renewable fuel is due to the following advantages of vegetable oil as diesel fuel: liquid nature-portability, readily availability, renewability, higher heat content (about 88% of no.2 diesel fuel), lower sulphur content, lower aromatic content and biodegradability [2]. The production of biodiesel as a substitute for petroleum diesel has increased in recent times. One problem arising from the production route is the generation and disposal of the crude glycerol, which is a by-product of biodiesel synthesis. This also plays a crucial role in the process economics. Currently, the crude glycerol is either disposed as waste or sold as glycerol after purification. Since biodiesel production capacity is expanding, the cost of glycerol has diminished due to its increased production. This has in turn affected the economic viability of commercial biodiesel production, because the by-product market is not encouraging in terms of returns on investment to offset production cost. However, in line with the objectives of green chemistry, alternative routes for crude glycerol utilization for the production of some chemical intermediates have been the subject of research in recent times. Such chemical intermediates include the production of 1,2-propanediol and 1,3-propanediol. These chemicals are feedstocks for a variety of products of industrial and domestic applications. The objective of this study is to examine the effect of copper chromite ratio in synthesis process for the hydrogenolysis of glycerol in a one pot-synthesis route with the multifunctional catalyst.

1.1 Hydrogenolysis of glycerol to propanediols

The conversion of glycerol to propanediols is an important route for obtaining chemical intermediates from renewable feedstocks. The use of chemical catalyst for this transformation has been the subject of a lot of research in recent years. The most common route of production these chemicals is through the dehydration and hydrogenation

(denoted as hydrogenolysis) of sugars or sugar alcohols at high temperatures and pressures in the presence of metal catalyst producing propylene glycol and other lower polyols [3]. This reaction scheme is seen in Fig 1.

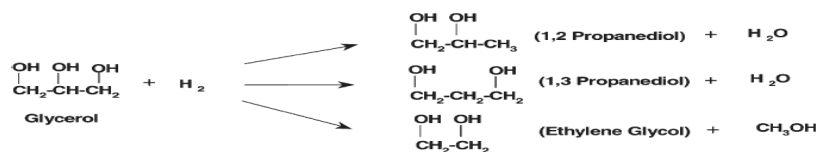


Fig1. Hydrogenolysis of glycerol to propanediols [3]

2 Experimental/methodology

2.1 Preparation of copper chromite mixed oxides of various atomic ratios

Mixed oxides of varying Cu:Cr atomic ratios (1:1, 3:1, 1:3) were prepared by coprecipitation of aqueous solutions of Cu (NO₃)₃·2H₂O and Cr (NO₃)₃·9H₂O using a procedure adapted from literature [4-5]. Stoichiometric amounts of the precursor of both nitrates of copper and chromium were dissolved in 1000ml beakers with distilled water. Sodium bicarbonate was added dropwise to the stirred aqueous solutions of mixtures of Cu^{II} + Cr^{III} nitrates of molar concentrations 0.1M for [Cu-Cr (1:1)], 0.5M [Cu-Cr(3:1)] and 0.5M [Cu-Cr(1:3)] at 70°C until pH 7 was reached, followed by aging of the suspension for 3 h at 70°C. The precipitates formed were collected on a filter, washed thoroughly with deionised water and dried at 100-104°C for 12 h. The Cu-Cr mixed hydroxides formed were thereafter calcined at 300°C for 5 h under nitrogen flow. The calcined samples were then reduced under hydrogen flow (30-40ml/min) at 300°C for 4 h. The prepared catalyst were characterised using BET surface area, Fourier transform infrared spectroscopy (FT-IR), thermo-gravimetric analysis (TGA) and x-ray diffraction. The hydrogenolysis of glycerol was carried out in the liquid phase using a batch reactor. A 50 ml Parr 4714 stainless steel autoclave reactor equipped with a pressure gauge and a magnetic stirrer. The reaction mixture consisted of 5.0 ml of an aqueous solution of glycerol and 0.5 g of catalyst. The autoclave was purged with H₂ then pressurised with H₂ and placed in an oil bath preheated to the required reaction temperature (100-200°C). The reaction was carried out for a specific duration (24 h), 180°C and 14 bar hydrogen pressure using 80% glycerol. Upon completion, the reactor was cooled to room temperature, placed in an ice bath for 30 min after which it was depressurised and opened. 0.2 g of n-butanol and 5 ml of deionised water were then added to the reaction mixture as external standard and solvent. The mixture was centrifuged using an Eppendorf minispin centrifuge at 13000 rpm for 20 min to separate the products and catalyst. The products were thereafter analysed using a Varian CP- 3800 gas chromatograph equipped with a flame ionisation detector, a 30m x 0.32mm x 0.5 μm CP-WAX 52 capillary column and a Star Varian chromatography 4.51 workstation software.

3 Results and discussion

It has been reported that Cu-Cr is a good hydrogenolysis catalyst [6]. In addition to the commercial Cu-Cr catalyst used in this reaction, Cu-Cr mixed oxides with varying Cu-Cr ratio was prepared as previously reported here and used to test for activity towards the glycerol hydrogenolysis reaction. The surface area results are presented in Table 1 and from Fig. 2 it is observed that the ratio of Cu-Cr greatly affects the conversion/ selectivity in the hydrogenolysis reaction. It also showed that Cu is the main active component for the reaction, as increased in Cu concentration increased the conversion to 79.68%. However, an increase in Cr ratio gave a corresponding decrease conversion to 18.62 %.

Table1: Shows the surface characteristics of the catalysts

Catalyst	Cu-Cr (Comm)	Cu- Cr(1:1)	Cu- Cr(3:1)	Cu- Cr(1:3)
S ^{BET} m ² /g	77.05	385.19	122.17	110.99
Pore size (Å)	68.65	67.19	74.84	53.42
Pore volume (cm ³ /g)	0.132	0.647	0.228	0.148

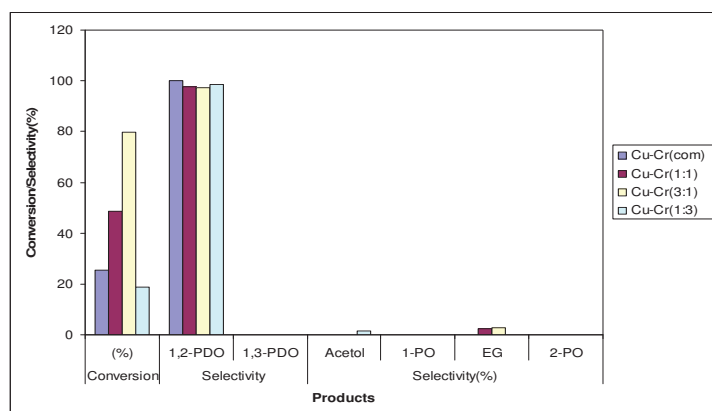


Fig.2. Effect of Cu-Cr ratio on conversion and selectivity of products at 180 °C, 14 bar hydrogen pressure using 80% glycerol

4 Conclusions

The hydrogenolysis of glycerol has been studied in this work using commercial and laboratory prepared copper chromite catalyst with optimum conversion and selectivity to 1,2-propanediol with Cu-Cr catalyst(3:1) at 14 bar hydrogen pressure, 180 °C, 24 h, 80% glycerol, 10% catalyst and 5mL of reaction mixture. The laboratory prepared Cu-Cr catalyst were observed to be very selective to 1,2-propanediol. In addition, it is further observed that in all the Cu catalyst the following products 1,3-propanediol, 2-propanol and 1-propanol were not detected.

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