



Glycerol carbonate production from transesterification of glycerol with diethyl carbonate catalyzed by Ca/Al-mixed oxides derived from hydrocalumite

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Abstract

A series of Ca/Al-mixed oxides derived from hydrocalumite (HC) with Ca/Al atomic ratio of 2 was prepared by calcination at different temperatures and they were evaluated in transesterification of glycerol with diethyl carbonate (DEC) to produce glycerol carbonate (GC). HC was tested as non-calcined and calcined at different temperatures (600, 700, 800, and 900 °C). The catalysts presented a well-crystallized structure with low specific surface area. Non-calcined hydrocalumite presented higher density of basic sites (571 $\mu\text{mol g}^{-1}$) with major proportion of strong basic sites; after calcination, catalyst basicity dropped dramatically. Reactions were performed with different temperatures (from 90 to 130 °C), catalyst amounts (5, 10, and 15 wt%), and solvents (dimethyl sulfoxide and dimethylformamide). Promising results were found using HC calcined at 700 °C, reaching 90% of glycerol conversion and 91% of GC selectivity at 130 °C.

Keywords Glycerol · Diethyl carbonate · Glycerol carbonate · Hydrocalumite · Ca/Al-mixed oxides

1 Introduction

Due to the depletion of the fossil resources and the growing search for less environmentally harmful chemicals, researchers have been looking for alternatives to supply this energy demand. An interesting alternative to fossil fuels is biodiesel that can be produced from a transesterification reaction using renewable sources such as vegetable oils, animal fats, algae, and fungi oil [1]. However, the increasing production of biodiesel also produces an excess of glycerol as the main byproduct [2]; each transesterified triglyceride molecule generates three ester molecules and one glycerol [3]. Glycerol is a versatile molecule, and it is a precursor to several compounds like glycidol, propanediol, glyceric acid, and glycerol carbonate [4, 5].

One of the alternatives for this glycerol surplus is its use for the production of glycerol carbonate (GC), which is an innovative product, being a sustainable solvent, due to its low

toxicity, good interaction with polar and nonpolar solvents, high boiling point, and water solubility. Furthermore, it can be used as polymer monomer [6] and battery carrier [7]. Usually, GC has been synthesized by reaction between glycerol and phosgene, but due to phosgene's high toxicity, alternative routes have been explored [5]. Another option is the use of urea as reactant, to avoid the use of phosgene, but the reaction produces 2 mol of ammonium as byproduct, which is undesirable in a green route [5, 6]. The use of CO₂, as carbonyl source, is attractive with high atom utilization efficiency. The main drawback of this reaction is the low conversion due to severe thermodynamic limitations [8, 9]. Several works in the literature present dimethyl carbonate (DMC) as reactant for GC production, using hydrotalcites, trisodium phosphate, LiCl/CaO, MgCe, among others, as catalysts [10–13]. Reaction produces 2 mol of methanol for each GC mole produced [14]. It is considered promising since reactions can be performed at milder conditions, and the methanol formed as byproduct can be easily separated [15].

Similar to dimethyl carbonate, diethyl carbonate (DEC) can be used as a source of alkyl carbonates for glycerol transesterification. Glycerol transesterification with DEC for GC synthesis is a green and promising route with nontoxic ethanol as the main byproduct and potential for high GC yield. Álvarez et al. [16] has studied the synthesis of glycerol

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