Research article

Continuous production of lactic acid from glycerol in alkaline medium using supported copper catalysts

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A B S T R A C T

With increasing demand for biodiesel, large quantity of crude glycerol has been produced both in Brazilian and world market, and this excess glycerol has become a problem that must be solved. Several studies have been performed with the objective to transform glycerol in value-added chemical products. Lactic acid has wide uses in chemical and food industries, and the hydrothermal transformation of glycerol to lactic acid is presented as an alternative to conventional production process. In this study, the production of lactic acid from glycerol under alkaline conditions, using copper (20 wt.% CuO) catalysts supported on Al_2O_3, ZnO and MgO in continuous flow reaction system was investigated. The catalysts were prepared by impregnation method and characterized by XRF, XRD, N_2 adsorption–desorption, TPR, and $TPD-CO_2$ and the dispersion of copper was determined by N_2O oxidation. The reaction was carried out at 240 °C, 35 atm, with space velocity (WHSV) of 2 h^{-1}, 10 vol.% glycerol solution and NaOH/glycerol molar ratio of 0.5, 0.75 and 1.0. All catalysts showed high conversion of glycerol with yield and selectivity to lactic acid in the range of 80 and 90%, respectively, when the reactions are performed with NaOH/glycerol molar ratio of 1.0.

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1. Introduction

Biomass has great potential to serve as a source of energy and sustainable carbon for our industrialized society. The production of fuels from biomass has potential to reduce emissions of greenhouse gases, compared to traditional fossil fuels. Furthermore, the CO_2 released is consumed during regeneration of the biomass. Thus, the development of renewable fuels and chemicals has become increasingly important over the last decade [1–7].

The biodiesel is typically produced by transesterification of vegetable oils or animal fats, and this process produces large amounts of glycerol as by-product. The production of a ton of biodiesel results in around 110 kg of crude glycerol, or 100 kg of pure glycerol [8]. In Brazil, according to National Agency of Petroleum, Natural Gas and Biofuels (ANP), the production of biodiesel (B100) in 2014 was approximately 3.45 million m^3, generating 345,000 m^3 of crude glycerol [9]. Biodiesel production is largely increasing in Brazil because of the compulsory addition of biodiesel to diesel: the addition of 2% biodiesel (B2) in diesel is mandatory since 2008, this amount increased to 5% (B5) in 2010 and after 1st of November of 2014, the percentage of biodiesel added to diesel reached 7% (B7). With the fast increase of glycerol supply in the world market the price of refined glycerol dropped from $1.20/kg in

2003 to $0.60/kg in 2006 [10], and in 2011 the price of crude glycerol in the United States reached the minimum value of $0.04–0.11/kg [11].

Glycerol is a very versatile raw material for producing various chemicals, polymers and fuels. Some of the processes described in the literature include polymerization; esterification to produce additives for fuels as octane; dehydration to produce acrolein, an important intermediate in the manufacture of polymers; selective oxidation to dihydroxyacetone, a versatile compound extensively used as a cosmetic ingredient, among others [12–14]. Furthermore, the catalytic conversion of glycerol with different metals under hydrogen or inert atmosphere can lead to a wide range of chemical products [15,16].

1,2-propanediol and lactic acid are two important chemicals that may be produced by catalytic conversion of glycerol. 1,2-propanediol is used in the food industry as antifreeze replacement of 1,2-ethanediol, being less toxic, and also used as a raw material in the production of films and polyester resins [17]. Lactic acid is widely used in cosmetic industry as moisturizing and in textile industry as a mordant (i.e. chemical that enhances the color durability of the tissue). Moreover, lactic acid is used in the dairy industry as a pH regulator, as a preservative or even as an inhibitor of bacterial spoilage. It is currently being used as a precursor of "green" solvents such as ethyl lactate, and also employed in the synthesis of poly lactic acid (PLA), which is increasingly used in the production of biodegradable packaging [18].

Currently commercial production of lactic acid is carried out by anaerobic fermentation of carbohydrates, such as glucose, sucrose

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or lactose [19]. Although the fermentation has a high yield (90%) into lactic acid, several problems are associated with the process, such as the high cost of culture media, due to the specific requirements of lactic acid producing bacteria [20], inhibition by the product [21], and high cost of purification process, besides being a non-ecological process [22].

The hydrothermal conversion of glycerol to lactic acid has recently been studied as an alternative to fermentative route, as well as presents an alternative for the use of glycerol obtained from the biodiesel production process. The hydrothermal process of glycerol conversion has the advantage of not requiring purification steps of glycerol derived from biodiesel production, which has impurities such as water, alcohol, salts and alkali compounds [23,24]. In addition, for environmental reasons, some researchers point to a growing demand for lactic acid, because it is a raw material for the production of a biodegradable polymer (PLA) [25].

Kishida et al. [26] were the first to describe the chemical route of the hydrothermal conversion of glycerol in strongly alkaline media. In this work, a mixture of water and glycerol was converted into sodium lactate using an autoclave reactor system and employing NaOH or KOH as catalyst at temperatures around 300 °C. After 90 min of reaction, using 1.25 M NaOH or KOH and 0.33 M glycerol solution, the yield of sodium lactate was higher than 90 mol% with 100% glycerol conversion. Ftouni et al. [27] evaluated the conversion of glycerol under alkaline conditions employing platinum-based catalysts and obtained a yield of lactic acid up to 84% after a reaction time of 24 h at 180 °C and NaOH/glycerol molar ratio of 1.8.

It is also possible to perform direct transformation of glycerol to methyl lactate in the absence of a base, by chemocatalytic conversion of glycerol in methanol [28]: 73% of yield was obtained at 160 °C using Au nanoparticles supported on USY.

Most of the works in the literature of glycerol conversion to lactic acid was carried out using batch reactor. Some exceptions are the studies presented by Zhang et al. [29] and Shimanouchi et al. [30], which employed continuous flow reactor, but with alkaline homogeneous catalysis. In the case of Shimanouchi et al. [30] rapid conversion and high yield (90% in 2 min) were achieved at 350 °C and 200 atm, resulted from the inhibition of side reactions by the rapid temperature-shift.

The objective of this study is to investigate the production of lactic acid from glycerol in alkaline medium, using copper catalyst supported on Al$_2$O$_3$, ZnO and MgO, in continuous flow reaction system and evaluate the effect of different molar ratios of NaOH/glycerol on yield and selectivity to lactic acid. Some literature reports have shown that the use of these catalyst supports might be promising in glycerol transformation to lactic acid. Additionally, copper has been shown effective as catalyst [24]. Thus, with this work we intend to show the performance and chemical stability of these catalysts when employed a continuous flow reaction system.

2. Experimental

2.1. Catalyst preparation

The supported copper catalysts (Cu/Al$_2$O$_3$, Cu/ZnO and Cu/MgO) were prepared by wet impregnation method with a loading of 20 wt.% of CuO in calcined sample. The ZnO and MgO supports were obtained from calcination of zinc nitrate (Zn(NO$_3$)$_2$.6H$_2$O) (Vetec) and magnesium nitrate (Mg(NO$_3$)$_2$.6H$_2$O) (Vetec), respectively. Both supports were pre-calcined in a muffle furnace at 350 °C for 1 h with the aim of removing most of the hydration water. Afterwards, the supports were calcined at 500 °C for 3 h under flowing air (60 mL min^{-1}). The alumina support used was a γ-alumina (Al$_2$O$_3$) (BASF), which was calcined at 500 °C for 3 h under flowing air. Then, an appropriate amount of copper nitrate (Cu(NO$_3$)$_2$.3H$_2$O) (Vetec) was solubilized in 80 mL of distilled and deionized water and added to the catalyst support. The water was

removed on a rotary evaporator (TECNAL TE – 211). Initially, the flask containing copper nitrate solution and support (Al$_2$O$_3$ or ZnO or MgO) was kept in rotation for 1 h to homogenize the mixture, and then the mixture was heated to 80 °C under vacuum and maintained at this temperature until complete evaporation of the water. Finally, the catalysts were dried at 110 °C overnight and then calcined at 500 °C for 3 h using a heating rate of 10 °C min^{-1} under flowing air (60 mL min^{-1}).

2.2. Catalyst characterization

The chemical composition of the catalysts was determined by X-ray fluorescence (XRF) using a Rigaku Primini spectrometer, equipped with X-ray generator tube of palladium.

X-ray powder diffraction (XRD) patterns were recorded in a Rigaku Miniflex II X-ray diffractometer equipped with a graphite monochromator using CuKα radiation (30 kV and 15 mA). The measurements were carried out with steps of 0.05° using a counting time of 1 s per step and over the 2θ range of 5° to 90°. Reduced catalysts were analyzed after ex situ reduction under the same conditions used before the catalytic tests and spent catalysts were analyzed without any other treatment after reaction. The mean crystallite sizes of Cu^0 were calculated using the Scherrer equation, using the (200) plane.

The textural characteristics, such as BET specific area and pore volume (BJH method), were determined by N$_2$ adsorption–desorption at −196 °C in a Micromeritics TriStar 3000. Prior to the analysis the samples were outgassed for 24 h at 250 °C in vacuum.

The reducibility of the catalysts was analyzed by temperature-programmed reduction (TPR), carried out in a microflow reactor operating at atmospheric pressure. TPR analysis was carried out in a conventional apparatus equipped with a thermal conductivity detector (TCD). The samples (~50 mg) were firstly dehydrated at 150 °C under Argon (Ar) flow before the reduction. The samples were then cooled at room temperature. Afterwards, the heating was initiated up to 1000 °C with a rate of 10 °C min^{-1}, using a mixture of 1.8% H$_2$/Ar flowing at 30 mL min^{-1} through the sample.

The catalyst basicity was investigated by temperature programmed desorption of carbon dioxide (CO$_2$-TPD), which was performed using a mass spectrometer QMG-220 (Pfeiffer).The samples were firstly reduced by a mixture of 1.8% H$_2$/Ar up to 450 °C at a heating rate of 10 °C min^{-1} with an isothermal at 450 °C for 30 min and then cooled down to room temperature. Carbon dioxide adsorption was carried out at room temperature with 10% CO$_2$-He (30 mL min^{-1}) for 30 min, followed by purging with He for 1 h. The desorption of chemisorbed CO$_2$ was realized by heating up to 1000 °C at 20 °C min^{-1}, under flowing pure He (30 mL min^{-1}). The ratio m/z = 44 was used for quantification of carbon dioxide. Decomposition of the peaks was performed using Gaussian shaped components considering each shoulder as a peak. Agreement factors were in all cases higher than 0.99.

Copper dispersion on the catalyst was obtained following similar procedures as shown by Gervasini and Bennici [31] and López-Suárez et al. [32]. Firstly, the copper oxide was reduced by a mixture of 1.8% H$_2$/Ar from 30 to 450 °C (10 °C min^{-1}), holding the maximum temperature for 30 min and then cooled down to room temperature. Then, the selective oxidation of the copper surface to Cu$_2$O was carried out under 10% N$_2$O gas mixture (9.89% N$_2$O and balance helium) with flow of 30 mL min^{-1} at 50 °C for 1 h. Finally, the surface copper oxide (Cu$_2$O) was reduced by heating up to 1000 °C at 10 °C min^{-1}, under flowing 1.8% H$_2$/Ar (30 mL min^{-1}). The ratio m/z = 2 was used for quantification of hydrogen, with mass spectrometer QMG-220 (Pfeiffer). The dispersion is calculated as a ratio between the amount of surface copper and total copper obtained by XRF analysis (Eq. (1)).

$$\text{Dispersion } (\%) = \frac{\text{Cu}_{surface}(g)}{\text{Cu}_{total}(g)} \times 100 \qquad (1)$$