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Cu catalysts supported on CaO/MgO for glycerol conversion to lactic acid in alkaline medium employing a continuous flow reaction system

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The production of lactic acid (LA) from glycerol in alkaline medium was investigated using Cu catalysts supported on CaO, MgO and $x\text{CaO/MgO}$ ($x = 5, 10, 15$ wt%), employing a continuous flow reaction system over a period of 30 h. In addition to assessing the effect of the composition of the catalytic support, the influence of the temperature (200–260 °C), NaOH/glycerol molar ratio (0.5–1.5), hydroxide type (NaOH and KOH), as well as the influence of concentration (10 and 20 vol%) and purity of glycerol was investigated. The catalysts were prepared by a wet impregnation method and characterized by XRF, XRD, N_2 adsorption–desorption, H_2 -TPR and CO_2 -TPD. The catalytic tests showed that the use of NaOH results in higher yields to LA. Cu catalysts supported on $x\text{CaO/MgO}$ exhibited better catalytic performance than the CuCa and CuMg catalysts. The LA yield increases with the increase of the reaction temperature from 200 to 240 °C, and then decreases with a subsequent increase to 260 °C. NaOH/glycerol molar ratios greater than 1.25 are not necessary, since high yield to LA (96.9%) was obtained in the catalytic test performed using a molar ratio of 1.25. The catalysts showed excellent stability without evidence of deactivation over the evaluated period.

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1. Introduction

2-Hydroxypropanoic acid, also named lactic acid (LA), is widely used in the cosmetic industry as a moisturizer and in the textile industry as a mordant (*i.e.* a chemical that enhances the color durability). Moreover, LA is used in the dairy industry as a pH regulator, 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.¹ In addition, LA is considered a platform molecule from which valuable industrial oxygenated compounds are obtained such as: acrylic acid, 2,3-pentanedione, pyruvic acid, propanoic acid, 1,2-propanediol and acetaldehyde.²

Market studies conducted in the early 2000s pointed to a growth of 19% per year in the consumption of LA for chemical applications.³ The worldwide consumption of LA in 2005 was estimated at 130 000–150 000 tons;³ in the year 2010 the worldwide demand for LA was around of 300 000–400 000 tons.⁴ The global LA market is expected to grow from 714.2 kilotons in 2013 to 1960.1 kilotons in 2020.⁵ According to the report of Global View Research (California, USA), the production of PLA is

expected to direct the increased demand for LA in the coming years. The global LA market size was valued at 1.29 billion USD in 2016 and is expected to reach 9.8 billion USD in 2025.⁵ European demand for PLA in 2010–2012 was around of 25 000 tons per year, and could potentially reach 650 000 tons per year in 2025.⁶

The physical properties of PLA depend on the isomeric purity of LA ($\text{l}(+)$ - or $\text{D}(-)$). For example, $\text{l}(+)$ -LA with high purity gives PLA of high melting point and high crystallinity.⁷ Furthermore, pure $\text{l}(+)$ -LA can be polymerized to a high crystal polymer suitable for fiber and oriented film production and is expected to be useful in the production of crystal liquids.⁸

Currently, commercial production of LA is based on chemical synthesis or fermentation processes.^{4,9} Production by the fermentation processes has the advantage that a pure isomers ($\text{l}(+)$ - or $\text{D}(-)$ -LA) can be obtained by choosing an appropriate strain of LA bacteria,¹⁰ while chemical synthesis always results in a racemic mixture of LA.¹¹ The fermentation has a high yield (90%) into lactic acid but several problems are associated with the process, such as the high cost of culture media, due to the specific requirements of LA producing bacteria,¹² inhibition by the product,¹³ and high cost of purification process, besides being a nonecological process.¹⁴ In addition, the fermentation route may not be able to meet the growing demand for LA of the chemical industry.¹⁵

Research of new alternatives for chemical routes to produce LA has been of great interest in the last decades.¹⁶ One of the

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