



Recyclable biocatalytic composites of lipase-linked magnetic macro-/nano-particles for glycerol carbonate synthesis

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ARTICLE INFO

Article history:

Received 24 April 2012

Received in revised form 11 June 2012

Accepted 12 June 2012

Available online 19 June 2012

Keywords:

Biocatalyst

Magnetic nano-/micro-particles

Lipase

Glycerol carbonate

ABSTRACT

Lipase immobilized biocatalysts were prepared *via* enzyme binding onto functionalized surface of magnetic micro-/nano-particles. In order to achieve an efficient biocatalytic composite the immobilization parameters (*e.g.* lipase concentration, pH of the immobilization phase, activation reagent) were correlated with support morphology and type of the functional group on the support surface. The characterization of the lipase-particle composites was made using FTIR and UV–Vis techniques. The biocatalyst activity was evaluated in the transesterification reaction of glycerol with DMC (dimethyl carbonate). Under solvent-free conditions the conversion of glycerol was of 48.6% with the selectivity in glycerol carbonate (GlyC) of 85%. The biocatalyst composites were easily recycled using the magnetic properties of the support. Compared to free enzyme, recycling experiments demonstrated that the operational stability of the heterogeneous biocatalyst was improved (fifteen cycles for bio-composites vs. four cycles for free enzyme).

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1. Introduction

Glycerol carbonate (GlyC) is a rather new compound with promising high potential in the chemical industry [1]. It is included in the category of so called “green solvents” due to the low toxicity, good biodegradability and high boiling point. Up to date it has been investigated as an additive of coatings, paints and detergents as well as component of gas separation membranes [2]. Also, it is part of the technological processes of polycarbonates and polyurethanes production as monomer [3].

Nowadays, the common routes to GlyC production involve glycerol carboxylation with various compounds delivering acyl groups (*e.g.* ethylene carbonate [4], urea [1] and carbon dioxide [5]). Dimethyl carbonate (DMC) is another acyl donor for glycerol carboxylation. Scheme 1 presents the synthesis route of GlyC (4). Glycerol dicarbonate (5) and diglycerol tricarbonate (6) are secondary products. Typically, this requires large quantities of Brønsted base as catalyst (*e.g.* K_2CO_3 , $n-Bu_2Sn(OCH_3)_2$, macroporous resins or alkaline X/Y zeolite [6–8] and results in moderate yields of targeted product. In addition, the synthesis is carried out under harsh reaction conditions.

Recently, biocatalytic preparation of GlyC has been accomplished based on lipase-catalyzed glycerol and DMC reaction, thus

facilitating the synthesis under mild reaction conditions. So far, there are only few reports on this topic. The lipase from *Candida antarctica* source immobilized on resins (Novozyme 435) catalyzed the transesterification of glycerol with DMC in THF [9] or solvent-free [10] conditions. *Aspergillus niger* lipase is also able to catalyze this reaction under solvent-free conditions [11]. In fact it is already obvious that a biocatalytic synthesis occurs under green conditions.

The immobilization of the enzyme onto a solid support makes even greener the biocatalytic synthesis of GlyC. Immobilization provides a physical support for enzymes conferring additional stability against their denaturation and sometimes modulating the catalytic activity [12–14]. However, in most of the cases the design of such biocatalysts is not trivial. Generally, it involves binding the enzyme *via* simple adsorption or covalent bonds [15] to a carrier (support) with different composition and geometry (*e.g.* ion exchange resin, mesoporous silica, polypropylene hollow fiber, glass balls, cellulose membrane and magnetic beads) [16]. The main advantages of immobilization are the easy separation of the enzyme from the reaction mixture and the reusability for tens of time. These lead to a reduction of the amount of used enzyme and, indirectly, of the process cost [17]. In the particular case of lipase, the immobilization can lead to changes of the enzyme activity and stability depending on the source of the enzyme, the type of the support and the immobilization method [13,14,18,19]. The selection of the proper support and of the immobilization method is thus very important.

In recent years, magnetic supports (*i.e.* Fe_3O_4 micro-/nanospheres coated with polymeric layer(s)) have showed attractive

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