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Hybrid composites octyl-silica-methacrylate agglomerates as enzyme supports

Oscar Fernández[a,b], Isabel Díaz[a], Carlos F. Torres[b], Montserrat Tobajas[c], Víctor Tejedor[a,c], Rosa M. Blanco[a,*]

[a] Instituto de Catálisis y Petroleoquímica, CSIC, c/Marie Curie 2, 28049 Madrid, Spain
[b] Instituto de Investigación en Ciencias de la Alimentación (CIAL), CSIC-UAM, Nicolás Cabrera 9, 28049 Madrid, Spain
[c] Sección de Ingeniería Química, Universidad Autónoma de Madrid, 28049 Madrid, Spain

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ABSTRACT

The use of immobilized enzymes as catalysts may be limited by particle size which must be larger than the mesh that retains them in the reactor. Octyl-silica (OS) beads of 70 μm average size were agglomerated to obtain hybrid organic–inorganic composites with particle sizes between 100 and 200 μm. The agglomeration process has been achieved by polymerization of methacrylate from glycidyl methacrylate and ethylene dimethacrylate in the presence of silica beads and further functionalization of the composite with octyl groups.

Methacrylate content of the composite (20%) is high enough to stick OS beads, and low enough to preserve the advantages of these particles as supports. The properties of the octyl silica particles for lipase immobilization have been very closely reproduced with the octyl-silica-methacrylate (OSM) composite. Enzyme loading of 210 mg lipase per gram of support has been achieved on OSM vs 230 mg/g on OS. Also catalytic activity values are close for both catalysts, OSM-lipase remaining fully active and stable after 15 cycles in acetonitrile.

1. Introduction

Current application of immobilized lipases is of doubtless interest in fields like the syntheses of pharmaceuticals or food additives and nutraceuticals [1]. Industrial use of these biocatalysts requires optimization of catalytic activity and stability in a number of reaction cycles [2]. In this regard, the choice of a suitable support is of utmost relevance to obtain catalysts with the best properties [3–5]. Leaving aside the chemical nature, the main limiting factors are the textural and morphological features of the support and indeed the real possibilities of application for the same enzyme can vary a lot as a function of this material. The distribution of the enzyme along inner surfaces and therefore the loading capacity of the support may be a challenge especially when using materials with large particle size and/or narrow pore diameter. The diffusion of substrates and products through the porous network of the support is also highly dependent on the particle size [6] and particle size distribution [7]. Although larger particles contributes to easier handling, the diffusion of the enzyme or substrates and products through internal pores may be limited and the enzyme loading and the apparent catalytic activity can be diminished compared to the smaller ones. Particle size may become a controlling step for catalysts in reactors where they must be retained within a mesh, and it must be large enough to enable an easy design of the reaction. But it must be small enough to prevent serious mass transfer restrictions. A large pore diameter may contribute to minimize this unwished effect [8], and indeed, it has been described [3] that this effect disappears when pores are larger than 100 nm diameter.

Gross et al. [9,10] have recently established that the enzyme-support affinity may also significantly affect immobilization of lipases on supports with different bead sizes: for high affinity no effect of the particle size on the immobilization rate was observed, but the distribution of the enzyme is uneven and limited to external bark. However, with moderate affinity between enzyme and support, immobilization rates are higher on the smaller particles; in this case the enzyme distribution is homogeneous only in particles of 75 μm diameter or less. In particles over this size the enzyme can only diffuse along the external shell.

Amorphous meso-macroporous silica MS3030 has been successfully used to immobilize lipases upon grafting with octyl groups. The textural properties of the silica combine high surface area and a high average pore diameter (of 27 nm), which is almost four fold the diameter of the molecule of lipase from *Candida antarctica* B [11]. By pre-wetting this octyl-silica (OS) with ethanol the restrictions of the aqueous enzyme solution [12] to diffuse through the hydrophobic environment of pore channels efficiently

* Corresponding author. Tel.: +34 91 5854636; fax: +34 91 5854760.
E-mail address: rmblanco@icp.csic.es (R.M. Blanco).

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