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Biocatalysts based on nanozeolite-enzyme complexes: Effects of alkoxysilane surface functionalization and biofuel production using microalgae lipids feedstock

Adriano de Vasconcellos[a], Alex Henrique Miller[a], Donato A.G. Aranda[b],
José Geraldo Nery[a,*]

[a] Laboratory for Clean Energy Technology (LACET), Physics Department, São Paulo State University–UNESP, Campus de São José do Rio Preto, SP, 15054-000, Brazil
[b] Greentec Laboratory, School of Chemistry, Federal University of Rio de Janeiro, RJ, 21941-972, Brazil

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ABSTRACT

Nanozeolites with different crystallographic structures (Nano/TS1, Nano/GIS, Nano/LTA, Nano/BEA, Nano/X, and Nano-X/Ni), functionalized with (3-aminopropyl)trimethoxysilane (APTMS) and crosslinked with glutaraldehyde (GA), were studied as solid supports for *Thermomyces lanuginosus* lipase (TLL) immobilization. Physicochemical characterizations of the surface-functionalized nanozeolites and nanozeolite-enzyme complexes were performed using XRD, SEM, AFM, ATR-FTIR, and zeta potential measurements. The experimental enzymatic activity results indicated that the nanozeolitic supports functionalized with APTMS and GA immobilized larger amounts of enzymes and provided higher enzymatic activities, compared to unfunctionalized supports. Correlations were observed among the nanozeolite surface charges, the enzyme immobilization efficiencies, and the biocatalyst activities. The catalytic performance and reusability of these enzyme-nanozeolite complexes were evaluated in the ethanolysis transesterification of microalgae oil to fatty acid ethyl esters (FAEEs). TLL immobilized on the nanozeolite supports functionalized with APTMS and GA provided the most efficient biocatalysis, with FAEEs yields above 93% and stability during five reaction cycles. Lower FAEEs yields and poorer catalytic stability were found for nanozeolite-enzyme complexes prepared only by physical adsorption. The findings indicated the viability of designing highly efficient biocatalysts for biofuel production by means of chemical modulation of nanozeolite surfaces. The high biocatalyst catalytic efficiency observed in ethanolysis reactions using a lipid feedstock that does not compete with food production is an advantage that should encourage the industrial application of these biocatalysts.

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1. Introduction

The production of liquid biofuels from biomass is one of the options available to help meet the increasing energy demands caused by the life styles in industrialized countries and by the rapid economic growth of populous developing countries. This high energy demand currently mainly relies on fossil fuels, but environmental concerns and the depletion of fossil fuel resources have stimulated the search for alternative renewable fuels that are environmentally benign and sustainable. Biodiesel can play a major role in this challenge of finding a viable alternative for the replacement of the fossil fuels used in the transportation sector [1,2].

The task of searching for new sources of clean and renewable energy is not straightforward and needs to consider various factors including the economic viability of non-edible biomass sources, the development of new catalysts, and the use of low cost processing technologies [3]. First generation biodiesels are produced from biomass feedstocks consisting of food and oil crops, using conventional chemical technologies [4,5], and a large proportion (95%) of biodiesel production still relies on edible oil sources [6]. The use of edible feedstocks has raised many ethical and economic questions, due to its negative impacts on global food markets and food security [7]. Alternative biomass sources such as non-food crops [8], animal fats [9,10], and waste cooking oils [11,12] are employed in the production of second generation biodiesel, but the use of

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* Corresponding author at: Rua Cristóvão Colombo 2265, São José do Rio Preto, SP, 15054-000, Brazil.
E-mail address: nery@ibilce.unesp.br (J.G. Nery).

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Table 1
Synthesis parameters of the nanozeolite materials.

Sample	Silica Source	Aluminum or Titanium Source	Cation Type	Synthesis time (h)	Temperature (°C)	Ref.
Nano-TS1	TEOS	TBOT	TPA$^+$	24	100	[45]
Nano-GIS	TEOS	AlIso	TMA$^+$	312	100	[46]
Nano-BEA	Silica Fumed	TEA	TEA$^+$	120	140	[47]
Nano-LTA	Ludox	AlIso	TMA$^+$	24	60	[48]
Nano-X	Silica Fumed	Sodium aluminate	Na$^+$	48	60	[49]

TEOS = tetraethylorthosilicate; TBOT = tetrabutylorthotitanate; AlIso = aluminumisopropoxide; TMA$^+$ = tetramethylammonium; TEA$^+$ = tetraethylammonium, TPA$^+$ = tetrapropylammonium; Ludox = aqueoussilicasolution (Ludox HS-30, 30 wt%).

these feedstocks has drawbacks related to the processing costs in large-scale commercial operations [13,14].

The third generation of biodiesel proposes the use of microalgae as an alternative biomass feedstock [15]. This is considered by experts in the energy field as a technically feasible alternative capable of overcoming the main difficulties associated with the feedstocks employed in first and second generation biodiesel production [16].

Heterotrophic and photoautotrophic microalgae are viable candidates for biodiesel production, due to their high photosynthetic efficiency, rapid formation of large amounts of biomass, high lipid contents that can be equivalent to that of soybean, and faster large-scale growth compared to other energy crops [17,18]. In addition, some heterotrophic microalgae can be cultivated in the absence of light, using a non-photosynthetic process, while others can be produced during fermentation of a reduced carbon source [19]. For practical and economic reasons, heterotrophic microalgae have several advantages over photoautotrophic organisms, including faster biomass accumulation under controlled conditions that decrease the likelihood of common problems affecting large-scale microalgae cultivation, such as variations in light intensity and the available carbon source [20]. Another advantage of heterotrophic microalgae is that genetically modified strains are capable of producing lipid yields higher than 80%, while photoautotrophic cultures of native algae yield only 20–50% of lipids [21,22]. Although heterotrophic microalgae are incapable of capturing CO_2 emissions, the overall heterotrophic process is cyclic, because the initial organic substrates are produced by photosynthetic plants [23].

There are four different catalytic routes in triacylglycerides transesterification reactions: (i) base-catalyzed processes, (ii) acid-catalyzed processes, (iii) enzyme-catalyzed processes, and (iv) use of supercritical conditions. The advantages and disadvantages of these different routes have been discussed in several review papers [24,25]. Currently, industrial biodiesel production mainly employs the homogeneous base-catalyzed process, using sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium methoxide ($NaOCH_3$), or sodium ethoxide ($NaOCH_2CH_3$) as the catalyst [26]. However, there are several drawbacks associated with this process, especially when low quality feedstocks with high contents of water and free fatty acids (FFAs) are used. In this case, the use of base catalysts increases the energy cost and the likelihood of soap and emulsion formation, which can lead to the generation of large amounts of wastewater during the processes of cleaning and separation of the glycerol (byproduct) and biodiesel (product) [26,27]. Hence, in order to overcome these drawbacks, alternative and more sustainable catalytic routes for biodiesel production are being sought.

The use of lipases as catalysts in biodiesel production is an attractive option, due to their higher specificity for the transesterification of triacylglycerides to fatty acid methyl esters (FAMEs) or fatty acid ethyl esters (FAEEs), compared to the conventional chemical catalysts employed in industrial biodiesel production. Enzymes exhibit greater selectivity and higher catalytic activity in transesterification reactions under mild operational conditions (25–60 °C), compared to homogeneous basic catalysts [28]. In addition, lipases can catalyze the transesterification of raw materials that contain high levels of FAAs and water, with decreased risk of soap and emulsion formation [28]. However, despite all the advantages of the enzymatic process, there are important issues that hinder its use in industrial scale processes for biodiesel production. These include: a) the high costs of enzymes, b) problems in separating the product from the reaction medium, c) difficulty in recovering and reusing enzymes, and d) deactivation of the active sites of enzymes by the substrates (short-chain alcohols such as methanol and ethanol) [29] and by the glycerol byproduct [30]. One way to overcome these obstacles is to immobilize the enzymes on solid carriers [31,32]. The selection of suitable solid supports needs to consider aspects including the overall enzymatic activity of the immobilized enzyme, the cost of the immobilization procedure, identification of the best operating conditions in order to avoid enzyme inactivation, and the ability to regenerate and reuse the enzyme-support complex [33].

Zeolites [34,35] and enzymes [36,37] are capable of catalyzing the transesterification of triacylglycerides into FAEEs or FAMEs. These different classes of materials have inherent characteristics that determine the yield of the desired final product under different experimental conditions [38]. Nonetheless, the combination of these different classes of catalysts can result in zeolite-enzyme complexes that offer outstanding catalytic performance [38].

Nanozeolites are hydrophobic supports with high external surface areas, whose high dispersibility in both aqueous solutions and organic media allows better access of the enzymes to the substrate. This also acts to reduce the adsorption of glycerol molecules onto the biocatalyst microenvironment, and electrostatic and hydrophobic interactions within the zeolite-enzyme system contribute to its stability. Several mechanisms have been proposed for the immobilization of lipase on zeolitic supports: a) electrostatic and acid-base linkages [38], b) formation of strong enzyme-support ionic interactions [39–41], and c) covalent bonding of lipases to the zeolite surface by functionalization of the zeolite surface with alkoxysilane, followed by crosslinking with glutaraldehyde [42]. Among the available immobilization methods, covalent attachment is the most effective in terms of enhancing uptake of the enzyme and its retention on the solid support. The covalent bonding of enzymes to solid matrices can improve the feasibility of using enzymes in industrial applications, considering aspects such as denaturation of the enzyme by heat or organic solvents, pH control of the medium, stability during storage, and reduction of leaching [43].

Studies of biocatalysts based on nanozeolite-lipase complexes for the purpose of biodiesel production have not been widely reported in the literature. Transesterification of palm oil to FAEEs using lipases of *Thermomyces lanuginosus* (TLL) and *Rhizomucor miehei* (RML) immobilized on nanosized NaX zeolite (FAU) ion-exchanged with different transition metals has shown positive results. This has encouraged further synthetic and catalytic studies of enzyme-nanozeolite complexes with supports derived from different zeolite structures, and their application in the catalytic conversion of different non-edible biomasses to biodiesel [44]. Nev-

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