

Transesterification of soybean oil using ethanol and mesoporous silica catalyst

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ABSTRACT

Mesoporous silica catalyst was evaluated in the ethanolysis of soybean oil. Ethanol can be environmentally advantageous over methanol (more frequently used as reagent in biodiesel production) because it can be obtained from renewable sources whilst methanol is usually derived from mineral sources. A silica molecular sieve containing lanthanum oxide as active phase (La₅₀SBA-15) was obtained by isomorphous substitution into the SBA-15 network using Pluronic (P123) dissolved in aqueous HCl solution with tetraethyl orthosilicate and a given amount of hydrated lanthanum chloride (Si:La = 50) at 333 K. The reaction was performed using the molar ratio ethanol:soybean oil of 20:1 at inert atmosphere (N₂) at 343 K with 1wt% of catalyst mass relative to total oil mass added to the reaction mixture. The reaction was evaluated for ethyl ester conversion after 6 h. The ethyl esters content was measured using low frequency ¹H NMR spectroscopy (60 MHz). The La₅₀SBA-15 heterogeneous catalyst presented conversion of soybean oil in ethyl esters as high as 80% after reaction time of 6 h., comparing well with previous reports for methanolysis of soybean oil. Moreover, lixiviation of the active phase was not observed, thus excluding the contribution of the homogeneous catalysis to the studied transesterification process.

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1. Introduction

Biodiesel can be defined as a fuel composed of monoalkyl esters of long chain fatty acids derived from vegetable oils or animal fats, used in compression ignition engines. The most common process for biodiesel production consists in a transesterification reaction in which a triglycerides source (vegetable oil or animal fat) reacts to a short chain alcohol (usually methanol) in catalyst presence [1–3]. Since ethanol is largely obtained in Brazil from renewable sources (mostly sugarcane) it might be advantageous to replace methanol in the transesterification reaction for biodiesel production [4].

The transesterification reaction may be catalyzed by acids, bases or enzymes [5]. Industrially, basic homogeneous catalysts such as potassium hydroxide and sodium hydroxide are often used in biodiesel production, because they display high reactivity, low cost and mild reaction conditions. However, as usually observed in homogeneous catalyst systems, they require downstream separation of the catalyst and byproducts, thus increasing the process complexity and cost [6–9]. Therefore process development for biodiesel production from heterogeneous catalysts has been largely

studied in recent years [5,6,10–12]. Albuquerque et al. [11] studied calcium oxide catalytic properties supported on several SBA-15 mesoporous silica in transesterification of castor and sunflower oil with methanol. Yan et al. [6] studied the use of calcium oxide modified with lanthanum in the transesterification reaction with methanol. The mixture CaO–La₂O₃ showed higher catalytic activity than when using pure calcium oxide or pure lanthanum oxide. Yan et al. [7] also studied the use of ZnO–La₂O₃ as heterogeneous catalyst in the transesterification of unrefined or waste oil with methanol with noticeable strong interaction between zinc and lanthanum species. The catalyst sample with a 3:1 zinc lanthanum molar ratio displayed higher activity compared to pure metal oxides. Sun et al. [13] studied the properties of ZrO₂ impregnated with La₂O₃ as a catalyst in sunflower oil transesterification with methanol. The best methyl ester conversion was found when using a catalyst concentration of 21 wt.% La₂O₃ on ZrO₂.

However, a key aspect in the search of heterogeneous catalysts for biodiesel production is to rule out a possible contribution of the homogeneous catalysis. Most studies concerning the use of solid catalysts for biodiesel production lack information about the lixiviation of the catalyst in the reaction medium, which could demand additional steps to remove metal ions from the biodiesel [11,14,15].

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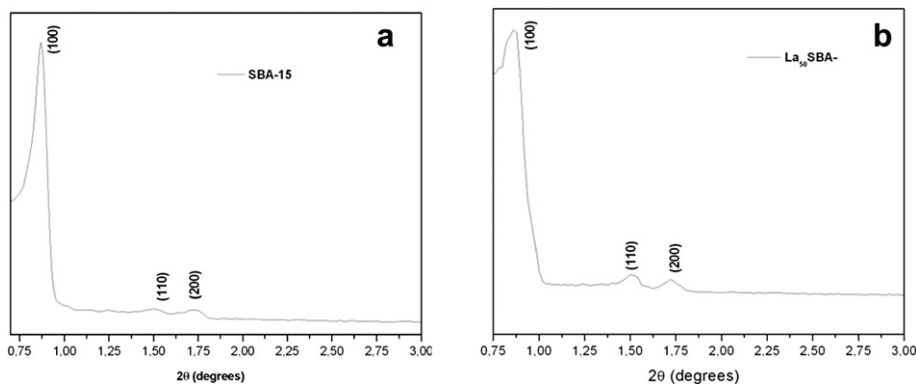


Fig. 1. X-Ray Diffractograms: (a) SBA-15; (b) La₅₀SBA-15.

This study intends to investigate the use of La₅₀SBA-15 in soybean oil transesterification using ethanol. The La₅₀SBA-15 has lanthanum oxide as active phase inserted into SBA-15 framework by isomorphous substitution.

2. Materials and methods

2.1. Catalyst preparation and characterization

The SBA-15 modified with lanthanum was synthesized by hydrothermal method using 4.0 g of Pluronic P123 (BASF Co.), 10.3 mL of HCl PA (VETEC, Brazil) and distilled water were mixed until dissolution of the Pluronic P123. Thereafter 10.3 mL of tetraethyl orthosilicate (Sigma–Aldrich) and a given amount of previously dissolved hydrated lanthanum chloride (VETEC, Brazil) were added (Si/La = 50), and the mixture stirred for 22 h at a temperature of 333 K. The resulting gel was placed into a Teflon container and submitted to hydrothermal treatment at a temperature of 373 K for 48 h. The solid was then filtered at room temperature, washed with a solution of HCl in ethanol 2 wt%, dried at 333 K for 1 h, and finally the solid was calcined at 823 K (heating rate = 10 K/min). The samples, designated as La₅₀SBA-15 (where 50 refers to the Si/La molar ratio) were characterized through X-ray diffraction (DRX), N₂ adsorption and desorption isotherms at 77 K, and scanning electron microscopy (SEM). Further details may be found in Quintella [17].

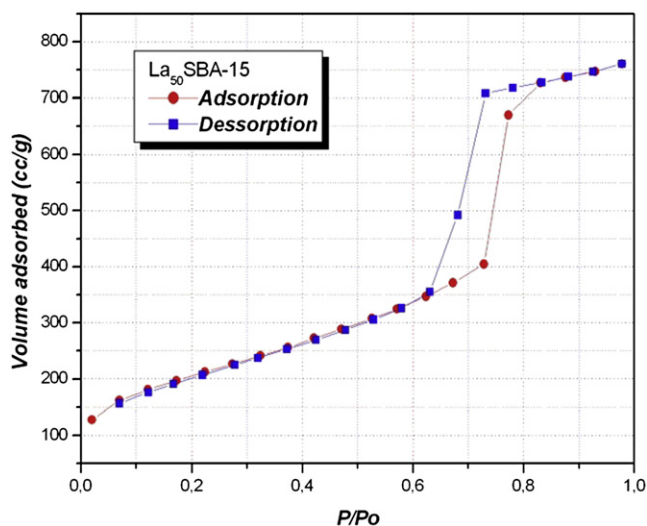


Fig. 2. N₂ adsorption and desorption isotherms of La₅₀SBA-15.

2.2. Reaction

The reaction experimental set-up consisted of a 100 mL round-bottomed flask with four outlets. A thermometer was attached to the first outlet for temperature control. The reflux condenser was inserted into the second one to minimize the ethanol loss through evaporation and the third received nitrogen flow providing inert atmosphere. The fourth outlet was used to introduce the catalyst and remove aliquots in order to monitor the reaction.

Initially the catalyst was activated at 1073 K, under inert atmosphere, during 1 h in order to convert carbonates eventually formed by atmosphere contact into oxides since carbonates do not show catalytic activity [10]. In the transesterification reactor, 30.3 g of commercial soybean oil (Liza, Brazil) were added to 99.6% ethanol (J.T.Baker, Mexico). The molar ratio of ethanol and soybean oil used was 20:1. The reaction was carried out at inert atmosphere using 1000 rpm agitation. When the oil and ethanol mixture reached the desired temperature, 343 K, the catalyst was inserted to the reaction mixture using a catalyst/oil mass ratio of 0.01. Samples of 5 mL were taken after 6 h, filtered under vacuum to extract the catalyst from the reaction mixture. To improve the phase separation in the reaction mixture, dichloromethane (Cromolina, Brazil) was added, and this mixture was agitated and set aside to develop two phases: the non-polar phase containing dichloromethane, mono-, di-, and triglycerides and ethyl esters (and traces of ethanol and glycerol) and the polar phase containing water, glycerol and ethanol (and traces of esters). The dichloromethane was then vaporized from the ester phase at 373 K.

On the other hand, the presence of catalyst in solution might imply on possible homogeneous contribution to the reaction, which requires additional steps of washing and purification of the biodiesel fraction [16]. For this reason, an experimental procedure to evaluate lixiviation was employed. It consisted in putting in contact the catalyst with ethanol under the same experimental conditions as used in the transesterification process, except for the presence of the oil. After 6 h of reaction, the catalyst was quickly removed by filtration, and ethanol was mixed with the necessary volume of soybean oil, and maintained at 343 K for 6 h, under inert atmosphere. If catalysts were lixiviated, some conversion would be observed due to a homogeneous contribution in the system.

Table 1
Textural characterization of synthesized samples.

Sample	a_0 (nm)	D_p (nm)	V_p (cm ³ g ⁻¹)	S_{BET} (m ² g ⁻¹)
SBA-15	11.88	4.33	0.95	931.3
La ₅₀ SBA-15	11.88	7.29	1.09	735.2

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