Applied Catalysis A: General 450 (2013) 114–119

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Investigation of biodiesel production by HUSY and Ce/HUSY zeolites: Influence of structural and acidity parameters

Luciana D. Borges[a], Nayara N. Moura[b], Andréia A. Costa[b], Patrícia R.S. Braga[b], José A. Dias[a], Sílvia C.L. Dias[a], Julio L. de Macedo[a,*], Grace F. Ghesti[a,*]

[a] Universidade de Brasília, Campus Darcy Ribeiro, Instituto de Química, Laboratório de Catálise, Caixa Postal 4478, Brasília, DF 70904-970, Brazil
[b] Universidade de Brasília, Faculdade UnB – Gama, Engenharia de Energia, Brasília, DF 72405-610, Brazil

ARTICLE INFO

Article history:
Received 3 August 2012
Received in revised form
25 September 2012
Accepted 6 October 2012
Available online 9 November 2012

Keywords:
Biodiesel
Transesterification
USY zeolite
Cerium
Catalytic cycles

ABSTRACT

In this work, activities of HUSY and Ce/HUSY zeolites were studied in transesterification cycles of soybean oil and ethanol to produce biodiesel. The characterization of the materials was performed by FT-IR, XRD, BET method and pyridine adsorption followed by thermal analyses. TG/DTG results indicated a decrease of acid sites for both samples after each reaction cycle. However, Ce/HUSY zeolite showed a superior stabilization of acidic sites after three catalytic cycles and intermediary activation procedures. Biodiesel production exhibited high conversion levels (>96%) for both zeolites in all transesterification cycles. Surface area and pore volume measurements evidenced that cerium incorporation reduced the number of acid sites by interacting with OH groups in the micropore and external area of the zeolitic surface. This interaction resulted in an acid and structural stability, which provided a better activity (99%) than HUSY (96%). The higher conversion values obtained by zeolites showed a final product with a different distribution when compared with the traditional transesterification process. The identification of free fatty acids, diethyl and glycerol ethers in the final products and the reduction of unsaturated compounds indicated that parallel reactions also occurred in the studied systems. Nonetheless, the biofuel produced showed high ester content and did not present changes in its calorific power.

1. Introduction

Environmental concerns and restrictive legislations have lead researches to develop clean technologies for energy production. Biodiesel, a biodegradable fuel and renewable form of energy, consists of mono alkyl esters of fatty acids that have been used as an alternative fuel in several countries [1–5].

The most widely used method to produced biodiesel is the transesterification of triacylglycerides using a homogeneous or heterogeneous catalyst [6]. Alkaline and acidic compounds are the two categories of catalysts used for the production of commercial available biodiesel [7,8]. Due to its low cost and high rate conversion at low temperature, homogeneous alkaline catalysts are commonly used in the industry for this purpose [9]. However, these catalysts cannot be recycled or regenerated and require a low content of free fatty acids (<0.5 wt.%) in the feedstock [10] to avoid soap formation. Besides, the glycerin obtained has a certain degree of impurity and the costs for its purification are very expensive [11–13].

Brønsted acid catalysts can be applied in both transesterification and esterification reactions to obtain biodiesel [4–8] and have been used as an alternative to alkaline catalysts, especially in cheap feedstocks (e.g., unrefined oil, soapstock and waste cooking oil) [10].

Based on the above premises, the development of new heterogeneous acid catalysts is an appropriate solution to overcome the problems associated with homogeneous catalysis. As a consequence, the products do not contain impurities from the catalyst and the final cost of separation is reduced. These materials are easily regenerated, reused and environmental friendly [5,7]. Additionally, the degree of glycerin purity obtained is about 98%, which provides a higher market value for this byproduct [12–14].

Among several heterogeneous acid catalysts, zeolites have been used for the production of biofuels from renewable sources [13,15–20], e.g., the cracking of biomass to generate products in the diesel or gasoline fraction, using large (Y and β) and medium to small (ZSM-5) pore zeolites, respectively [20].

The main objective of this study was to investigate the activity of zeolitic catalysts (HUSY and Ce/HUSY) in transesterification cycles of soybean oil with ethanol and to evaluate their properties after each cycle. The materials were characterized by XRD, XRF/EDX, surface area by BET, and gas adsorption of pyridine followed by TG/DTG and FT-IR measurements.

* Corresponding authors. Tel.: +55 61 9277 2610; fax: +55 61 3368 6901.
E-mail addresses: julio@unb.br (J.L. de Macedo), grace@unb.br (G.F. Ghesti).

0926-860X/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apcata.2012.10.009