Applied Catalysis A: General 425–426 (2012) 199–204

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

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

Levulinic acid esterification with ethanol to ethyl levulinate production over solid acid catalysts

D.R. Fernandes[a], A.S. Rocha[a], E.F. Mai[a], Claudio J.A. Mota[b], V. Teixeira da Silva[a,*]

[a] Universidade Federal do Rio de Janeiro, NUCAT – Programa de Engenharia Química – COPPE, P.O. Box 68502, 21941-914, RJ, Rio de Janeiro, Brazil
[b] Universidade Federal do Rio de Janeiro, Instituto de Química, Av. Athos da Silveira Ramos 149, CT Bloco A, 21941-909, Rio de Janeiro, Brazil – INCT de Energia e Ambiente, UFRJ, 21941-909, RJ, Brazil

ARTICLE INFO

Article history:
Received 21 January 2012
Received in revised form 10 March 2012
Accepted 13 March 2012
Available online 23 March 2012

Keywords:
Levulinic acid
Ethyl levulinate
Esterification
Acid solids
Sulfated stannia
Bio-ethanol

ABSTRACT

Levulinic acid is considered as a versatile building block because it can be used for the synthesis of several organic chemicals. In particular, its esterification with ethanol produces ethyl levulinate that can be used as diesel miscible biofuel (DMB), preventing global warming by decreasing atmospheric CO_2 generated from the consumption of fossil fuels. This article explores the use of two groups of solid acid catalysts (sulfated oxides and zeolites with different pore structures) in the esterification of levulinc acid with ethanol aiming for ethyl levulinate production. It was found that while there is a correlation between the number of acidic sites and activity for the sulfated oxides, the same is not true for the studied zeolites where the pore channels play a more important role. Among the catalysts tested, Amberlyst-15 and sulfated SnO_2 showed a remarkable high yield of ethyl levulinate that was probably due to the strong acidity provided by SO_3H functional groups and SO_4 species, respectively.

1. Introduction

Conversion of biomass and its derivatives has received a great deal of attention in the last years due to the possibility of becoming an alternative source for the sustainable production of chemicals and fuels [1–8]. Levulinic acid can be produced by the acid hydrolysis of cellulose and is a molecule containing two functional groups, a ketone and a carboxylic acid, making it a versatile building block for the synthesis of several organic chemicals such as levulinate esters, γ-valerolactone, α-angelica lactone, acrylic acid and 1,4-pentanediol [9,10].

Esters of levulinic acid are important compounds that are used, amongst others, in the flavoring industry and as solvents and plasticizers. In particular, ethyl levulinate is quite attractive because this ester can be used up to 5 wt.% as a diesel miscible biofuel (DMB) directly in regular diesel car engines. Since levulinic acid can be easily obtained from biomass [11], its esterification with bio-ethanol could be a very attractive green process for ethyl levulinate production.

Esterification reactions are usually carried out in liquid-phase using mineral acids such as H_2SO_4, H_3PO_4 or HCl [12–15], but substitution of homogeneous by heterogeneous catalysts is highly desirable because solids are easier to separate and there is no need for neutralization, can be used several times, and are less corrosive than mineral acids.

Reaction of levulinic acid with primary alcohols, such as ethanol (Scheme 1), occurs even at room temperature, but the reaction is very slow and needs to be accelerated either by using high temperature or by using a catalyst to achieve the equilibrium conversion in a reasonable period of time [12,16–18].

Various solid acids have been used for several esterification reactions but to the best our knowledge only recently for the levulinic acid esterification with bio-ethanol [19].

The main objective of this work was to evaluate and compare the activities of different zeolites (HUSY, HBEA, HMOR, HZSM-5, HMCM-22) and sulfated oxides (SnO_2, ZrO_2, Nb_2O_5, TiO_2) to that presented by a commercial sulfonic resin (Amberlyst-15) in the esterification of levulinic acid with bio-ethanol.

2. Experimental

2.1. Catalysts

H-form zeolite materials (HZSM-5, HBEA, and HUSY) were supplied from Zeolyst, whereas HMOR was purchased from Tricat. Amberlyst-15, an ion-exchange sulfonic resin, was supplied from Rohm and Haas.

* Corresponding author. Tel.: +55 21 2562 8344; fax: +55 21 2562 8300.
E-mail address: victor.teixeira@peq.coppe.ufrj.br (V. Teixeira da Silva).

0926-860X/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcata.2012.03.020