Chemical Engineering Journal 215–216 (2013) 491–499

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

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

Fish bone derived natural hydroxyapatite-supported copper acid catalyst: Taguchi optimization of semibatch oleic acid esterification

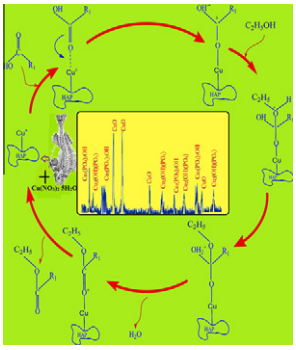
R. Chakraborty *, D. RoyChowdhury

Department of Chemical Engineering, Jadavpur University, Kolkata 700 032, India

HIGHLIGHTS

- Natural hydroxyapatite (NHAp) was derived from fish (*Lates calcarifer*) bone.
- NHAp supported efficient, cost-effective, reusable copper Lewis acid catalyst.
- Catalyst preparation through Tungsten–halogen-irradiation-assisted freeze-drying.
- Optimization of semibatch ethyl oleate synthesis through Taguchi robust design.
- Enhanced oleic acid conversion by in situ water removal employing adsorbent.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 20 August 2012
Received in revised form 9 November 2012
Accepted 14 November 2012
Available online 23 November 2012

Keywords:
Fish bone-natural HAp
Tungsten–halogen-irradiation-assisted freeze-drying
Cu–natural HAp catalyst
Oleic acid esterification
Taguchi optimization

ABSTRACT

Natural hydroxyapatite (NHAp) derived from waste fish (*Lates calcarifer*) bone has been effectively utilized as a support for preparation of low-cost, recyclable, heterogeneous copper acid catalyst. The novel catalyst has been prepared through wet-impregnation method involving tungsten–halogen-irradiation assisted freeze-drying. The catalyst was characterized through TGA, SEM, XRD, BET–BJH and FTIR analyses. The catalyst possessed 16.78 m^2/g specific surface area, 0.0313 cc/g pore volume and 33.14 nm modal pore size with an acidity of 11.22 mmol KOH/g catalyst. The developed acid catalyst demonstrated excellent efficacy in the semibatch esterification of oleic acid with ethanol. The Taguchi robust design method (L_9 orthogonal array) was applied to optimize process parameters governing oleic acid conversion. The maximum oleic acid conversion over a span of 1 h was 91.86% corresponding to the parametric values viz. 90 °C freeze-drying temperature, 1.0 weight ratio of copper nitrate to NHAp, 0.8 mL/min ethanol flow rate and 1000 rpm stirrer speed. Moreover, in situ water removal within the reactor through use of silica-gel desiccators could significantly enhance oleic acid conversion. The innovative Cu–NHAp catalyst demonstrated excellent reusability and regeneration characteristics. Thus, the article explores an innovative and environmentally-benign utilization avenue of waste fish bone as a promising heterogeneous catalyst support.

1. Introduction

Fatty acid esters generated through reversible esterification reactions form an industrially important class of substances [1]. Ethyl oleate derived from ethanol and oleic acid, can be used as industrial solvents for pharmaceutical manipulations, as lubricant or plasticizer, water resisting agent and hydraulic fluids [2]. Due to its excellent properties, synthesis of ethyl oleate had been studied by many researchers employing different heterogeneous catalyst viz. modified ZnO Nanoparticles [3], 12-tungstophosphoric acid supported on zirconia [4]. Among the possible sources of

* Corresponding author. Tel./fax: +91 3324146378.
E-mail address: rajat_chakraborty25@yahoo.com (R. Chakraborty).

1385-8947/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cej.2012.11.064