



Optimization of biological-hydroxyapatite supported iron catalyzed methyl oleate synthesis using response surface methodology

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ABSTRACT

Innovative biological-hydroxyapatite (BHAp) derived from *Catla catla* (abundantly aqua-cultured freshwater species in South Asia) bone was employed to prepare cost-effective, reusable supported iron solid acid catalyst using $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ through wet impregnation method employing infrared (IR) irradiation assisted freeze-drying protocol. The catalytic effectiveness was assessed and optimized through response surface methodology (RSM) in synthesis of methyl oleate through esterification of oleic acid with methanol. Catalyst characterization involved TGA, FESEM, EDX, XRD, BET–BJH and FTIR analyses. The catalyst that rendered optimal performance possessed $14.9 \text{ m}^2/\text{g}$ specific surface area, $0.0335 \text{ cm}^3/\text{g}$ pore volume and 33.13 nm modal pore size with an acidity of $10.336 \text{ mmol KOH/g}$ catalyst. Esterification attained a maximum 93.0% conversion at 70°C freeze-drying temperature, 1.85 weight ratio of ferric sulphate to BHAp and 2.0 wt.% catalyst concentration within 60 min batch time. Application of recyclable solid desiccant during esterification could further significantly augment methyl oleate yield at the derived optimal conditions. The novel catalyst exhibited appreciable reusability and rejuvenation attributes. The present research demonstrates successful application of *C. catla* bone as a potential support for economical preparation of solid iron acid catalyst, creating an innovative avenue for recycling of this municipal solid waste.

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1. Introduction

Heterogeneous catalysis is imperative in the field of chemical technology owing to ease of catalyst recovery and subsequent reusability [1,2]. Over recent past, development of highly effective and reusable heterogeneous acid catalyst for esterification of oleic acid with monohydric alcohol viz. methanol attracted the attention of the researcher across the globe as methyl oleate can be used as blending stock for biodiesel [3]. Biodiesel production through esterification of oleic acid with methanol using various heterogeneous catalysts viz. cation exchange resin [4], sulphated zirconia [5] and pure or sulphated lanthanum oxide (SLO), pure HZSM-5 and SLO/HZSM-5 [6] have been reported in recent past.

Hydroxyapatite (HAp) has been found useful as a catalyst support, because of its unique properties like structural stability, ionic substitution ability, acid–base properties and adsorption capacity [7]. Several works had been conducted using HAp as a support for heterogeneous catalyst viz. Knoevenagel reaction [8], Friedel–Crafts alkylation [9] and Michael's addition [10]. HAp impregnated Ruthenium [11] and Tin [12] catalysts were

employed for complete hydrogenation of quinoline and transformation of trioses in alcohols to yield alkyl lactates, respectively. More recently, reports were made on reusable Fe-HAp catalyst for photo catalytic application [13] and for oxidative dehydrogenation of propane [14]. Magnetite (Fe_3O_4) had been successfully demonstrated as an excellent recyclable Lewis acid catalyst for the dehydrogenation of ethylbenzene to styrene [15] and in the reactions of primary alkylamines, heterocumulenes, and isatoic anhydride [16]. Nevertheless, all the preceding research works employed reagent-grade chemicals for preparation of HAp as a catalyst support. To the best of our knowledge, preparation of reusable $\text{Fe}_3\text{O}_4/\text{Ca-HAp}$ solid acid catalyst employing waste fish bone derived cost-effective biological-HAp has not been reported previously.

Usages of fish bone for preparation of HAp as a coating material for 316 L SS surface [17] and for elimination of heavy metals [18] had been accounted. In recent times, calcined animal bone was utilized for biosorption of safranin as cationic dye from aqueous solutions [19]. Of late, we have reported for the first time, the application of fish (*Lates calcarifer*) bone for development of HAp supported Cu acid catalyst [20]. Conventional freeze-drying was advantageously applied for Cobalt impregnated HAp catalyst [21]. In spite of salient advantages of freeze-drying for catalyst preparation, scanty information is available in scientific database on HAp supported Fe catalyst.

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Nomenclature

A	concentration of oleic acid
$A_{\text{Oleic Acid}}$	acid value of oleic acid = 200
C_{OA}	oleic acid conversion, %
M	normality of potassium hydroxide
V	volume of potassium hydroxide consumed from burette, mL
m	weight of ester phase, g
j_1	coded form for freeze-drying temperature
j_2	coded form for Ferric sulphate to BHAp wt ratio
j_3	coded form for catalyst concentration.
J_C	catalyst concentration, wt.% of oleic acid
J_{FDT}	freeze drying temperature, °C
J_{FL}	ferric sulphate to BHAp weight ratio

The response surface methodology (RSM) optimizes process response (dependent variable) corresponding to different process independent variables [22]. Several authors have followed this technique for finding optimal process conditions with low-cost catalyst [23], regeneration of activated carbon [24], continuous biosynthesis of biodiesel from waste cooking oil [25] and for water-gas shift reaction using Cu–Zn–Fe composite-oxide catalysts [26].

The objective of the present work is to prepare highly efficient and cost-effective biological-HAp (BHAp) supported iron catalyst (Fe-BHAp), wherein BHAp has been economically derived from waste Catla fish (*Catla catla*) bone. This fish is an important and abundantly aqua-cultured freshwater species in South Asia. The novel iron catalyst has been prepared using $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ through wet impregnation method incorporating the application of infrared (IR) irradiation supported freeze-drying operation. The characterization of developed catalyst has been performed through TGA, XRD, BET–BJH, FTIR, FESEM and EDX analyses. The catalytic activity has been demonstrated through esterification of oleic acid with methanol for methyl oleate (MO) production. Statistical multivariate correlation between oleic acid conversion and process factors viz. weight ratio of $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ to BHAp, catalyst concentration and freeze-drying temperature has been formulated and optimal result has been evaluated by RSM through face centred central composite design (FCCD). Effect of solid desiccant (silica gel) usage on methyl oleate formation has also been assessed.

2. Methods

2.1. Materials

Catla Fish (*C. catla*) bone was stockpiled from local fish-filleting market. The chemicals viz. 25% aqueous ammonia solution, KOH, methanol (>99% purity), silica gel (water adsorbent) and oleic acid were purchased from Merck; and $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ was procured from Loba Chemie, India.

2.2. Catalyst preparation

C. catla bone, a municipal solid waste (MSW), was pre-treated through repeated washing with hot distilled water to eliminate the adhering organic matters and subsequently trampled into paste form employing a laboratory grinder to obtain the biological hydroxyapatite (BHAp). The BHAp was next put in a 1 L three-neck glass flask equipped with two reflux condensers and centrally

mounted mechanical stirrer. In a representative Fe 1.85 catalyst preparation procedure a measured quantity of the active metal precursor viz. 37 g $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ was dissolved in 92.5 mL water; subsequently, the prepared solution was drop-wise added to 50 g BHAp kept in the above-mentioned glass flask as per wet impregnation method [27] under vigorous mixing for 30 min. Then the sample pH was adjusted to 10 by using 25% aqueous ammonia in order to form a dark-brown precipitate; subsequently, mechanically stirred for 2 h at 700 rpm and 60 °C. Afterwards, the sample was ripened for 24 h and eventually, vacuum filtration was performed to remove mother liquor to obtain the sticky precipitate mass (SPM) which was subsequently freeze-dried using infrared (IR) irradiation (80 W) at 70 °C for 2 h. The freeze-dried solid was finally subjected to calcination at 700 °C for 4 h to develop catalyst. Identical procedure was applied for making catalysts with different ferric sulphate to BHAp weight ratio in order to analyze the effects of ferric sulphate loading on the properties of catalyst. Thus, according to the five weight ratio of $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ to BHAp, i.e. 0.5:1, 1.25:1, 1.85:1 and 2:1 the catalysts are here after designated as Fe 0.5, Fe 1.25, Fe 1.85 and Fe 2.0, respectively.

2.3. Catalyst characterization

To evaluate the effect of calcination temperature on SPM, thermo-gravimetric analysis (TGA) of representative SPM was performed with Perkin-Elmer TGA analyzer (Pyris Diamond TG/DTA) in a platinum crucible, under nitrogen atmosphere (150 mL/min) from 30 °C to 800 °C with an increasing temperature rate of 12 °C/min. The mass of the sample used was 4.794 mg approximately using alpha alumina as reference powder. Identical protocol was adopted for TGA of BHAp.

The specific surface area of the generated catalyst sample was measured by BET methods (Quantachrome make NOVA 4000e). X-ray diffraction (XRD) patterns of the prepared catalyst obtained by calcination at 700 °C were analyzed (Rigaku Miniflex Co., Japan) using $\text{Cu K}\alpha$ source outfitted with an Inel CPS 120 hemispherical detector. The analysis was performed at 2θ ranging from 20° to 80° at a scanning speed of 1 min⁻¹. The infrared spectra of the catalyst was analyzed by FTIR-Shimadzu (alpha) from 4000 cm⁻¹ to 400 cm⁻¹ while the morphology was studied by a field Emission Scanning Electron Microscope (FESEM) at 10 kV (JEOL Ltd., Japan, model JSM 6700F). The elemental composition of developed catalyst was analyzed by Energy dispersive X-ray (EDX) analyzer. The catalyst samples developed by varying freeze-drying temperature were tested before and after calcination for acidity [28].

2.4. Experimental design

The efficacy of the developed catalyst was tested in the esterification of oleic acid with methanol deploying the following three process factors: i.e. freeze-drying temperature, weight ratio of ferric sulphate to BHAp and catalyst concentration (Table 1). The experiments were programmed as per FCCD layout, and conversion of oleic acid was selected as the response variable (Design

Table 1

Experimental ranges and levels of the factors (process variable) for response surface study.

Factors	Name	Units	-1 level	0 level	+1 level
J_{FDT}	Freeze drying temperature	°C	70	80	90
J_{FL}	Ferric sulphate to BHAp wt. ratio	-	0.5	1.25	2.0
J_C	Catalyst concentration	wt.% of oleic acid	2	3	4

-1 (low level value), $j_1 = \frac{J_{\text{FDT}} - 80}{10}$, +1 (high level value), $j_2 = \frac{J_{\text{FL}} - 2}{0.75}$, 0 (centre points), $j_3 = \frac{J_C - 4}{1}$.

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