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Al grafted natural hydroxyapatite for neem oil transesterification: Kinetic study at optimal point

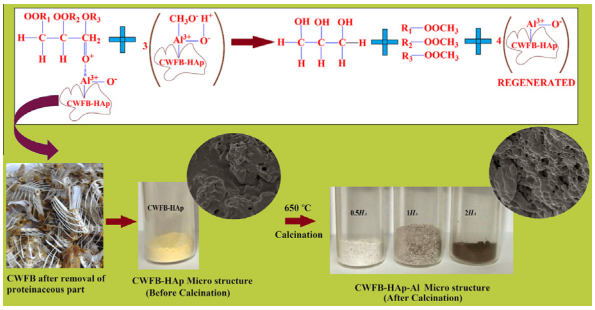
Himadri Sahu, Kaustubha Mohanty *

Department of Chemical Engineering, Indian Institute of Technology Guwahati, Guwahati 781039, India

HIGHLIGHTS

- Waste fishbone derived hydroxyapatite was used to prepare heterogeneous catalyst.
- Al was doped on to the catalyst to increase its surface properties.
- Doped catalyst resulted in higher surface area and was more thermally stable.
- RSM was used to optimize the response during transesterification of neem oil.
- Developed catalyst showed good reusability.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, Al metal ions were doped on natural hydroxyapatite by wet chemical impregnation route. The hydroxyapatite was obtained from waste cooked fish bones after proper treatment. The developed catalyst was characterized. From BET analysis it was found that the surface area and pore volume has increased up to 157.96 $m^2\,g^{-1}$ and 0.8062 $mL\,g^{-1}$ after Al doping followed by calcination. The FE-SEM micrographs showed the homogenous porous structure distribution on the surface of the Al doped catalyst. From TGA analysis, it was found that the catalyst was stable up to 1000 °C. A comparison of the developed catalyst with other catalysts reported in literature confirmed the superiority of this catalyst. Doping of Al ion and calcination played a significant role during transesterification of neem (*Azadirachta indica*) oil which was clearly envisaged. The kinetics of transesterification was thoroughly studied at optimal condition, which was found out using response surface methodology. The physical properties of the transesterified product were calculated by following the usual ASTM protocols. The catalyst reusability was also studied.

1. Introduction

Heterogeneous catalysts have the prospective to beat several of the barriers that impede the catalytic performance of homogeneous catalysts [1]. Heterogeneous catalysts are mostly solid and can be prepared from various materials such as industrial squanders (e.g. red mud, aluminum dross, fly slag, blast furnace and steel slag) and natural squanders (e.g. chicken egg shells, rice husks, fish skeletal substance, crab shell, oyster shell, snail shell, shrimp shell, biont shell) etc. [2]. The use of such wastes to develop catalysts can be a win–win situation as this takes care of the disposal issues and the high volume waste can furnish an economical track to dynamic frameworks. As these squanders are to be used for catalyst preparation it is necessary to know the potential influence of its composition. Though industrial squanders are readily available, it may not contain the required precursors (such as MgO, Al_2O_3 etc.), whereas the natural squanders contain high amount of required precursors (such as CaO, $Ca_5(PO_4)_3(OH)$ etc.). Natural squanders are also low cost alternatives, which is why many researchers

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* Corresponding author. Tel.: +91 361 2582267; fax: +91 361 2582291.
E-mail address: kmohanty@iitg.ernet.in (K. Mohanty).

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focused their attention on these materials. Moreover, there are plenty of alternate natural squanders available which can be exploited for preparing catalysts.

Apatite is a group of phosphate minerals which is available both in the form of synthetic as well as natural [3]. Hydroxyapatite ($Ca_5(PO_4)_3(OH)$) is one of such apatite which is the mineral form of calcium apatite and is a potential candidate for catalyst preparation [4]. About 50% by weight of bone contains hydroxyapatite. Fish bone is an imperative wellspring of hydroxyapatite which can be used for the preparation of catalysts. From a global market study, it was found that 90% of fish resources is marine and rest are from fish farming and fresh water [5]. Human consumption of fish is about 75% whereas the rest 25% is used for the production of fish oil. This generates a huge amount of waste which creates an adverse effect on the environment. Hence, there is scope available for the use of such waste into value-added product. Commercial hydroxyapatite as catalyst was reported by several researchers [6], however there is scant information available on the use of waste fish bone as a precursor for catalyst preparation. Waste fish bone after proper treatment was used as catalyst earlier, however with limited success due to poor surface area [7]. Literature reveals that various metals were doped on to the surface of Mg–Al hydrotalcites [8], fly ash [9], coal fly ash [10], and egg shell [11] to increase the surface area. Thus, there is a wide scope available to test various metals for doping on the surface of waste fish bone with an aim to increase the surface area. Chakraborty and RoyChowdhury [12] prepared copper supported hydroxyapatite for semi-batch oleic acid esterification. They prepared the catalyst by freeze drying followed by wet impregnation method. Although they tried to prepare an acidic catalyst, however they used 25% Ammonia solution to make the solution pH 4.0, which is bit abrupt for the acid catalyst preparation process. Jazie et al. [13] used waste animal bone for transesterification of peanut and rapeseed oils. Obadiah et al. [14] also used waste animal bone for biodiesel production from palm oil. However, the stability of these catalysts was a major issue, although the transesterification conversion was above 80%.

In this work, waste fish bone was used as the precursor for the preparation of metal doped catalyst. Calcium phosphate is the main component of fish bone which has relatively high catalytic activity, good thermal and chemical stability, and can be used for various applications. Aluminum oxide (Al_2O_3) was used for doping due to its high specific surface area and defective crystalline property [15]. It can be used as active phase during catalysis which influences the selectivity and activity of catalytic reactions [16]. Moreover, Al_2O_3 nanoparticles are used as a carrier and support because of its high thermal stability. In the present investigation, the waste fish bone-derived catalysts were characterized in detail and used for the transesterification of neem oil (*Azadirachta indica*). The reusability of the catalyst was also thoroughly studied and reported.

2. Materials and detailed methodology

2.1. Materials

The cooked waste fish bone (CWFB) was collected from Indian Institute of Technology (IIT) Guwahati hostel messes. The chemicals viz. 25% aqueous ammonia solution, KOH, methanol and aluminum nitrate ($Al(NO_3)_3{\cdot}9H_2O$) were procured from Sigma Aldrich, India and were used as it is without any further treatment.

2.2. Preparation methodology

The CWFB was washed under the tap water to remove the attached flesh and adhered proteinaceous part and dried under sun for 2 days. This was followed by treatment with acetone for 24 h and again dried at 60 °C for complete evacuation of oily matters. The CWFB was consequently crushed and biological hydroxyapatite (CWFB-HAp) was obtained. Aluminum was doped on CWFB-HAp to prepare the doped catalyst (CWFB-HAp-Al) using the wet impregnation method. For this, 0.5:1, 1:1 and 1:0.5 wt. proportions of CWFB-HAp and the concerned oxide, aluminum nitrate were mixed followed by calcination at 650 °C temperature. For preparation of 1:1 CWFB-HAp-Al catalyst, 30 g of $Al(NO_3)_3{\cdot}9H_2O$ was added to 100 mL of water to get a ready solution of aluminum nitrate. To this solution, 30 g of fine powder of CWFB-HAp was added gradually according to the wet chemical precipitation technique and blended rigorously using a mechanical agitator under aggregate reflux time of 30 min. The pH was maintained at 11.0 by using 25% aqueous ammonia solution. The entire solution was again mechanically mixed at 700 rpm at 60 °C for 2 h. The resultant solution was kept for 24 h at room temperature so as to allow the deposition of aluminum ions on CWFB-HAp. Then the mother liquor was removed by vacuum filtration and a sticky precipitate was obtained which was then subjected to drying using a hot air oven. The dried mass was then subjected to calcination at 650 °C for 3 h [17]. Similar procedure was applied for making catalysts with different CWFB-HAp to aluminum nitrate loading in order to analyze the effects of aluminum nitrate loading on the properties of catalyst. Thus, as per the three weight proportions *i.e.* 0.5:1, 1:1 and 1:0.5 of CWFB-HAp to aluminum nitrate, the catalyst were herein after designated as $0.5H_A$, $1H_A$ and $2H_A$, respectively. Also a calcined CWFB-HAp was prepared to compare the catalytic effects of catalysts with and without Al doping. So, finally five catalysts viz. CWFB-HAp, CWFB-CHAp, CWFB-HAp-Al ($0.5H_A$, $1H_A$ and $2H_A$) were prepared and stored in air tight containers for further use.

2.3. Catalyst, raw neem oil (RNO) and transesterified neem oil (TNO) characterization

2.3.1. Catalyst delineation

Powder X-ray diffraction information for structural analysis were gathered with a Bucker X-ray D8 advance diffractometer. A Cu Kα ($\lambda = 0.154$ nm, 45 kV, 40 mA) anode was utilized as the X-ray radiation source, ranging 2θ between 2° and 90° with scan rate of 0.5 s/step with increment 0.05. ICDD-JCPDS database was used for diffraction profiles.

The porous properties, for example BET surface area, average pore measurement and pore volume (*t*-plot strategy) were calculated by physical adsorption–desorption of N_2 at the boiling point (77 K) utilizing an Beckman-Coulter; Model: SA3100 surface analyzer device. Preceding the examination, the reactant was subjected to preheating at 423 K under vacuum for 90 min.

The thermogravimetric analysis of the powder sample was carried out by NETZSCH (STA449F3 Jupiter) thermal analyzer. The TGA was performed under Argon flow with a heating rate of 10 K min^{-1} using a ceramic crucible up to 1000 °C.

The powder morphology studied under the specified conditions was contemplated by a field emission scanning electron microscope (JEOL-JSM-6390LV) furnished with an EDAX PV 9760 detector for Energy dispersive X-ray spectroscopy (EDX) to investigate nearby chemical arrangement. When mounting on a sample holder for FE-SEM investigation, the samples were dispersed in methanol and deposited on an aluminum foil and then coated with Gold–Palladium to make the specimen fit for microstructures investigations. The microcrystalline nature of the developed catalyst was observed from transmission electron micrographs (TEM) and selected area electron diffraction (SAED) pattern. It was acquired from JEM 2100 electron microscope operated at 200 kV.