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Sodium modified hydroxyapatite: Highly efficient and stable solid-base catalyst for biodiesel production

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ABSTRACT

The present study focuses on the transesterification of rapeseed oil into biodiesel using sodium-modified hydroxyapatite (NaHAP) as a new highly efficient solid base catalyst. The catalyst was prepared by a simple impregnation of $NaNO_3$ on the HAP support followed by the calcination at different temperatures. The prepared solid-base catalysts were characterized using the X-ray powder diffraction, thermogravimetric analysis, Fourier transform infrared (FTIR) scanning electron microscopy (SEM), ^{31}P solid-state NMR, BET, and basicity measurement by phenol adsorption to determine their physical and chemical properties. Characterization results revealed that the catalyst loaded with 50 wt% of $NaNO_3$ and calcined at 800 °C exhibited the highest amount total basicity, which is 121 μmol/g. The suitable reaction condition for maximum biodiesel yield up to 99% were methanol to oil molar ratio of 6:1, 4 wt% of catalyst and reaction temperature of 100 °C. The catalyst has good stability and strong ability to be reuse for more than five cycles. Moreover, some of the most important physicochemical properties of the produced biodiesel fuel were determined according to the European standard and were found to be within the recommended EN14214 specifications.

1. Introduction

Fossil fuels are the most used sources of primary energy in the world, they account around 80% of the total energy consumed [1]. In fact, the transportation sector is mainly dependent on energy from petroleum (96%) and represents the major consumer of fossil fuels [2]. Besides the growing energy demand due to the ever-increasing human population [3] and the unsteady cost of fossil fuels resources, other worrying issues related to the use of the petroleum derived fuels include the increase in greenhouse gases in the atmosphere generated by the human activities mainly electricity production, transportation and industrial transformation.

These concerns have led to the search for feasible substitutes of petroleum-derived fuels especially green and renewable ones. The aims of these researches are the reduction of our dependence on fossil fuels *via* the development of a new renewable and sustainable fuel such as biodiesel. Since its discovery by Rudolf Diesel [4], biodiesel has attracted much attention and received renewed interest and intensive researches. Nowadays, the biodiesel industry becomes the fastest growing industry worldwide by the implantation of many biodiesel plants, which make biodiesel an attractive alternative to petrodiesel.

Biodiesel or fatty acid methyl ester (FAME) has attracted considerable interest all over the world since it can significantly reduce global warming, environmental pollution, and the dependence on fossil resources. It has been widely accepted as an excellent and renewable alternative to fossil diesel due to its environmental benefits such as renewability and biodegradability [5]. Biodiesel shares similar physicochemical properties, in term of kinematic viscosity, specific gravity, calorific value and cetane number as petroleum-based diesel fuel [6,7]. Moreover, it also possesses a higher flash point (>130 °C), decreases the emission of carbon monoxide, unburned hydrocarbons and particulates during the combustion process when compared with conventional diesel. The catalytic transesterification of vegetable oils to the corresponding methyl esters is an efficient and economical route from an industrial point of view. Traditionally, the transesterification

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reaction has already been conducted using homogeneous acids and bases, such as H_2SO_4, HCl, NaOH, and CH_3ONa. Currently, the industrial transesterification processes are performed on a commercial scale using homogeneous base catalysts such as NaOH and KOH due to their rather high catalytic activity under mild conditions [8,9]. Despite their high performance, the conventional homogeneous base catalysts are corrosive and sensitive to water and free fatty acids, which have a negative effect on the catalyst performance [10]. In addition to this, the homogeneous transterification process has many environmental drawbacks since it requires additional neutralization and purification steps [11]. Thus, a considerable amount of water is required, which further increases the production cost [12]. Besides, homogeneous base catalysts produce soap instead of biodiesel and become deactivated in the presence of moisture and free fatty acid (FFA). To address this issue, recently, much more attention has been devoted to the development of new ecofriendly chemical processes that can overcome the problems associated to the homogenous catalysis and improves the biodiesel production process using heterogeneous catalysis [13]. These eco-friendly approaches were found to have several advantages like easy separation and purification of the reaction products without further washing and neutralization steps. Moreover, a heterogeneous catalyst can be regenerated and reused several times without any loss in its activity, makes the process cheaper, practical and sustainable [14]. However, the heterogeneously catalyzed transeterification reaction is very complex catalysis system because it occurs in a three-phase system consisting of oil-methanol-catalyst. At present, a variety of heterogeneous base catalysts are used such as single transition metal oxides, mixed metal oxides, zeolites and modified zeolites, hydrotalcites, anion exchange resins, lipase immobilized on/in various supports and so on [15–22]. Unfortunately, some of the reported catalytic systems require prolonged reaction time, high methanol to oil molar ration and high cost of catalyst, thus only a few of them were being used on commercial scale.

Alkali metal (Li, Na, K) or alkali earth salts have shown high catalytic activity in the transesterification reaction and could be supported on Al_2O_3, SiO_2, bentonite, palygorskite or attapulgite and activated carbon to generate a new highly efficient heterogeneous catalyst with improved catalytic activity in the transesterification reaction [23–27]. These studies demonstrated that loading an alkali metal or alkali earth salts on catalysts support resulted in the improvement of their catalytic performance towards the transesterification reaction.

Additionally, the catalysts derived from natural sources such as eggshell, mollusk shells, coral, ash and animal bone, have been widely accepted as a cost-effective catalyst for biodiesel production [28–31]. These catalysts have shown good performance and stability in the transesterification reaction but require higher catalyst amount, a longer reaction time and higher methanol/oil molar ratio thereby raising the cost of biodiesel production [31].

Calcium phosphate (CP)-based catalysts derived from biological resources such as animal bones and eggshells are abundant in the nature. Their low cost and relative high surface area allow them to serve as promising heterogeneous catalysts for the biodiesel synthesis since they possess a good catalytic activity and low solubility in methanol [32–35].

These studies provided an impetus to search for a new highly efficient solid base catalyst with high selectivity and reactivity. Among these, calcium phosphate derived catalysts such as hydroxyapatite (HAP) appear very attractive due to their ion-exchange ability, acid base adjustability, adsorption capacity, non-toxicity and thermal stability [36]. This variability of properties enables the possibility to use of HAP in diverse applications, especially heterogeneous catalysis. Indeed, several researches have been focused on the use of HAP-based materials as heterogeneous catalysts for base-catalyzed reactions [37–39]. Recently, we have reported an efficient protocol for the synthesis of naphthopyran derivatives catalyzed by hydroxyapatite or sodium-modified-hydroxyapatite in water [40]. In spite of active research efforts in the development of highly efficient heterogeneous catalysts for biodiesel production, only a few studies have been documented in literature related to the investigation of the utilization of hydroxyapatite based alkaline catalyst to synthesis solid catalyst for biodiesel production till date.

In the present study, we first investigate the catalytic activity of sodium-modified hydroxyapatite as a new heterogeneous catalyst for biodiesel production. A series of NaHAP catalysts, with different $NaNO_3$ loading, were prepared and their activities towards transesterification reaction were examined. The effect of $NaNO_3$ weight ratio and calcinations temperature on the catalytic activity and the leaching behavior of NaHAP catalyst were investigated. Both screening of the reaction conditions and reusability of the catalyst has also been carefully studied and combined with the physicochemical properties of the prepared catalysts. Finally, several physicochemical properties of the obtained biodiesel were determined and compared with EN14214 standard. This study may increase the novelty of using calcium phosphate and more precisely hydroxyapayite as support for catalysts especially in transesterification of high-grade oil to biodiesel.

2. Experimental

2.1. Chemicals and materials

Vegetable oils used in this work were purchased from a local company in Mohammedia, Morocco and were directly used without further treatment and purification. Chemical reagents such as $Ca(NO_3)_2{\cdot}6H_2O$, $(NH_4)_2HPO_4$, Cetyltrimethylammonium bromide (CTAB), $NaNO_3$, KNO_3, KF and NH_4OH were provided by Aldrich Chemical Company and were used as received. All chemicals were analytical grades and used directly without further purification. Methanol was of HPLC grade. Methyl 10-Undecanoate used as an internal standard for GC analysis was purchased from Aldrich Chemical Company and used as received.

2.2. Feed stock's characterization

The main properties of the used vegetable oils determined by using the standard methods are summarized in Table S1. As shown in this table, the water content of the refined rapeseed oil (RO), soybean oil (SBO) and sunflower oil (SFO) used in this study was very low which avoid soap formation and leaching of active species into water. Moreover, it can be seen that the refined oils have very low free fatty acid content, calculated in terms of mg KOH/g, which limits the catalyst deactivation by acid-base neutralization and avoids the separation of the biodiesel product from the glycerol [41]. The average molecular weight (MW) of RO, SBO and SFO was calculated according to the following equation [42]:

$$MW = (56.1 \times 1000 \times 3)/(SV - AV) \quad (1)$$

where SV and AV represent the saponification and the acid values of the oil.

2.3. Catalyst preparation

The NaHAP catalysts were prepared using the following two-step method. Firstly, mesoporous hydroxyapatite was prepared by a pseudo sol gel process based upon the following procedure: Briefly, CTAB (5 mmol) and $(NH_4)_2HPO_4$ (0.06 mol) were dissolved in 100 mL deionized water and stirred for 30 min to form a clear