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Modified fluorapatite as highly efficient catalyst for the synthesis of chalcones via Claisen–Schmidt condensation reaction

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ABSTRACT

In the present study, we investigated the synthesis of fluorapatite using a pseudo sol–gel process and the chemical modification of this new catalyst support via impregnation of sodium nitrate followed by calcination at 550 °C in order to enhance its catalytic performance. This approach was used to obtain a bi-functional catalyst for Claisen–Schmidt condensation. Indeed, this heterogeneous catalyst exhibited excellent catalytic activity and high selectivity for the synthesis of chalcones from direct aromatic aldehydes with substituted ketones at room temperature. The operational simplicity, excellent yields of the products and the recyclability of the catalyst are the main advantages of this method.

Introduction

Due to their wide application in pharmaceutical and biological sectors, the synthesis of chalcones has drawn tremendous interest over the past years [1,2]. Indeed, these compounds have been reported to possess abroad spectrum of biological activities such as anti-inflammatory, anti-invasive, antitumor and antibacterial properties [3–6]. They are also considered as potentially important synthetic intermediates for the preparation of flavonoids and isoflavonoids, which are widely, present in inedible plants [7–9]. Moreover, they have recently been used as simple building blocks for the synthesis of dihydropyridones [10]. Traditionally, chalcones compounds are synthesized through Claisen–Schmidt condensation between aldehydes with substituted ketones using homogeneous catalysts such as NaOH, KOH and $Ba(OH)_2$ [11–17]. However, recently many synthetic methods have been developed for the preparation of chalcones using heterogeneous catalysts such as magnesium oxide [18], hydrotalcites [19,20], hydroxyapatite [21], solid derived from coal combustion fly ash [22], and modified natural phosphates [23,24]. Most of heterogeneous catalysts used are recyclable but they possess poor selectivity to chalcone due to the competitive Cannizzaro reaction of aldehyde and other undesired side reactions like the Michael addition reaction. On the other hand, fluorapatite (FAP) has attracted tremendous interest due to its potential biomaterial application for bone repair due to its bioactivity and its biocompatibility as well as its antibacterial activity [25,26]. It is structurally and chemically similar to hydroxyapatite, but it has better physic-chemical stability such as lower solubility in an acidic medium. Fluorapatite offers other advantages such as high stability at high temperatures and insolubility in organic solvents as well as water. However, one of the main properties of apatites is their ability to exchange anions or cations in the structure leading to the design of specific materials that have new catalytic properties. Many methods regarding the synthesis of fluorapatite have been reported

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including: sol–gel process [27], solid-state reaction [28,29] and the hydrothermal process [30]. The replacement of traditional homogeneous catalysts by heterogeneous catalysts is a field of growing interest from both an industrial and an academic point of view. In contract to the acid heterogeneous catalysis, the application of solid basic catalysts to organic synthesis is far less developed. In the contrast to hydroxyapatite, little attention has been given to the usage of FAP as a solid support or as a catalyst in organic reactions [31,32]. The performance of FAP in organic chemistry is influenced by its structural features such as size and morphology. In an effort to develop new heterogeneous catalytic systems, we initiated a program aimed at introducing natural or synthesized fluorapatite as it is or conveniently modified that can catalyze several organic transformations. Some examples include Friedel–Crafts alkylation [33], Michael-addition [34], Knoevenagel [35], and nitrile hydration [36]. In the present paper, we report the synthesis of fluorapatite through a pseudo sol–gel method using a hydrosoluble surfactant such as cetyltrimethylammonium bromide. This synthesized fluorapatite was impregnated with sodium nitrate, which lead to sodium-modified-fluorapatite that exhibited good catalytic activity in Claisen–Schmidt condensation between aldehydes with substituted ketones.

Experimental

Materials and apparatus

High purity $CaNO_3$, $NaNO_3$, NH_4OH, $(NH_3)_2HPO_4$ and $(C_{16}H_{33})N(CH_3)_3$ Br were purchased from Aldrich chemical company and were used without further purification. X-ray diffraction (XRD) patterns of the catalyst were obtained at room temperature on a Bruker AXS D-8 diffractometer using Cu-Kα radiation in Bragg–Brentano geometry (θ–2θ). Scanning electron microscopy (SEM) analyses were recorded on a FEI Helios NanoLab microscope after few nanometers of gold palladium metallization. The transmission electron microscopy (TEM) micrographs were obtained on a Tecnai FEI microscope operating at 200 kV. Specific surface areas were determined from the nitrogen adsorption/desorption isotherms (at 77 K) and measured with a Quantachrome Autosorb-1 automatic analyzer using the BET equation at $P/P_0 = 0.98$. The ^{31}P NMR experiments were carried out at 298 K under magic angle spinning (MAS) using Bruker Avance 400 WB spectrometer at resonance frequencies of 160 MHz equipped with a 4 mm probe. The spectra were recorded under high-power proton decoupling conditions using pulse delays of 30 s.

Preparation of FAP and NaFAP catalysts

A solution containing cetyltrimethylammonium bromide (0.045 g, 0.12 mmol) and diammonium hydrogen phosphate (7.92 g, 60 mmol) in 250 mL of deionized water was stirred for 60 min at room temperature. The solution was maintained at a pH higher than 12 by adding ammonium hydroxide. To this solution, an aqueous solution containing ammonium fluoride (1 g, 27 mmol) and calcium nitrate (23.8 g, 145 mmol) was added dropwise over 30 min under continued mechanical stirring. The resultant milky solution was refluxed for 4 h. After this time, the mixture was cooled to room temperature and the white precipitate formed was filtered, washed several times with distilled water and ethanol and air dried overnight at 80 °C under vacuum. The as-synthesized sample that was calcined at 550 °C for 4 h resulted in a white powder. The modified fluorapatite (Na/FAP = 1/2, w/w) was prepared by the addition of an aqueous solution of sodium nitrate (5 g, 1.17 M) to an aqueous solution of FAP (10 g, 10 mmol). The resulting mixture was vigorously stirred at room temperature for 30 min, and then the water was evaporated under vacuum. The resulting solid was calcined in open air at 700 °C.

Synthesis of chalcones via Claisen–Schmidt condensation with NaFAP

The NaFAP catalyst (0.05 g) was added to a mixture of an arylaldehyde (2.5 mmol) and ketone (2.5 mmol) in methanol (3 mL). The reaction was stirred at room temperature for 24 h. The reaction progress was monitored using GC analysis. After completion of the reaction, the catalyst was removed by filtration, the solution was concentrated under vacuum and purified by recrystallization in ethanol. The products were identified by ^1H NMR, ^{13}C NMR, IR spectroscopy and by mass spectrometry.

Results and discussion

The preparation of this material was carried out by a pseudo sol–gel method in high yield. The lattice parameters for pure FAP are measured as $a = 9.375$ Å and $c = 6.887$ Å [37,38]. The FAP structure belongs to P63/m space group and its structure is hexagonal [39]. It takes the form of an arrangement of a large Ca site and phosphate (PO_4) tetrahedral surrounding a channel containing F^- as anion (Fig. 1).

The spatial distribution of FAP structure is an assembly of the CaO_6 and PO_4 tetrahedra which give rises of the corners connected units which create tunnels in the c-axis direction (Fig. 2) [40].

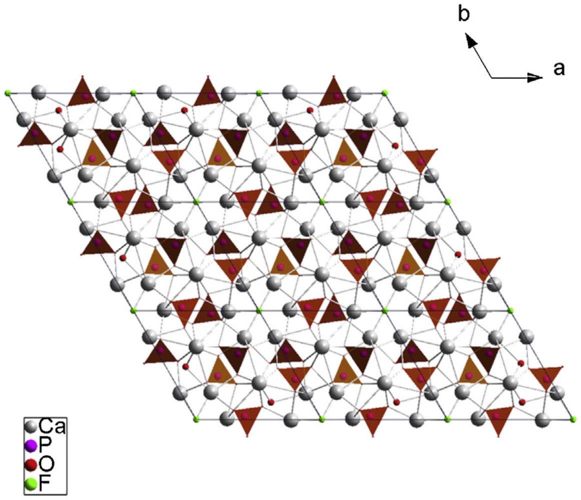

Fig. 1. The projection of fluorapatite represented by PO_4 units linked to other cations and anions.

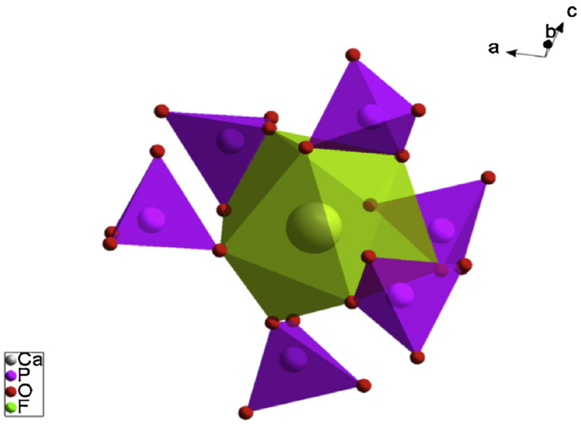

Fig. 2. The assembling of CaO_6 and PO_4 tetrahedra that are connected by corners.