Acid treatment halloysite nanoclay: Eco-friendly heterogeneous catalyst for the synthesis of pyrrole derivatives

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Abstract

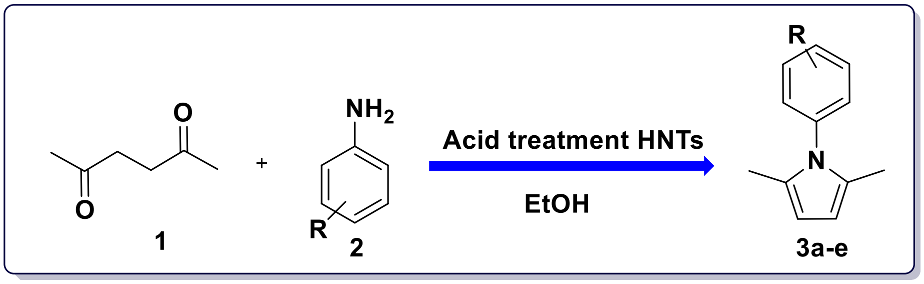
In this study, halloysite nanotubes (HNTs) as a green and available nano-mineral were used. The hydroxyl groups of HNTs were increased by acid treatment. So, the efficiency of HNTs was improved. The catalyst application of acid treatment HNTs was investigated in the synthesis of pyrrole as an important heterocycle compound. The catalyst was characterized by Fourier transforms infrared spectroscopy (FT-IR). Easy and simple method, high efficiency and eco-friendly are the advantages of this report.

Keywords: Halloysite nanotubes, Acid treatment, Nanocatalyst, Pyrrole.

1. Introduction

Halloysite ($Al_2Si_2O_5(OH)_4.nH_2O$) is a subset of aluminosilicate minerals. Halloysite nanotubes (HNTs) was mined from natural deposits in countries like China, New Zealand, America, Brazil, and France. Nanotube structure, availability, eco-friendly and porosity are the very important features for HNTs [1]. HNTs used in as a catalyst application in different reaction [2,3]. The external surface and the internal of HNTs are composed of silicon-oxygen tetrahedron and alumina oxygen octahedrons, respectively. The reaction of the acid with both the outer and inner surfaces of the nanotubes causes the AlO_6 octahedral layers to dissolve and dealumination occurred [4]. The acid treatment of halloysite has been used as a traditional chemical activation method for improving the performance of its catalytic activity. Nowadays, nanocatalysts have attracted much attention as a beneficial strategy in green chemistry [5].

Nitrogen based heterocyclic compounds, which have been widely used in the pharmaceutical industry [6]. Therefore, pyrrole as a nitrogen-based heterocyclic with biological activities was more considerable by the scientist [7]. Several methods and catalyst have been reported for the synthesis of this important framework [8]. In continuation of our research [9-14] and due to the importance of pyrrole scaffold, herein, an efficient synthesis of pyrrole derivatives was carried out in the presence of a catalytic amount of acid treatment halloysite nanocatalyst in ethanol at room temperature in high yields. The solid nanocatalyst can be recovered easily and reused without any significant loss of the catalytic activity (Scheme 1).



Scheme 1. The synthesis of pyrroles in the presence of halloysite nanoclay catalyst.

2. Experimental

2.1. General

All raw materials and solvents required were provided from Merck and Aldrich. The FT-IR spectrum of the product was taken by Shimadzu IR-470 spectrometer on KBr pellet. Melting points were measured with an Electrothermal 9100 apparatus and are uncorrected.

2.2. *Synthesis of acid treatment HNTs*

At first, 0.5 g of halloysite was added to a 10 mL deionized water. The mixture was stirred for 10 min and the uniform solution was achieved. Then, 50 mL of HCl solution (3 M) was added to the halloysite solution, and the mixture was stirred for 3 h. The nanoclay powder washed with distilled water 2 times. Finally, the obtained nanocomposite was dried at 100 °C for 4 h.

*2.3. General procedure for the synthesis of pyrrole derivatives **3a-e***

Acetonylacetone (1 mmol, 0.114 g), aniline (1 mmol, 0.093 g) and catalyst (0.06 g) were mixed in ethanol. The mixture was stirred in an air atmosphere at room temperature for 1 h. After the completion of the reaction, as indicated by TLC, the catalyst was removed easily by filtration. The crude product was filtered and recrystallized from ethanol to give products in good to high yields.

3. Results and discussion

FT-IR spectroscopy was used to confirm the synthesis of acid treatment HNTs (Fig. 1). The bands at 1035, 794, 792 and 692 cm^{-1} were attributed to the stretching vibrations of Si-O in both HNTs and acid treatment HNTs. As can be seen in HNTs spectrum the peak at 912 cm^{-1} was assigned to the bending vibration of Al-OH, while, this peak was disappeared in acid treatment HNTs. Also, acid treatment increased the hydroxyl groups and the broad and intense band around 3000 cm^{-1} can confirm this result.

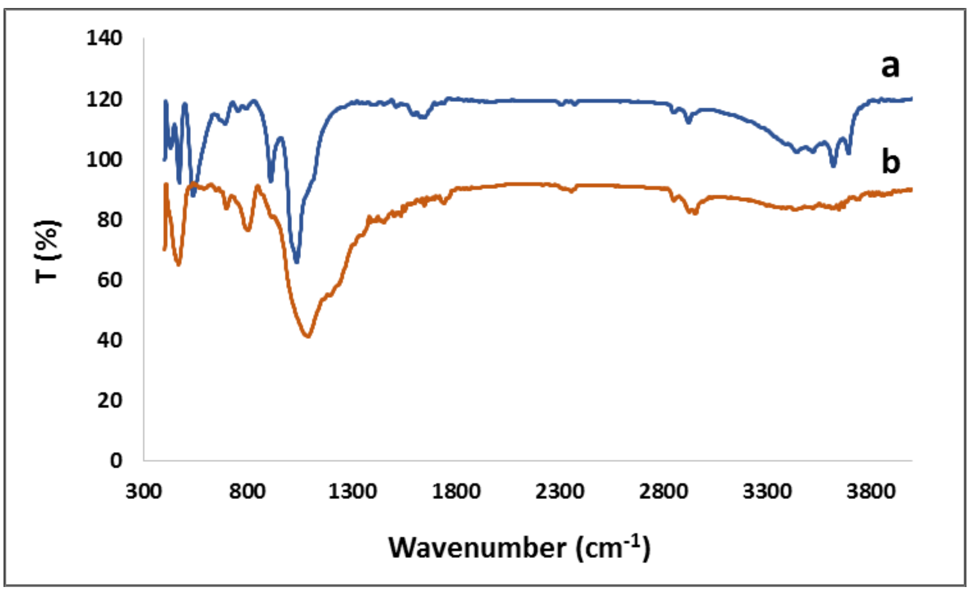


Fig. 1. FT-IR spectra of: a) HNTs and b) acid treatment HNTs

4. Conclusions

In summary, the green, eco-friendly, available and efficient nanocatalyst base on HNTs nanoclay was introduced. The acid treatment HNTs with high performance was used in the synthesis of pyrrole derivatives. High yield, green media and short reaction time are the benefits of this study. This research is under progress in our research laboratory.

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