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Halloysite nanotubes modified by chitosan as an efficient and eco-friendly heterogeneous nanocatalyst for the synthesis of heterocyclic compounds

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Abstract

In this study, halloysite nanotubes (HNTs) were modified by chitosan as a natural cationic amino polysaccharide. Halloysite nanotubes/chitosan (HNTs/Chit) was characterized by Fourier transform infrared (FT-IR) spectroscopy and energy dispersive X-ray (EDX) analysis. Also, its performance as a heterogeneous catalyst was investigated in the synthesis of pyranopyrazole derivatives. Reusable and easily recoverable catalyst, eco-friendly, high efficiency, and mild reaction conditions are some advantages of the present work.

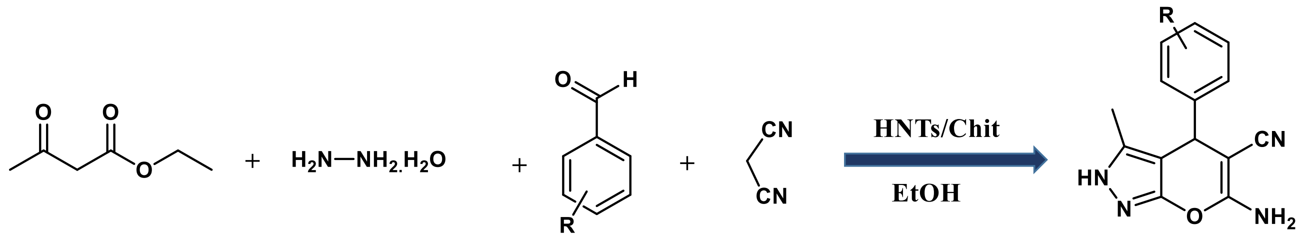
Keywords: Halloysite nanotubes, Chitosan, Nanocatalyst, Heterocyclic compounds.

1. Introduction

Halloysite nanotubes (HNTs) a natural aluminosilicate with a hollow tubular structure and the same ratio of tetrahedral and octahedral sheets [1]. HNTs were applied in various applications due to their special properties such as green, nanotube morphology, accessibility, biocompatible, porosity, and mechanical stability [2]. Moreover, different chemistry of the outer and inner of halloysite nanotube lead to selective modification [3]. HNTs were functionalized with organic and inorganic materials like chitosan, poly(ethylene imine) and alginate [4-6].

Chitosan (CS) is a natural cationic amino polysaccharide obtained by alkaline N-deacetylation of chitin [7]. Chitosan with the sheet structure like cellulose was achieved by a combination of β-1,4-linked 2-acetoamino-2-deoxy-D-glucopyranose and 2-amino-2-deoxy-glucopyranose units [8]. Recently, Chitosan with excellent features such as non-toxic, biocompatible, hydrophilic, antibacterial activity and biodegradable attract more attention among scientists [9]. Chitosan was applied in different applications including drug delivery systems, wound healing and tissue engineering [10,11].

The synthesis of pyranopyrazole compounds with pharmacological and medicinal properties was suggested by new catalysts similar to magnetic Fe_3O_4 nanoparticles and isonicotinic acid, recently [12]. Multicomponent reactions (MCRs) with most noteworthy features such as atom economy, short reaction time and simplicity in the synthesis of complex structures are applied in the synthesis of heterocyclic materials as an important class of organic compounds. In continues to our research on MCRs and nanomaterials and due to the importance of heterocyclic compounds [13-30], herein, HNTs/Chit as a green, reusable and efficient nanocatalyst was used in the synthesis of pyranopyrazole derivatives in the mild condition (Scheme 1).



Scheme 1. The synthesis of pyranopyrazole derivatives in the presence catalyst.

2. Experimental

2.1. General

HNTs, chitosan and all other materials and solvents were obtained from Merck and Aldrich company. The FT-IR spectrum of the product was taken by Shimadzu IR-470 spectrometer on KBr pellet. EDX spectra were provided with a Numerix DXP–X10P. Melting points were measured with an Electrothermal 9100 apparatus and are uncorrected.

2.2. *Synthesis of HNTs/Chit*

At first, 0.5 g of chitosan was added to a 20 mL deionized water. Then, acetic acid solution (0.5 M) was added dropwise until chitosan is completely dissolved. 1 g HNTs were dispersed in mL 20 mL deionized water and added to the chitosan solution. The mixture was stirred overnight. Subsequently, it was frozen into ice at -20 °C.

*2.3. General procedure for the synthesis of pyranopyrazole derivatives **5a-e***

The mixture of ethyl acetoacetate (2 mmol), hydrazinehydrate (2 mmol), aromatic aldehyde (1 mmol) and malononitrile (1 mmol) was stirred in 5 mL of EtOH in the presence of HNTs/Chit (20 mg) under reflux condition for 30 min. The reaction progress was checked by thin-layer chromatography (TLC). After the completion of the reaction (as indicated by TLC) the catalyst was separated by filtration. The crude product was recrystallized from EtOH to yield a pure product.

3. Results and discussion

As can be seen in Fig. 1, The result of the EDX analysis of HNTs/Chit nanocomposite confirms the presence of Al, Si, O, C and N elements in the synthesis nanocatalyst.

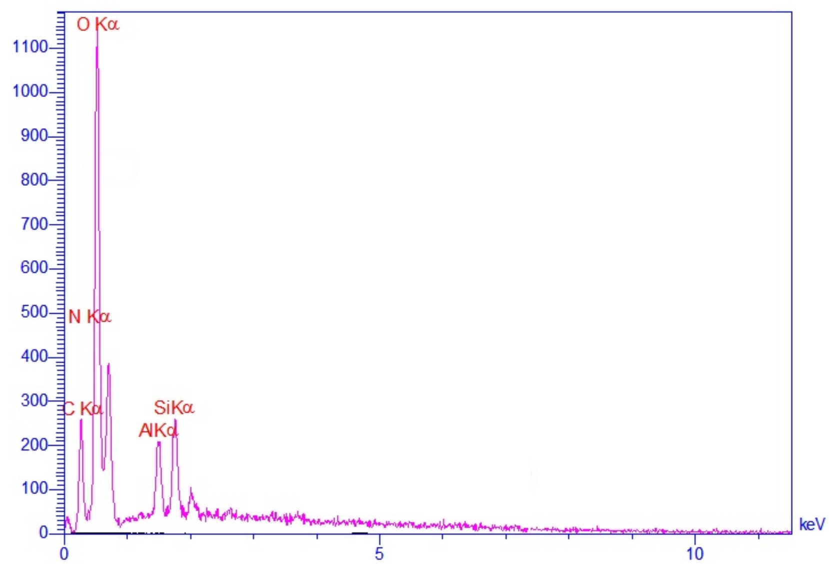


Fig. 1. EDX analysis of HNTs/Chit nanocatalyst.

Furthermore, FT-IR spectroscopy was used as a common analysis. The FT-IR spectrum of HNTs was shown in Fig. 2a. The bands at 520, 460, 1030 and 910 cm^{-1} are related to Al-O-Si, Si-O-Si, Si-O, and Al-OH, respectively. The stretching vibrations of inner-surface Al–OH were shown at 3690 and 3620 cm^{-1}. As can be seen in the HNTs/Chit spectrum (Fig. 2b) the vibrational stretching of the C=N appeared at 1650 cm^{-1}. Also, the absorption band at 1550 cm^{-1} was related to the distortion vibration of N-H groups of chitosan.

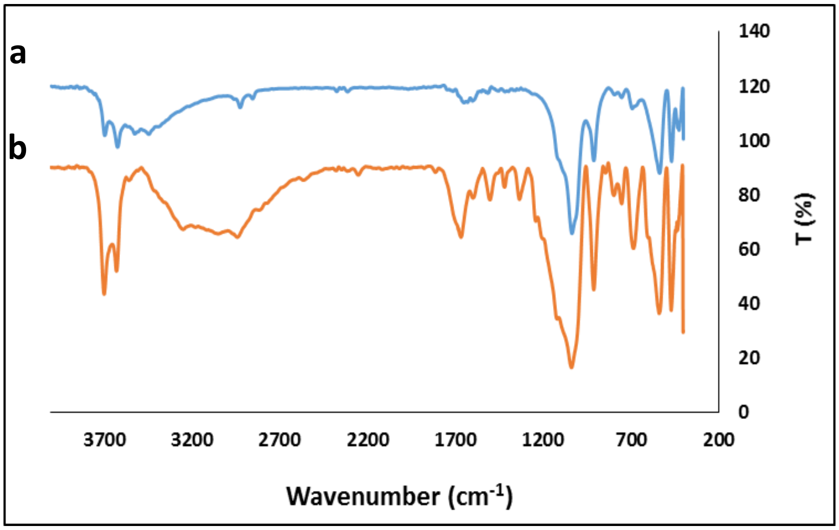


Fig. 2. FT-IR spectra of: a) HNTs and b) HNTs/Chit.

Catalytic application of HNTs/Chit in the synthesis of pyranopyrazole derivatives

Repeatability the efficiency of this strategy was confirmed by using different aromatic aldehydes with electron-withdrawing and electron-releasing substitutions and the synthesis of various pyranopyrazole derivatives under mild conditions with great yields. The results were summarized in Table 1.

Table 1. Synthesis of various pyranopyrazole derivatives.

Entry	R	Product	Yield[a] (%)	Mp (°C)
1	H	**5a**	95	244-246
2	3-NO_2	**5b**	93	234-235
3	4-NO_2	**5c**	91	247-249
4	4-Cl	**5d**	90	230-232
5	4-Me	**5e**	90	220-222

[a] Isolated yield.

4. Conclusions

In summary, the synthesis of nanocomposite based on natural and green materials was suggested in this research. Halloysite nanotubes were modified easily by chitosan and applied as an efficient nanocatalyst in organic reaction. Mild reaction condition, reusability of the catalyst and eco-friendly are some of the advantageous of this study.

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