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Alkylaminopyridine-grafted on HY Zeolite: Preparation, characterization and application in synthesis of 4*H*-Chromenes

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ABSTRACT

In this work, we functionalized acidic HY Zeolite (Z-HY) by alkylaminopyridine base that is excellent heterogeneous catalyst for synthesis of 4*H*-chromenes. The prepared catalyst was well characterized by Scanning electron microscopy (SEM), Energy dispersive X-ray analysis (EDX), Fourier transform infrared (FT-IR), Thermogravimetric analysis (TGA), X-ray diffraction (XRD) and Brunauer-Emmett-Teller (BET) techniques. The results showed that the alkylaminopyridine moiety was supported on HY Zeolite successfully. Hence, this catalyst was used for preparation of 4*H*-chromenes and obtained results showed that the reaction was carried out in the mild and solvent free condition with short reaction times, high yields and pure products. Furthermore, reusability of the catalyst and solvent free condition makes this method to be green and environmental friendly procedure.

1. Introduction

Organic-inorganic hybrid materials are of great interest as green, heterogeneous and recyclable catalysts in organic synthesis, due to the functional diversity merged with thermal and mechanical stability of inorganic solids [1,2]. There are different methods to preparation of heterogeneous catalyst such as functionalization homogenous catalyst on surface of alumina, silica, Fe_3O_4 and porous materials. Also, functionalization is used to change the surface properties of materials in order to improve the behavior and overall performance of materials adding new functions and overcoming deficiency while maintaining the bulk material properties.

Although, functionalization of some homogenous catalysts such as -SO_3H, Schiff base on porous material created fine heterogeneous catalyst but successful functionalization of alkylaminopyridine on HY Zeolite surfaces has not yet been reported [3]. Zeolites and related compounds with attractive nanoscale pores structure and free surface silanol groups (Si-OH), which are highly accessible to the common silyl agents and suitable substrate for functionalization [4].

2-amino-4*H*-chromene derivatives have a great attracting due to their biological activities such as anticoagulant, anti-HIV, anti-inflammatory, anti-asthmatic, antibacterial, anti-fungal, antioxidant and cancer therapy [5]. In recent years, several synthesis methods have been developed to access of 4*H*-chromene with different catalytic systems, DBU [6], PEG-400 [7], KF/Al_2O_3 [8], MCM-41-NH_2 [9], potassium phosphate tribasic trihydrate [10], Mg/Al hydrotalcite [11], nanosized magnesium oxide [12], methanesulfonic acid [13], tetrabutylammonium chloride (TBAC) [14], cetyltrimethylammonium bromide (CTABr) [15], poly (4-vinylpyridine) [16], and $Fe(HSO_4)_3$ [17], $CuSO_4.5H_2O$ [18], [EMIM][OH] ionic liquid [19], piperazine and microwave [20] and Preyssler heteropolyacid [21]. Although some reactions are satisfactory in terms of yield, but the use of high temperatures, expensive metal precursors, catalysts that are harmful to the environment, long reaction times, harsh reaction conditions, effluent pollution and tedious workup procedures are drawbacks of these methods.

Herein, for the above reasons and as a part of our works on design and development of novel heterogeneous catalysts and green chemical methods [22,23], we reported the synthesis and characterization of organic base-functionalized acidic HY Zeolite to give access to valuable 4*H*-chromenes as a new eco-friendly method (Scheme 1). This novel designed catalyst provided a heterogeneous system with a green synthetic aspect by avoiding the use of hazardous conditions for accessing target heterocyclic compounds.

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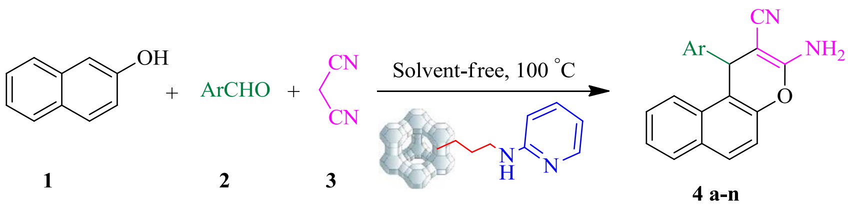
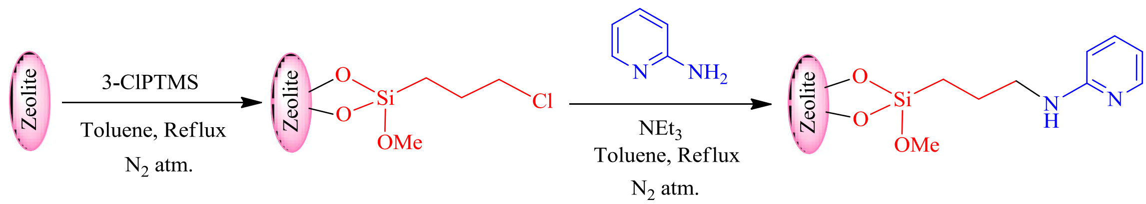


Scheme 1. Synthesis of 4*H*-chromenes.



Scheme 2. Alkylaminopyridine-grafted on HY Zeolite.

Table 1
The FT-IR of NaY Zeolite, HY Zeolite, Z-HY@SiO_2-PrCl and Z-HY@SiO_2-Pr-Py

NH,CH, CN band	*External vibrations*			*Internal vibrations*			*Sample*
	Pore opening	D-R	T-O_{sym}	T-O_{asym}	T-$O_{υsym}$	T-O bend	
–	384	577	791	1022	721	459	NaY
–	386	577	791	1026	723	459	HY
3389,3216,2950,1330	390	579	789	1030	723	459	Z-HY@SiO_2-PrCl
3385,3215,2959,1321	388	581	789	1040	725	461	Z-HY@SiO_2-Pr-Py

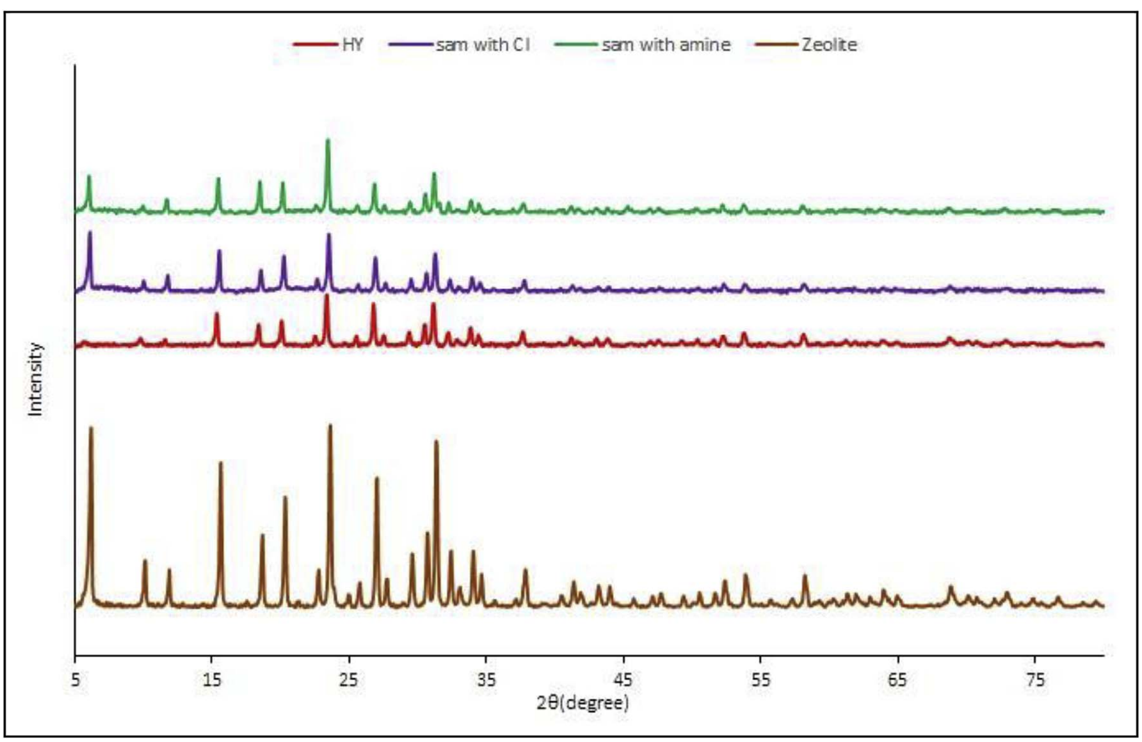


Fig. 1. The XRD for NaY (a), HY(b), Z-HY@SiO_2-PrCl (c) and Z-HY@SiO_2-Pr-Py(d)

Table 2
The EDX of NaY Zeolite, Z-HY@SiO_2-PrCl and Z-HY@SiO_2-Pr-Py

Compounds	Si/Al	C/N	O	Cl
NaY	2.53	–	39.87	–
HY@SiO_2-PrCl	2.80	3	44.02	3.92
HY@SiO_2-Pr-Py	2.86	2.73	44.07	1.33

2. Experimental

2.1. Materials and instruments

All materials and solvents were purchased from Aldrich or Merck while NaY Zeolite was purchased from SPAGE Company (Tehran, Iran). X-ray powder diffraction patterns were recorded on an X-Ray diffract