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Nano-CrY zeolite as a new and reusable catalyst for synthesis of 2-aryl-1*H*-benzothiazoles

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ABSTRACT

The Nano-CrY zeolite synthesized and characterized by Fourier transfer infrared (FT-IR), X-ray diffraction (XRD),and Scanning electron microscopy (SEM).The result show that nano catalyst prepared with mainly particles size about 30-80 nm. The XRD show the structure of the zeolite does not collapse. This Nano-CrY zeolite has been used as new, and nontoxic catalyst for catalyzes of synthesis of 2-aryl-1H-benzothiazoles at mild condition. This procedure is simple, effective, inexpensive and green. The products were obtained in high yields and the catalyst is reusable. Since products were obtained by aqua work-up in good purity, complex purification methods are not necessary.

***Keywords**: Nano-CrY zeolite, 2-aryl-1H-benzothiazoles, Nanocatalyst, 2-aminothiophenol, Cyclocondensation.*

1. Introduction

2-Substituted benzothiazoles are an important class of compounds in medicinal and industrial chemistry [1]. The compounds with benzothiazole cores have been known as antitumor drugs [2], antibacterial [3], antiglutamate/antiparkinson [4], broad spectrum Ca^{+2} channel antagonist [5], inhibition of enzymes such as aldose reductas [6], monoamineoxidase [7], lipoxyenase [8], cycloxygenase [9], acetyalcholoine esterase [10], thrombine [11], proteases [12], H^+-K^+ ATPase [13], carbonic anhydrase [14], HCV helicase [15], plant growth regulation [16].

As the importance of benzothiazoles, for synthesis of these compounds several methodologies have been reported [17]. The two major methods are condensation of 2-aminothiophenol with aldehydes and cyclization of thiobenzanilides [18].

Several reagents have been used for catalyzes of this condensation that include DMSO/120°C [19a], ionic liquid 1-phenyl-3-methylimidazoliumbromide ([pmIm]Br) [19b], scandium triflate [19c], silicagel [19d], MnO_2/SiO_2 [19e], molecular iodine [19f], molecular oxygen promoted by activated carbon [19g], p-TSOH [19h], SiO_2/graphite [19i], electrochemical synthesis in methanol containing sodium acetate as supporting electrolyte [19j], water/110°C [19k], carboxylic acid [20], acid chlorides [21] or esters [22].

Also, some methods such as micro wave-mediated reaction of 2-aminothiophenol with β-chloro-cinnamadehydes [23], palladium-catalyzed Suzuki biaryl coupling of 2-bromobenzothiazoles with aryl bromides [24], coupling of benzothiazoles with aryl bromides [25] and reaction of thiophenol with aromatic nitriles [26] have been used.

Unfortunately, many of these procedures suffer from several defects such as the use of toxic and/or expensive catalysts [17,18], using of hazardous and carcinogenic organic solvent and multistep process for reaction. [19]. Therefore, investigating the optimized methodology for synthesis of benzothiazoles is still important.

The use of heterogeneous solid catalysts in the organic synthesis and industrial manufacturing of chemicals is interesting and important, because of their suitable acidity, insolubility to all organic solvents, thermal stability, and low cost; they also provide a green alternative to homogeneous catalysts [28]. A literature survey on organic reactions catalyzed by heterogeneous catalyst indicates that in the majority of them, zeolite with Bronsted and Lewis acid centers are

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simultaneously important in the catalytic activity [29]. Zeolites are crystalline hydrated alumina silicates of the alkaline earths. The acid sites center can be increased by exchange of monovalent ions with polyvalent cations with the different process [30].

As the importance and high efficiency of zeolites, in this work we have used CrY zeolite as a green, effective and reusable catalyst for catalyze one-pot synthesis of benzothiazoles (Scheme 1).

2. Experimental

Solvents, reagents, and chemical materials were obtained from Aldrich and Merck chemical companies and purified prior to use.

2.1. Preparation of nano-CrY Zeolite

About 100 ml of 0.01 M solution of metal salt $CrCl_3.6H_2O$ was added to 1.0 g of NaY zeolite that prepared in our laboratory according to a previously reported procedure in a 250-mL flask [33-35]. The mixture was stirred for 24 h and then filtered. The obtained solid was washed with water. The final zeolite products were dried at room temperature. The CrY zeolites were initially produced under ultrasound to obtain nano-size.

2.2. General procedure for synthesis of 2-aryl-1H-benzothiazoles

To a mixture of 2-amnomthiophenole, aldehyde (1 mmol) in DMF (4 ml), 0.1 g of nano-CrY Zeloite added and stirred for 90 minutes. The progress of reaction was followed by TLC. After completion of reaction, zeolite has been filtrated, washed and dried for reusing, and then 15 ml of water was added. Benzothiazoles are not solvable in water, therefore, the participated products were filtrated as nearly pure corresponding benzothiazoles. For more purification, products recrystallized in ethanol (96%) if needed.

3. Results and Discussion

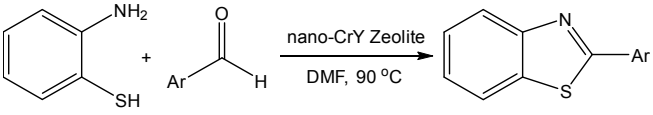
The results indicated that CrY zeolite shows the high activity for preparation of benzothiazoles reaction. Because of the small ions, such as Cr^{3+}, Zn^{2+}, Cu^{2+}, etc, high degrees of ion exchange are observed. It seems that $CrCl_3$ has dispersed completely onto the surface of NaY zeolite under ion exchange proceeding [31].

The scanning electron microscopy (SEM) image of the CrY zeolite nano-particles is shown in (Fig. 1). The particles size was mainly about 30-80 nm. Also, FT-IR of the CrY zeolite nano-particles is shown in Fig. 2 that an intense band at ca.1022 cm^{-1} attributable to the asymmetric stretching of Al–O–Si chain of zeolite. The symmetric stretching and bending frequency bands of Al–O–Si framework of zeolite appear at ca. 791 and 463 cm^{-1}, respectively. Transition metal /complexes encapsulated in the zeolite nano cage did not show any significant shift in functional groups stretching bond of zeolite, but anew band appear at 846 cm^{-1} related to Cr–O–Si or Al [30].

XRD pattern of nano size CrY zeolite show in Fig. 3. As we can see, the structure of the zeolite does not collapse and six characteristic peaks appear at 2 theta of 30.1, 35.5, 43.1, 53.4, 57.0, and 62.6, which are marked by their indices ((2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0)) [32].

After optimization tests, DMF has chosen as the best solvent. Results were summarized in Table 1.

As the shown in Table 1, it is notable that both electron-withdrawing and electron-relaxing group were reacted in this method. But, clearly, electron-relaxing



Scheme 1. Nano-CrY Zeolite catalyzes the synthesis of 2-aryl-1*H*-benzothiazoles.

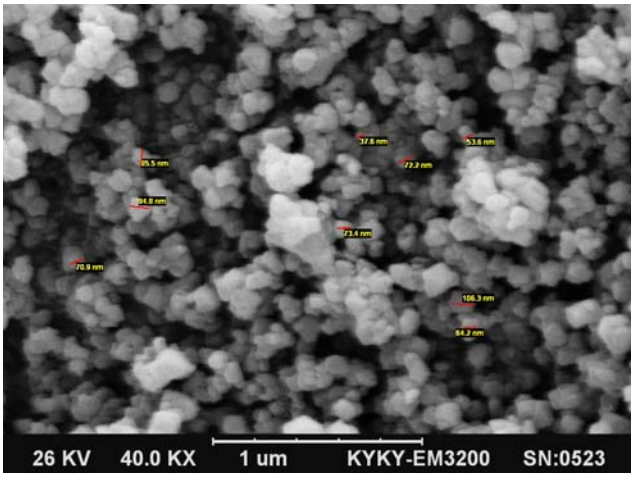


Fig 1. The scanning electron microscopy (SEM) image of the CrY zeolite nanoparticles.

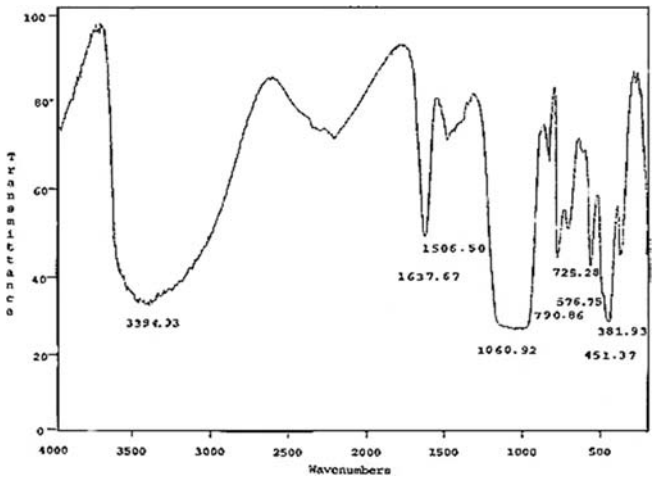


Fig 2. FT-IR of the CrY zeolite nanoparticles.

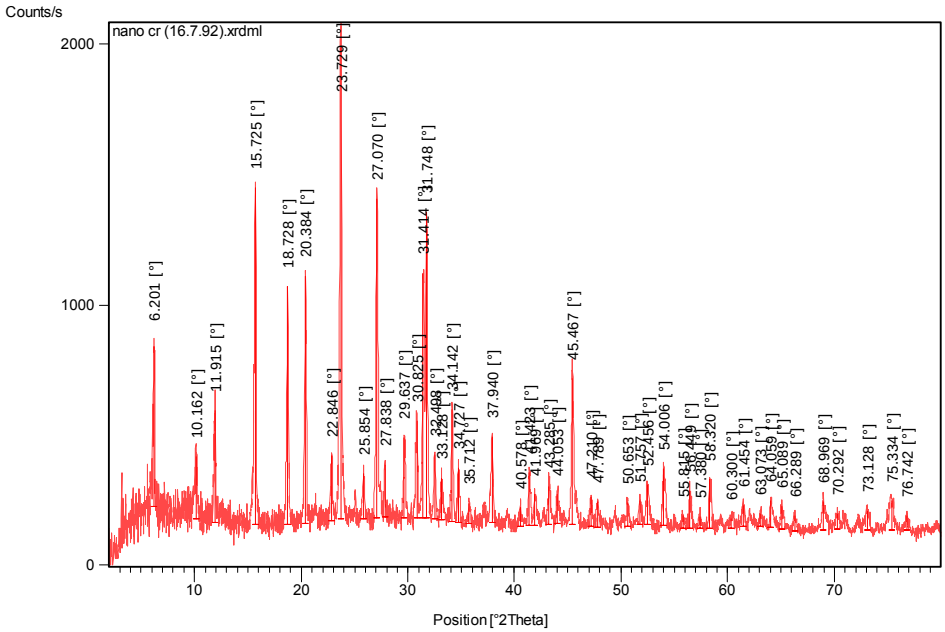


Fig 3. XRD pattern of nano size CrY zeolite.

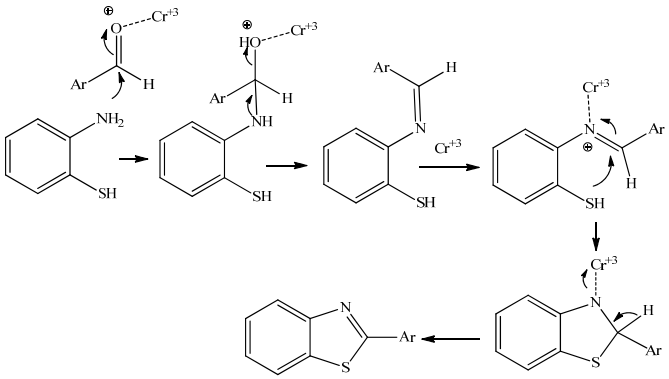
Table 1. Synthesis of 2-aryl-1*H*-benzothiazoles in optimized conditions.

Product[a]	Ar	Time (min)	Yield (%)[b]	m.p. (°C)	
				Found	Reported[c]
2a	C_6H_5	90	71	118-123	114-116
2b	4-$NO_2C_6H_5$	90	87	232-235	230-231
2c	2,4-$Cl_2C_6H_5$	90	85	154-158	150-152
2d	4-$MeOC_6H_5$	90	57	123-126	122-124
2e	4-$N(CH_3)_2C_6H_5$	90	27	169-172	175-177
2f	2-ClC_6H_5	90	50	119-120	128-129
2g	4-ClC_6H_5	90	44	113-116	114-116
2h	3-$NO_2C_6H_5$	90	88.50,71,64[d]	186-192	181-183

[a]The products were characterized by their physical properties and spectral analysis and compared with authentic samples.
[b]Isolated yields.
[c]Reported from Ref. 27.
[d]Reused for three times.

groups such as methoxy or *N*,*N*-dimethyl substituent (Table 1,entries 2d and 2 e) cause that yield is very poorer than electron-withdrawing group such as nitro substituent (Table 1, entries 2b and 2h). As these results, we suggests an acceptable mechanism that shown below (Scheme 2).

As the shown in scheme 2, the Cr^{+3} as a Lewis acid activates the carbonyl group of the aldehyde that placed in empty sites of zeolite. On the other hand, the amino group in 2-aminothiophenol as a powerful nucleophile attacks to this activated carbonyl. Then, after removing of water that carry out by Cr^{+3} helping, the formed imine is activated by Lewis effect of Cr^{+3}.



Scheme 2. Suggested mechanism for catalytic effect Nano-CrY Zeolite.

Therefore, the sulphur atom of 2-aminothiophenole attack to this activated imine and the thiazole cycle is formed that are aromatized to corresponding benzothiazole under reaction conditions.

4. Conclusions

This procedure is simple, effective, inexpensive and green. The products were obtained in high yields and the catalyst is reusable. Since products were obtained by aqua work-up in good purity, so, complex purification methods are not necessary.

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