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Original article

Propylsulfonic acid functionalized nanozeolite clinoptilolite as heterogeneous catalyst for the synthesis of quinoxaline derivatives

Seyed Meysam Baghbanian

Department of Chemistry, Ayatollah Amoli Branch, Islamic Azad University, Amol, Iran

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ABSTRACT

In this work, the natural nanozeolite clinoptilolite (Nano CP) was successfully functionalized by propylsulfonic acid and applied as efficient heterogeneous catalyst for the synthesis of quinoxaline derivatives in aqueous media. The nanocatalyst was characterized by various techniques such as CHN, XRD, FT-IR, BET, TGA/DTA, SEM, TEM and TEM-EDS. The results show its applicability as green, reusable and promising catalyst in organic synthesis. It was found that the nanocatalysts could be recycled and reused eight times without significant loss of catalytic activities.

1. Introduction

Quinoxaline derivatives are important components of pharmacologically active compounds, including antiviral, antibacterial, anti-inflammatory, anti-protozoal, askinase inhibitors, anticancer and anthelmintic agents [1]. In addition, quinoxaline derivatives are reported for their application in dyes, organic semiconductors, rigid subunits in macrocyclic receptors or molecular recognition, efficient electroluminescent materials, chemically controllable switches [2,3]. Generally, quinoxalines are synthesized by the condensation of aryl 1,2-diamines with 1,2-dicarbonyl compounds in MeOH/AcOH [4]. There are several methods for the formation of the quinoxaline ring system in the presence of various catalysts have been reported [5–15]. However, all these methods have some drawbacks in the light of current working performance such as application of toxic reagents, or reagents which are very expensive and less accessible, thermally unstable and formation of side products.

Nanozeolite clinoptilolite is attractive in material supports because of the excellent properties such as ease of availability of the natural, inexpensive, high specific surface area, large pore volumes, good thermal and chemical stability, and non-toxicity. Although many kinds of zeolites were used as catalysts or catalysts supports such as HB, A, NaY, X, Y and ZSM-5, the main drawbacks of these catalysts are low selectivity and using expensive or toxic materials for the synthesis of them on a large scale [16]. Acid treatment causes a modification in morphology of nanozeolite CP by the destruction of channel-blocking impurities and the development of secondary porosity [17]. Therefore, acid treatment increases the number of Si–OH groups, which can be used for the immobilization process. To explore its capability, we intended to investigate on the functionalization of natural nanozeolite clinoptilolite by propylsulfonic acid and applied as catalyst for the synthesis of quinoxalines.

2. Experimental

All chemicals such as 3-mercaptopropyltrimethoxysilane (MPTS), hydrogen peroxide (33 wt%) were purchased from Merck Chemical Company. The raw zeolite material was an Iranian commercial clinoptilolite (Afrandtooska Company) obtained from deposits in the region of Semnan (*ca.* 1 $ per kg). All the other solvents and chemicals were obtained from analytical reagent grade chemicals unless specified otherwise and purchased from Merck Company.

2.1. Synthesis of activated Nano CP

The nanozeolite clinoptilolite (5 g) was taken into a 250 mL round bottom flask and 100 mL 4 mol/L sulfuric acid was added to it. The flask mixture was refluxed for 1 h. After cooling, the

E-mail address: s.m.baghbanian@iauamol.ac.ir.

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supernatant was discarded and the activated nanozeolite CP was repeatedly washed with deionized water (250 mL) until the solution became neutral and finally dried in oven at 80 °C overnight to obtain the white solid product. The activated nanozeolite CP was designated as AT-Nano CP.

2.2. Synthesis of propylsulfonic acid functionalized AT-Nano CP (NZ-PSA)

AT-Nano CP (2 g) was taken into a 50 mL round bottom flask. MPTS (2 mL) was dissolved in toluene (4 mL) and added slowly under vigorous stirring condition. The resulting mixture was stirred at 80 °C for 8 h. The mixture was then filtered and washed with toluene (4 mL) and double distilled water (5 mL) before drying at 100 °C. The oxidation was carried out by contacting the sample (1.0 g) with a solution of hydrogen peroxide (33 wt%) at room temperature and stirred for 12 h. The solid was then filtered, washed abundantly with distilled water, following by drying at 100 °C for overnight.

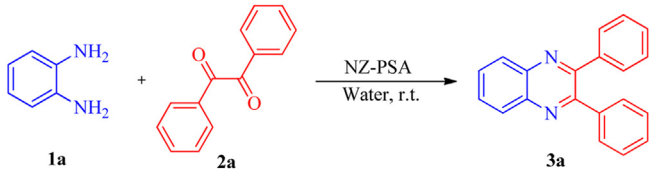
2.3. General procedure for the synthesis of quinoxalines

A mixture of aromatic *o*-diamine (1 mmol), 1,2-dicarbonyl compounds or phenacyl bromides (1 mmol) and NZ-PSA (0.01 g) in 5 mL of water was stirred at room temperature for an appropriate time (Scheme 2). The progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was filtered off. The solvent was evaporated under reduced pressure and the pure product was obtained without any further purification and their spectroscopic data are shown in supporting information.

3. Results and discussion

The nanozeolite CP was prepared according to a simple method developed recently by our group [18a] and subsequently activated with 4 mol/L sulfuric acid. The activated nanozeolite CP was designated as AT-Nano CP. AT-Nano CP was reacted with MPTS in toluene at 80 °C to afforded propylsulfonic acid functionalized nanozeolite CP (NZ-PSA). Afterwards, the NZ-PSA was characterized by various techniques such as CHN, XRD, FT-IR, BET, TGA/DTA, SEM, TEM and TEM-EDS (Supporting information). After synthesis and characterizations of NZ-PSA, the catalytic activities of these nanocatalyst were explored for the synthesis of quinoxaline derivatives. In order to determine the optimum reaction conditions, the reaction of benzene-1,2-diamine **1a** (1 mmol) with benzil **2a** (1 mmol) was examined as a model reaction in water at room temperature (Scheme 1).

The model reaction was carried out in the presence of different catalytic amounts of nanozeolite CP and NZ-PSA the results are presented in Table 1. In the absence of catalyst, only a trace amount of desired product was obtained even after in longer reaction time (entry 1). The results show that both nanocatalysts could promote the reaction, but NZ-PSA catalyst is significantly more effective than nanozeolite CP in the synthesis of quinoxaline **3a** and it provides better results with high yields and short reaction times. In order to optimize the reaction conditions, the catalytic efficiency



Scheme 1. The model reaction for the synthesis of quinoxaline **3a**.

Table 1
Optimization of reaction conditions for the synthesis of quinoxaline **3a**.[a]

Entry	Solvent	Catalyst (g)	Temp. (°C)	Time (min)	Yield (%)[b]
1	H_2O	–	25	120	Trace
2	H_2O	Nano CP [0.01]	25	80	30
3	H_2O	Nano CP [0.01]	80	60	55
4	H_2O	NZ-PSA[0.004]	25	30	85
5	H_2O	NZ-PSA [0.008]	25	15	90
6	**H_2O**	**NZ-PSA [0.01]**	**25**	**10**	**95**
7	H_2O	NZ-PSA [0.02]	25	20	95
8	H_2O	NZ-PSA [0.01]	50	15	95
9	H_2O	NZ-PSA [0.01]	80	15	95
10	EtOH	NZ-PSA [0.01]	25	30	85
11	DMF	NZ-PSA [0.01]	25	45	65
12	Toluene	NZ-PSA [0.01]	25	50	35
13	CH_2Cl_2	NZ-PSA [0.01]	25	45	40

[a] Reaction conditions: Benzene-1,2-diamine (1 mmol), benzil (1 mmol) and solvent (5 mL).
[b] Isolated yields.

was studied with various amounts of nano NZ-PSA in the model reaction (entries 4–6). The results reveal that 0.01 g of NZ-PSA provided the best effects in terms of economy of catalyst charge and purity of products (entry 6). Moreover, higher amounts of the catalyst (0.02 g) did not improve the yield and the reaction time (entry 7). The role of solvents in the reaction was also screened. As shown in Table 1, entries 10–13, it was found that water is a suitable solvent to produce the target products in high to excellent yields and relatively short reaction time in comparison with other solvents. Also, we carried out the model reaction at various temperatures ranging from 25 °C to 80 °C (entries 7–9). The results demonstrate that increase in the reaction temperature did not affect the product yield and reaction time. Consequently, the best results were afforded by the reaction of these components in water (5 mL) in the presence of 0.01 g of NZ-PSA at room temperature obtaining quinoxaline **3a** in a 95% yield (entry 6).

To assess the generality of this approach for the synthesis of quinoxalines, various substituted 1,2-diketones were reacted with structurally and electronically diverse *o*-phenylenediamines, and the results are summarized in Scheme 2, **3a**-**j**. It was observed that electron-donating groups had no significant effect on the reaction results (**3b**,**g**,**h**,**i**). Moreover, other 1,2-diketones such as 9,10-phenanthraquinone (**3c**,**h**,**i**), acenaphthoquinone (**3d**,**g**), and indantrione (**3e**,**f**) were examined in this reaction and corresponding quinoxalines were produced in the short time and excellent yield. In following to further explore the potential of this protocol, we also examined the synthesis of quinoxalines using another reactant, phenacyl bromide derivatives instead of 1,2-diketones under similar reaction conditions (Scheme 2). Results demonstrate that all *p*-chloro and bromophenacylbromide were reacted with *o*-phenylenediamines to provide the corresponding products in good yields (**5a**-**i**).

The reaction was clean and the products were obtained in high yields without the formation of any by-products. All the products prepared were known compounds and their structures were characterized with use of the spectral methods (^{1}H NMR and ^{13}C NMR) and comparison with authentic samples (Supporting information). The recyclability of the catalyst for reactions was investigated for the synthesis of quinoxaline under the optimized reaction conditions. The catalyst was recovered by filtration technique after each experiment and washed with hot distilled ethanol (2 mL) twice and drying at 80 °C in an oven to provide an opportunity for recycling experiments. The separated nanocatalyst was reused successively eight times without any significant loss of activity (Fig. S7 in Supporting information). The strong interaction of MPTS grafted on the surface of AT-Nano CP could be the reason