ORIGINAL ARTICLE

Conversion of acids to benzimidazoles with transition metal/zeolites

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Abstract Transition metal/Y zeolites were prepared using microwave solid state and aqueous solution ion exchange methods. The activity of these zeolites was investigated in a conversion of acids to benzimidazoles reaction between 4-methyl-1, 2-phenylenediamine and 3-nitrobenzoic acid. The yield of these reactions increased in order of $CuY < Fe^{2+}Y < NiY < CoY < NaY < CrY < MnY < ZnY$ for both methods. The solid state ion-exchanged zeolites showed higher activity in comparison to the aqueous solution exchange. Yields of products in the presence of the ZnY zeolite were of the order of 69–83%. It seems that the Lewis sites are better sites compared to the Bronsted sites for this reaction.

Keywords Benzimidazole · Ion-exchange · Acid sites · Zeolite

Introduction

A large variety of benzimidsoles are reported to exhibit chemotherapeutic [1–6] and biological effects [7–9]. Substituted benzimidazoles have commercial applications in veterinarian medicine as anithelmintic agents and in diverse human therapeutic areas such as treatment of ulcers and as antihistaminic [10]. Recently, it has been found that two groups of benzimidazoles,

namely the 5,6-dinitro and 2-trifiuoromethyl derivatives to be promising candidates for antimicrobial drugs [11].

Benzimidazoles are generally synthesized by cyclo-condensation reaction of *o*-phenylenediamines with carboxylic acids or derivatives. However, synthesis of benzimidazoles from carboxylic acids, especially aryl carboxylic acids and hindered alkanoic acids, and *o*-phenylinediamine needs vigorous reaction conditions or expensive non-available materials. Several authors have reported such different vigorous conditions for synthesis of different benzimidazoles [12].

Zeolites are crystalline hydrated aluminosilicates of the alkaline earths. It is well known that the acidic sites of zeolite can be catalyzed organic reactions. The acidity of the zeolite could be due to Bronsted and Lewis sites [13]. Study of the organic reactions catalyzed by zeolite indicated that the Bronsted and Lewis acid sites are both important in the catalytic activity of zeolite. The Bronsted acid sites can be increased by exchange of monovalent ions with polyvalent cations with the hydrolysis process [14], which is very useful for the under hydrolysis acid catalyst reactions such as acylation, alcohol dehydration [15], estrification [16] and Diels-Alder reaction [17].

Dehydration reaction, which is carried out above 875 K, decreases the number of the proton sites and increases the number of Lewis sites [18]. The ion exchange process between zeolites and metal-containing species undergoes in the solid state phase at high temperature for a long periods of time [19]. However, the time of the ion exchange process can be reduced under microwave irradiation [20]. The metal/zeolites are prepared in the solid state phase ion exchange under microwave irradiation, which Lewis sites increased [21]. Interestingly, in the other reactions,

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such as intramolecular acylation [16] and isomerization [22], Lewis centers are the active sites.

Hence, a literature review explains that rare earth elements have positive effect on zeolite thermal stability. In fact, it is acknowledged that cations have a more pronounced stabilizing effect than monovalent cations; whereas zeolites exchanged with trivalent cations tend to be the more stable ones [23–25].

In this study, conversion of acids to benzimidazoles was carried out in the presence of transition metal/Y zeolites, which have been prepared by solution ion exchange and solid state ion exchange methods. Microwave irradiation was used to reduce the periods of time for the solid state ion exchange methods. Also the effect of zeolites using the ion exchange method in conversion of acids to benzimidazoles reactions was investigated.

Experimental

^{1}H NMR spectra were recorded on a Bruker (300 MHz) Spectrometer. TMS was used as an internal standard. The IR spectra were recorded on Glaxy FT-IR 500 Spectrometer. All products were characterized by comparison of their spectra (IR, H^1 NMR) with those of authentic samples, or prepared under reflux.

Preparation of zeolite catalyst

Zeolite NaY was prepared and activated according to the procedure described previously [26]. Two different routes were used to prepare metal/Y zeolites.

(A) 200 ml of 0.01 M solutions of metal salts (CrCl$_3$.6H$_2$O, FeCl$_3$.4H$_2$O, MnCl$_2$.4H$_2$O, CoCl$_2$.6H$_2$O, NiCl$_2$.6H$_2$O, CuCl$_2$.2H$_2$O and ZnCl$_2$) were added to 2 g of NaY in a 250 ml flask. The mixture was stirred for 24 h and then filtered. The obtained solid was washed with water until a colorless filtrate was observed. The final zeolite products were dried at room temperature.

(B) 2 g of zeolite and 2 mmol of each metal salts listed above were mechanically mixed, ground and heated in a microwave oven for 10–20 min at 900 W power.

Last study showed that metal salts are completely dispersed and ion exchanged on zeolite [27].

General preparation of 3-nitrobenzimidazoles

To a solution of 4-methyl-1, 2-phenylenediamine (0.001 mol) in ethanol (30 mL), appropriate aromatic acid (0.00125 mol) and metal/zeolite Y (0.15 g) was added. The reaction mixture was refluxed for 10 h. The used catalyst was collected by filtration and then washed with ethanol. The crude product was recrystallized from water and ethanol (30:70 mL) or from benzene.

Results

Table 1 shows the results of a conversion of acids to benzimidazoles reaction between 4-methyl-1, 2-phenylenediamine and 3-nitrobenzoic acid. 2-Aryl substituted benzimidazole was the single product of this reaction. The zeolite, which was used as a catalyst in these reactions, was ion exchanged by microwave in the solid state and in the aqueous solution. The reaction was carried out 3–4 times, where the catalyst was activated for 2 h. In each case, yield was decreased about 4–5%. Also the results of measurement the concentration of cations in metal/zeolite that determined by using atomic absorption after reaction show approximation were similar to those reported before [27]. The infrared spectra of product showed that the peak of the carbonyl at about 1,680 cm^{-1} disappeared. ^{1}H NMR in DMSO-d$_6$: 6.1–8.6 (m, 7H); 2.05(s, 3H).

Discussion

Table 1 shows the following catalytic activity for ion exchange zeolite: CuY < Fe^{2+}Y < NiY < CoY < NaY < CrY < MnY < ZnY, with ZnY showing the highest activity for two sets of catalyst. The yield for this reaction was higher when solid state ion-exchanged metal zeolite was used. It appears that reactions are catalyzed by Lewis sites. Since these reactions are

Table 1 The yield (%) of the conversion of acids to benzimidazoles between 4-methyl-1, 2-phenylenediamine and 3-nitrobenzoic acid
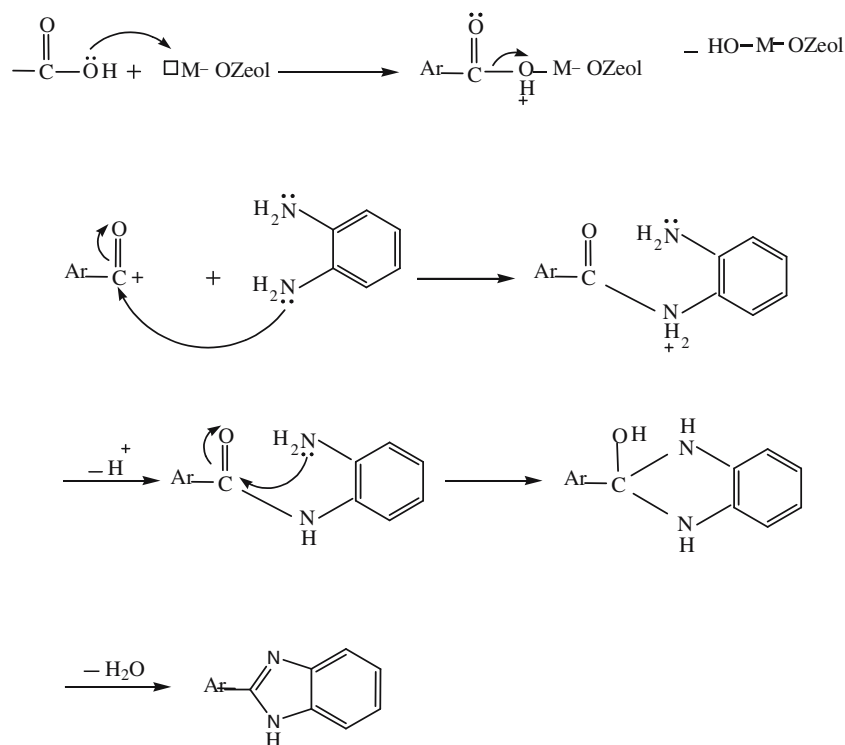
	CrY	Fe^{2+}Y	MnY	CoY	NiY	CuY	ZnY	NaY
Aq[b]	53.4	38.2	53.8	43.5	39.3	34.9	69.2	51.2
M.W[c]	64.3	56.2	76.6	62.1	61.8	52.6	83	

[a] All products characterized by ^{1}H NMR, FT-IR

[b] Ion-exchange in aqueous solution

[c] Ion-exchange in solid state by microwave

catalyzed by acid, the acidity is strongly linked with the type of cation and will vary with the degree of cation exchange. Furthermore, pervious studies showed a synergy between the Bronsted and Lewis acid sites, and the number of Bronsted sites increases by adsorption of water on Y zeolite [15, 27]. Interestingly, in the present study, we found that by using hydrated zeolite ion-exchanged under microwave condition, the yield of the reaction decreased by 10%. Apparently, in the microwave solid state ion exchange the water bonded to the zeolite decreases at high temperature and consequently the number of Lewis acid sites increases. Therefore, the nature of the acid site is related to the type of metal centers in addition to thermal pretreatement. It seems the ion exchange in solid state increases the Lewis acid sites [28]. These Lewis acid sites may be formed through the following mechanism

to form–O–Zn–Cl under microwave irradiation, which are as new Lewis acid sites [29].

Conclusion

The nature of cations and the method of exchange was influenced the catalytic activities of the transition metal cation exchanged zeolites. The good correlation between the yields of the reaction of 4-methyl-1, 2-phenylenediamine with 3-nitrobenzoic acid in the presence of different transition metal/zeolite cation exchanges in aqueous solution suggests that the active centers are mostly Lewis sites.

In conclusion, excellent rate was observed in the conversion of acids to benzimidazoles in the presence of the metal salt/zeolites.

The results indicated that ZnY zeolite shows the highest activity for conversion of acids to benzimidazoles reaction for the two sets of catalysts. Because of the small ions, such as Zn^{2+}, Cu^{2+}, etc, high degrees of ion exchange are observed. It seems to us that $ZnCl_2$ has dispersed completely onto the surface of NaY zeolite under microwave irradiation. Also some of the dispersed $ZnCl_2$ reacted with the oxygen ions of zeolite

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