

## Diels-Alder Reaction with Transition Metal/Zeolites

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### Abstract

Transition metal/Y zeolites were prepared by microwave solid state and aqueous solution ion-exchange methods. The activity of these zeolites was investigated in a Diels–Alder reaction of cyclopentadiene and maleic anhydride, anthracene and maleic anhydride. The yield of these reactions increased in order of (NaY < Fe<sup>2+</sup>Y < Fe<sup>3+</sup>Y < MnY < CuY ≈ NiY < CoY ≈ CrY < ZnY) for both methods. The aqueous solution ion-exchanged zeolites showed higher activity in comparison to solid state exchange. About 65–70% yield was observed for the Diels–Alder reaction with ZnY Zeolite. Endo-selectivity was observed for these reactions.

### Introduction

The Diels–Alder reaction is an important tool in the synthesis of cyclic compounds. Several inorganic compounds, such as silica gel [1], alumina [2], clays [3], mesopores [4], and zeolites [5] have been used as catalysts in Diels–Alder reactions.

According to literature reports, using zeolites, the conditions of reaction, such as temperature and pressure, are mild [6]. Moreover, use of these catalysts have afforded highly regioselective and diastereoselective reactions with good yields [7].

Extensive research shows that these reactions are catalyzed by the acidic sites of zeolite. The zeolite acidity could be due to Broensted and Lewis sites [8]. The exchange of monovalent ions with polyvalent cations creates very strong Broensted acidic centers by the hydrolysis phenomena [9]. The ion-exchange properties of zeolite are important for the acid catalyst reaction. It is well known that the dehydration reaction occur above 875 K, which decreases the number of proton sites and increases the number of Lewis sites [10]. Both Broensted and Lewis sites can be present simultaneously in the structure at high temperature.

The ion-exchange between zeolites and metal-containing species can be carried out in the solid state phase at high temperature for a long duration of time [11]. This time can be reduced by microwave irradiation [12]. The metal/zeolites prepared by solid state ion-exchange with use of microwave irradiation in Intramolecular Acylation reactions [13]. A literature survey on organic reactions catalyzed by zeolite indicates that in the majority of them, Broensted and Lewis acid centers are simultaneously important in the

catalytic activity of zeolites. Interestingly, it has been demonstrated that in some reactions, such as acylation, alcohol dehydration [14] and estrification [13], the Broensted centers of zeolites are the active sites; in the other reactions, such as isomerization [15] and intramolecular acylation [13], Lewis centers are the active sites.

In this work, we carried out Diels–Alder reactions with the use of transition metal/Y zeolites. These zeolites have been prepared by solution ion-exchange and solid state ion-exchange methods. Microwave heating was used to decrease the amount of time for the solid state ion-exchange methods. The purpose of present study is to understand the effect of zeolites using the ion-exchange method in Diels–Alder reactions. The results may allow for the tailoring of zeolites to specific reactions.

### Experimental

#### *Preparation of zeolite catalyst*

Zeolite NaY was prepared and activated according to the procedure described previously [16]. Two different routes were used to prepare metal/Yzeolites.

A. 200 ml of 0.01 M solutions of metal salts (CrCl<sub>3</sub>·6H<sub>2</sub>O, FeCl<sub>2</sub>·4H<sub>2</sub>O, FeCl<sub>3</sub>·4H<sub>2</sub>O, MnCl<sub>2</sub>·4H<sub>2</sub>O, CoCl<sub>2</sub>·6H<sub>2</sub>O, NiCl<sub>2</sub>·6H<sub>2</sub>O, CuCl<sub>2</sub>·2H<sub>2</sub>O and ZnCl<sub>2</sub>) 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.

Table 1. Diels–Alder reaction yields of cyclopentadiene with maleic anhydride<sup>a</sup>

	CrY	Fe <sup>2+</sup> Y	Fe <sup>3+</sup> Y	MnY	CoY	NiY	CuY	ZnY	NaY
Aq <sup>b</sup>	63	51	53	56	64	59	59	68	40
M.W <sup>c</sup>	60	45	47	55	60	50	50	65	

<sup>a</sup> All products characterized by <sup>1</sup>H-NMR, FT-IR.

<sup>b</sup> Ion-exchange in aqueous solution.

<sup>c</sup> Ion-exchange in solid state by microwave technique.

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

As shown in the previous study [16] metal salts completely disperse at such conditions and ions-exchange in zeolite.

### Diels–Alder reactions

1 mmol of dienophile (maleic anhydride) and 1 mmol of diene (freshly distilled cyclopentadiene and anthracene) were added to 20 ml of CH<sub>2</sub>Cl<sub>2</sub> containing 1 g of metal salts zeolite. The mixture stirred for 4 h under nitrogen atmosphere at 0 °C. After filtration, the filtrate was concentrated under reduced pressure by a rotary evaporator. Uncatalyzed Diels–Alder reactions showed only trace amounts of product.

### Characterization of the products

<sup>1</sup>H-NMR and FT-IR spectroscopy were used to characterize all products obtained from the Diels–Alder reactions. Infrared spectra were recorded on Galaxy serie FT-IR 5000. <sup>1</sup>H-NMR spectra were recorded on Broker 60. 500 MHZ.

Microwave solid state ion-exchanged zeolites were fully characterized and results will be reported elsewhere.

### Results

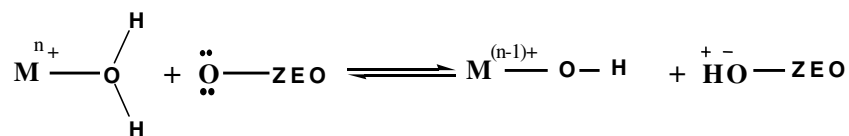
Table 1 shows the results of a Diels–Alder reaction between cyclopentadiene and maleic anhydride. The

zeolite, which was used as catalyst in these reactions, was ion-exchanged by microwave technique described above. The infrared spectra of the product showed that the peak of the conjugated double bond of the cyclopentadiene at about 1600 ~ 1650 cm<sup>-1</sup> disappeared. <sup>1</sup>H-NMR in DMSO: 6.3(M, 2H); 3.7(S, 2H); 3.35(S, 2H); 1.6(T, 2H).

Table 2 shows the results of a Diels–Alder reaction between anthracene and Maleic anhydride with metal salts/zeolite. <sup>1</sup>H-NMR in DMSO: 7.4(T, 2H); 7.3(T, 2H); 7.1(M, 4H); 4.9(M, 1H); 3.6(M, 1H); 2.5(T, 2H). The results show high endo-selectivity (> 95%) for these reactions.

### Discussion

Tables 1 and 2 show the following catalytic activity for ion-exchange zeolite: NaY < Fe<sup>2+</sup>Y < Fe<sup>3+</sup>Y < MnY < CuY ≈ NiY < CoY ≈ CrY < ZnY, with ZnY showing the highest activity for two sets of catalyst. The yield for these reactions was higher when aqueous solution ion-exchanged metal zeolite was used. It appears that these reactions are catalyzed with Broensted sites. Since these reactions are catalyzed with acid, the acidity is strongly linked with the kind of cation and will vary with the degree of cation-exchange. For the small ions, such as Zn<sup>2+</sup>, Cu<sup>2+</sup>, etc., high degrees of ion-exchange are observed. When zeolite is in the hydrated form, all the metal cations are solvated by water molecules, and Broensted acid sites are formed through the following mechanism [17].

Table 2. Diels–Alder reaction yields of anthracene with maleic anhydride<sup>a</sup>

	CrY	Fe <sup>2+</sup> Y	Fe <sup>3+</sup> Y	MnY	CoY	NiY	CuY	ZnY	NaY
Aq <sup>b</sup>	64	41	48	54	64	61	61	66	33
M.W <sup>c</sup>	63	39	45	48	61	50	50	64	–

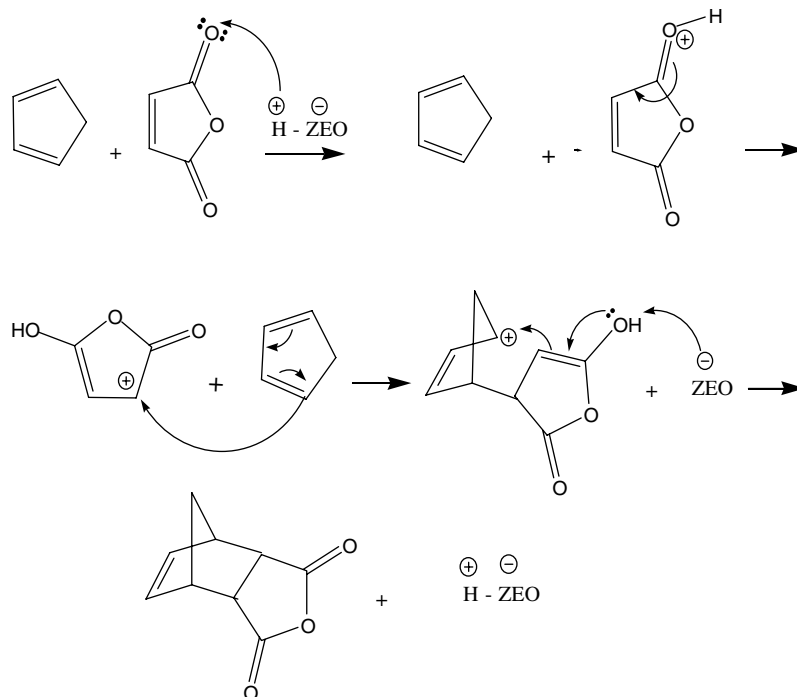
<sup>a</sup> All products characterized by <sup>1</sup>H-NMR, FT-IR.

<sup>b</sup> Ion-exchange in aqueous solution.

<sup>c</sup> Ion-exchange in solid state by microwave technique.

On the other hand, when the degree of ion-exchange increases, more acid sites develop in zeolite. In this work, the high degree of exchange with  $Zn^{2+}$ ,  $Cu^{2+}$ ,  $Cr^{3+}$ , etc., is reflected in the better catalytic activity. It has also been suggested that the increase in acidity is due to an increase in the electrostatic field of the cation [18].

The following mechanism may be proposed for the Diels–Alder reaction in the present study.



The predominant frontier molecular orbital interaction in a Diels–Alder reaction involves the diene HOMO and dienophile LUMO. The mode of action of the Brønsted acid appears to involve coordination of the carbonyl group of the dienophile. The interaction has the effect of lowering the energy level of the LUMO of the dienophiles, enabling it to be more efficient in overlapping with the HOMO of the diene. Therefore, the reaction proceeds with great efficiency. Results were observed for these Diels–Alder reactions show that there is high endo-selectivity. These results were observed for some of the Diels–Alder reactions with a variety of zeolites [7].

## Conclusion

The nature of cations and the method of exchange influenced the catalytic activities of the transition metal cation-exchanged zeolites. The good correlation between yields of Diels–Alder reactions with different transition metal/zeolite cation-exchange by aqueous solution suggests that the active centers are mostly Brønsted sites.

In conclusion, excellent rate and stereoselectivities were observed in the Diels–Alder reactions carried out with metal salt/zeolites.

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