

# ZnCl<sub>2</sub> supported on NaY zeolite by solid-state interaction under microwave irradiation and used as heterogeneous catalysts for high regioselective Diels–Alder reaction of myrcene and acrolein

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## Abstract

A novel catalyst preparation method is developed by solid-state interaction between ZnCl<sub>2</sub> and NaY zeolite under microwave irradiation. The solid-state interaction is investigated by powder X-ray diffraction, FT-IR spectroscopy, and by testing the catalytic properties in the Diels–Alder reaction of myrcene and acrolein. XRD patterns indicate that ZnCl<sub>2</sub> can disperse completely on the surface of NaY zeolite at the ZnCl<sub>2</sub> loading less than 2.75 mmol g<sup>-1</sup>. FT-IR spectra of pyridine adsorption on catalyst show that Lewis acid sites are the predominant acid sites. The catalyst of ZnCl<sub>2</sub>/NaY prepared by the treatment of microwave irradiation is proved to be an effective heterogeneous catalyst for high regioselective Diels–Alder reaction of myrcene and acrolein. The catalytic activity and the regioselectivity of *p/m* strongly depend on the ZnCl<sub>2</sub> loading. With an increase of the ZnCl<sub>2</sub> loading up to 0.92 mmol g<sup>-1</sup>, the activity and selectivity increase a little. In this case, the active site is deduced from the zinc ion species formed by solid-state ion exchange. The Lewis acid sites are too weak to catalyze efficiently the Diels–Alder reaction. Keeping an increase of ZnCl<sub>2</sub> loading from 0.92 mmol g<sup>-1</sup> to 1.84 mmol g<sup>-1</sup>, the activity and the regioselectivity of *p/m* increased markedly due to the formation of new zinc ion species of –O–Zn–Cl as Lewis acid sites on NaY zeolite. The catalysts leached with a mixture solvent of acrolein and dichloromethane show little loss of catalytic activity and selectivity. Thanks to the possibility of simple and safe handling of the ZnCl<sub>2</sub>/NaY and to its easy separation from organic products, it becomes an alternative Lewis acid catalyst for the Diels–Alder reaction to homogeneous Lewis acids.

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**Keywords:** Zinc chloride; NaY zeolite; Microwave irradiation; Diels–Alder reaction; Myrcene; Myrac aldehyde

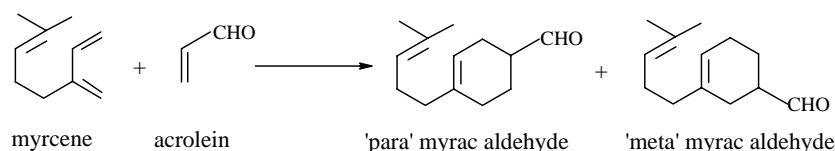
## 1. Introduction

The Diels–Alder reaction of myrcene (7-methyl-3-methene-1,6-octadiene) prepared by cracking β-pinene from turpentine oil, gives rise to a variety of fragrant compounds and their intermediates when reacting with a conjugated alkylene carbonyl compound [1–5]. The regiochemistry of the cyclohexene derivatives often include ‘*para*’ and ‘*meta*’ adduct, which is outlined in Scheme 1. In general, the ‘*para*’ adduct is more important than the ‘*meta*’ adduct in the synthesis of new perfumes, medical drugs, and biological active substances [1,2,6–9]. For example,

the ‘*para*’ myrac aldehyde (4-(4'-methyl-3'-pentyl)-Δ<sup>3</sup>-cyclohexenecarboxaldehyde) and their derivatives are often used “as is” in perfumery. Furthermore, the products with a pleasant ‘woody and fruity ambergris smell’, which is from the subsequent cyclization of the ‘*para*’ cycloadducts, have been found to be very useful in perfumes, colognes, cosmetic powders and dryer-added fabric softeners articles, as well as in cigarette and smoking tobacco articles [8]. How to improve the regioselectivity of ‘*para*’ cycloadduct for the Diels–Alder reaction therefore becomes considerable practical interest. Homogenous Lewis acids are often used as catalysts for accelerating the reaction and enhancing the regioselectivity and stereoselectivity. The catalyst of ZnCl<sub>2</sub> showed excellent regioselectivity and activity for the Diels–Alder reaction of myrcene and acrolein [10]. However, it is well known that the homogenous Lewis acids have

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Scheme 1. The Diels–Alder reaction of myrcene and acrolein.

serious drawbacks such as the use of more than one molar equivalent, laborious work-up procedures and problems with environmentally hazardous waste-streams.

It has been found that several inorganic solids, such as alumina [11], zeolite [12], clays [13], mesoporous aluminosilicate (Al-HMS) [14,15] are efficient catalysts in Diels–Alder reactions of cyclopentadiene. Mayoral and co-workers found that clay calcination improved the activity of the catalyst, which can be recovered without a loss of its catalytic activity [16]. However, in reactions of carbonyl-containing dienophiles, the activity is far less than that of traditional Lewis acids in homogeneous reactions. Given the interest of Diels–Alder reactions, it is important to search for solid with better catalytic properties for reaction of carbonyl-containing dienophiles. Lewis acids supported on solids can take the advantages of Lewis acids and inorganic solid, in which many studies have been carried out showing that the modified catalysts can be successfully used in obtaining the high reactivity and selectivity for the Diels–Alder reaction [13–22]. The modified Lewis acids catalysts are usually prepared by the reaction of mono- and di-surface hydroxyl group on the support of silica, alumina, K10 montmorillonites, zeolite, and Al-HMS with Lewis acids of  $\text{BF}_3$ ,  $\text{ZnCl}_2$ ,  $\text{FeCl}_3$ , aluminium and titanium derivatives (chlorides, ethyl and diethyl aluminium chlorides, titanium diisopropoxide dichloride, titanium tetraisopropoxide). The resulting catalysts contain mainly Lewis acid sites, which are effectively used in the Lewis acid-catalyzed organic reaction.

Recently, immobilization of anhydrous  $\text{AlCl}_3$  on mesoporous silicate of MCM-41 and anhydrous  $\text{ZnCl}_2$  impregnated on Mont-K10 were reported by Zhao and Choudhary, respectively [23,24]. The anhydrous chlorides supported on porous solid by the solvent impregnation method possess strong Lewis acid properties for the liquid-phase Lewis acid catalyzed reaction. One disadvantage of this method for industrial applications is the handling of large volumes of solutions during the preparation process of the catalysts. Thus, an alternative method of dispersing active species by solid-state reaction has attracted increasing attention in the last decade [25–30]. The solid-state interaction between  $\text{ZnCl}_2$  and NaY zeolite has been carried out in our early studies indicated that  $\text{ZnCl}_2$  can be completely dispersed onto the surface of NaY zeolite at the  $\text{ZnCl}_2$  loading less than 37.5 wt.% [28]. It is found that the dispersed  $\text{ZnCl}_2$  undergoes solid-state ion exchange with  $\text{Na}^+$  and coordinates with oxygen from the surface of the support. However, the surface acidic properties of the catalyst are still not defined.

Based on both practical and scientific interest, we reported here a more detailed investigation of the preparation method of  $\text{ZnCl}_2/\text{NaY}$  catalyst by activation of microwave irradiation and used as a heterogeneous catalyst for high regioselective synthesis of myrac aldehyde. The surface acidic nature created during the solid-state interaction under microwave irradiation was evaluated by the catalytic performance in the Diels–Alder reaction.

## 2. Experimental

### 2.1. Materials

Myrcene prepared by cracking  $\beta$ -pinene was described elsewhere [31]. Anhydrous  $\text{ZnCl}_2$  was prepared by using dichlorosulfoxide ( $\text{SOCl}_2$ ) to dehydrated  $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$  [10], the left  $\text{SOCl}_2$  was then removed by distillation under vacuum. The obtained anhydrous  $\text{ZnCl}_2$  was kept in a vacuum desiccator with potassium hydroxide over night prior to use. Acrolein was purchased from Aldrich and freshly distilled before use. NaY and Na-ZSM-5 zeolite (Si/Al ratio 2.6) obtained from Changling oil refine Corp., China, were calcined at  $550^\circ\text{C}$  for 5 h prior to use.

HY zeolite was prepared by NaY zeolite (20 g) suspended in 200 ml of 1 M ammonium chloride solution. The slurry was stirred at  $90^\circ\text{C}$  for 6 h, filtered and washed chloride free with deionised water. The ion exchange operation was repeated five times. The resulting solid was dried in an oven at  $110^\circ\text{C}$  for 6 h, and then calcined in a muffle furnace at  $550^\circ\text{C}$  for 3 h.

ZnNaY zeolite was prepared by ion exchange of a 1 M aqueous  $\text{ZnCl}_2$  solution and NaY (pH = 6.0) with a liquid/solid mass ratio of 10 at  $90^\circ\text{C}$  for 6 h. The mixture was then filtered and washed chloride free with deionised water. The following drying and calcined procedures were same to the preparation of HY zeolite. The degree of ion exchange of 71% was determined by atomic absorption spectrometry (AAS).

### 2.2. Preparation of catalysts

Mixtures of NaY zeolite and anhydrous  $\text{ZnCl}_2$  with different loading were ground in an agate mortar to obtain well-powder and homogenized samples. The resulting mixtures were irradiated in a microwave oven at 650 W, 2450 MHz for 15 min, and then the catalyst was removed from the microwave oven while hot and it was kept in a

desiccator to cool to room temperature prior to use. For comparison, another catalyst prepared by heating method was also involved in this study. The well-powder and homogenized sample of NaY zeolite and anhydrous  $\text{ZnCl}_2$  was heated in a muffle furnace at  $200^\circ\text{C}$  for 1 h, and then the catalyst was transferred to a desiccator to cool to room temperature. The physical mixtures sample of  $\text{ZnCl}_2$  and NaY was prepared by simple grinding the mixtures only.

### 2.3. Catalyst characterization

The powder X-ray diffraction (XRD) patterns of the samples were recorded on a Siemens D 500 diffractometer using  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.542 \text{ \AA}$ ). Infrared spectra were collected on a Nicolet 510P FT-IR spectrophotometer. Acidic properties of the samples were determined by chemical adsorption of pyridine as a probe molecule on self-supported wafers. The wafers were compressed under  $5 \text{ t/cm}^2$  pressure to obtain thin disks 12 mm in diameter with a thickness of ca. 3 mm. The resulting wafers were placed in cells (equipped with KBr windows and connected via stopcocks to a vacuum line) where the treatment of the catalysts was performed. Catalyst was activated in an IR cell at  $200^\circ\text{C}$  under vacuum for 1 h, cooled down to  $100^\circ\text{C}$ , followed by exposure to pyridine at this temperature for 30 min. The sample was then evacuated at this temperature under vacuum ( $10^{-5}$  Torr) for 1 h to remove physical adsorbed pyridine. Finally, the spectrum was recorded at room temperature.

### 2.4. General procedure for Diels–Alder reaction of myrcene

Under argon, 42.8 mmol of acrolein was added to a suspension of the catalyst (1 g) in 5.0 ml of freshly distilled dichloromethane with vigorously stirring in a magnetic stirrer. After the mixture was heated up to  $30^\circ\text{C}$ , 35.3 mmol of myrcene was added via a syringe. The reaction was monitored by gas chromatography (FID, SE-30 column,  $25 \text{ m} \times 0.25 \text{ mm}$ ), nitrogen as a carrier gas, injector temperature  $200^\circ\text{C}$ , the detector temperature  $180^\circ\text{C}$ , oven temperature program  $120^\circ\text{C}$  (4 min)  $\rightarrow 24^\circ\text{C}/\text{min} \rightarrow 190^\circ\text{C}$  (9 min), using *trans*-naphthene as an internal standard substance. After completion of the reaction, the catalyst was filtered, washed with dichloromethane. The filtrate was washed with saturated aqueous sodium chloride, and then dried with anhydrous magnesium sulfate. The resulting solution was distilled and purified under vacuum. The product of myrac aldehyde was identified with a GC-MS and FT-IR spectra, which is in good agreement with the authentic sample.  $m/z$ : 192 [ $M^+$  peak], 177 [ $192\text{-CH}_3$ ] $^+$ , 149 [ $177\text{-CHO}$ ] $^+$ , 122 [ $192\text{-CH}_2\text{CH=CHO}$ ] $^+$ , 93 [ $122\text{-CHO}$ ] $^+$ , 69 [ $(\text{CH}_3)_2\text{=CHCH}_2$ ] $^+$ , 41 [ $\text{CH}_2\text{=CH-CH}_2$ ] $^+$ , 29 [ $\text{-CHO}$ ] $^+$ . IR  $\text{cm}^{-1}$ : 2820, 2720, 1730, 1390, 1370, 1205 and 805.

## 3. Results and discussion

### 3.1. Catalyst characterization

Some salts can disperse spontaneously onto the surface of a suitable support with a highly specific surface after the heat treatment, which can be identified by the disappearance of the crystalline phase of the salts from their XRD patterns [32]. The XRD patterns of  $\text{ZnCl}_2$  and  $\text{ZnCl}_2/\text{NaY}$  samples prepared by different methods are shown in Fig. 1. It can be seen that the appearance of diffraction peak of  $\text{ZnCl}_2$  is apparent in the XRD pattern ( $2\theta = 16.3^\circ$ ) of the physical mixture sample of  $\text{ZnCl}_2/\text{NaY}$  (Fig. 1(a)). The peaks of crystalline  $\text{ZnCl}_2$  do not disappear but are slightly reduced after the heat treatment at  $200^\circ\text{C}$  for 1 h (Fig. 1(b)). It suggests that heating at this temperature can help  $\text{ZnCl}_2$  to disperse onto the surface of NaY zeolite, but not to diffuse sufficiently. However, The crystalline phase of  $\text{ZnCl}_2$  has vanished in the sample of  $\text{ZnCl}_2/\text{NaY}$  when the mixture of  $\text{ZnCl}_2$  and NaY zeolite was irradiated by microwave even at high  $\text{ZnCl}_2$  loading of  $2.75 \text{ mmol g}^{-1}$  (Fig. 1(c)). It is found that no solid solutions has been formed between  $\text{ZnCl}_2$  and NaY zeolite after the sample was treated via microwave irradiation. Our early studies revealed that the zinc ions took place solid-state ion exchange with the  $\text{Na}^+$  in NaY zeolite, and also some of the dispersed  $\text{ZnCl}_2$  reacted with the oxygen ions to form  $\text{-O-Zn-Cl}$  under microwave irradiation [28]. The surface bond between the dispersed  $\text{ZnCl}_2$  and the oxygen of support is usually strong enough which could be verified by IR spectra. Choudary et al. also found that an

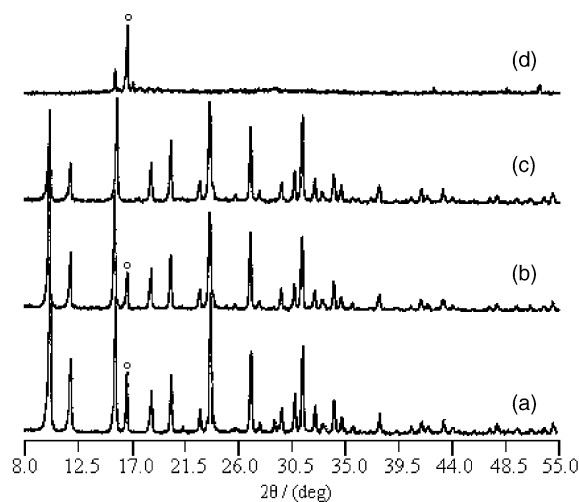


Fig. 1. XRD patterns of (a–c)  $\text{ZnCl}_2/\text{NaY}$  samples prepared by different methods and (d)  $\text{ZnCl}_2$ . (a) the physical mixture of  $\text{ZnCl}_2$  ( $0.92 \text{ mmol}$ ) and NaY zeolite (1 g), (b) the mixture of  $\text{ZnCl}_2$  and NaY zeolite prepared by heating method at  $\text{ZnCl}_2$  loading of  $2.75 \text{ mmol g}^{-1}$ , (c) the mixture of  $\text{ZnCl}_2$  and NaY zeolite prepared by microwave irradiation at  $\text{ZnCl}_2$  loading of  $2.75 \text{ mmol g}^{-1}$ . The symbol of ‘o’ in the XRD patterns is the crystal phase of  $\text{ZnCl}_2$ .

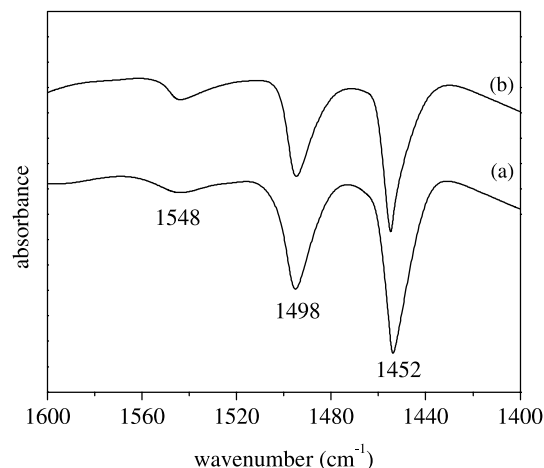


Fig. 2. FT-IR spectra of pyridine adsorbed on samples of (a)  $\text{ZnCl}_2/\text{NaY}$  prepared by microwave irradiation, and (b) the physical mixture of  $\text{ZnCl}_2/\text{NaY}$ .  $\text{ZnCl}_2$  loading in the two samples is  $2.75 \text{ mmol g}^{-1}$ .

occurrence of reaction between  $\text{ZnCl}_2$  and the surface hydroxyl groups of the Mont-K10 clay leading to formation of new Lewis acid sites ( $-\text{O}-\text{Zn}-\text{Cl}$ ) by the thermal activation [24]. And also, the solid-state ion exchange reaction by heating treatment makes zinc cation distributions more homogeneous than the conventional ion exchange from salt solution to form  $\text{ZnY}$  zeolite [33]. It is also noted that some loss of crystallinity of  $\text{NaY}$  zeolite take place in this sample, which can not be exclusively attributed to the dilution effects caused by high  $\text{ZnCl}_2$  loading.

Fig. 2 shows the pyridine-FTIR spectra of (a)  $\text{ZnCl}_2/\text{NaY}$  and (b) the physical mixture of  $\text{ZnCl}_2$  and  $\text{NaY}$  zeolite. It can be seen both of the two samples exhibit bands at 1548, 1498 and  $1452 \text{ cm}^{-1}$ . The band at  $1548 \text{ cm}^{-1}$  is attributed to Brönsted acid sites, the band at  $1452 \text{ cm}^{-1}$  is assigned to Lewis acid sites, and the band at  $1498 \text{ cm}^{-1}$  is assigned to a combination signal associated with both Brönsted and Lewis acid sites. Judged from the IR spectra, Lewis acid sites are the predominant acid sites for the two samples. However, the

intensity of the band around  $1548 \text{ cm}^{-1}$  in the  $\text{ZnCl}_2/\text{NaY}$  sample treated with microwave irradiation is less intense than that in the physical mixture. It is suggested that the Brönsted acidity in the physical mixture of  $\text{ZnCl}_2/\text{NaY}$  may be induced by polarization of their solvating water molecules when grinding the mixture.

### 3.2. Effect of catalyst preparation method on catalytic properties

The catalytic properties of the various catalysts are evaluated in terms of the conversion of myrcene (activity), the selectivity of the cycloadducts, and the regioselectivity ( $p/m$ ). The results of the Diels–Alder reaction between myrcene and acrolein in the absence or presence of various catalysts prepared by different methods are summarized in Table 1. Without catalyst, the thermal reaction is too slow and exhibits poor regioselectivity (entry 1). The parent  $\text{NaY}$  zeolite without acidic properties shows similar results to that of thermal reaction (entry 2). It is expected that the catalytic activity and regioselectivity increase over  $\text{HY}$  zeolite catalyst due to its relative strong acidic properties, but the selectivity of the cycloadducts decreases a little (entry 3). When  $\text{ZnNaY}$  zeolite prepared by solution ion exchange of  $\text{ZnCl}_2$  and  $\text{NaY}$  zeolite is used as a catalyst, the activity increases twofolds and the regioselectivity increases slightly (entry 4). This enhancement of catalytic activity can be explained by the Lewis acid sites of zinc ions in the  $\text{ZnNaY}$  zeolite created by ion exchange, but the acid strength of this type of zinc species bonded two oxygen are not strong enough to catalyze the reaction. The typical homogeneous Lewis acid of  $\text{ZnCl}_2$  shows good activity and regioselectivity, but the selectivity of cycloadducts is decreased (entry 5).

The physical mixture of  $\text{ZnCl}_2$  and  $\text{NaY}$  zeolite exhibits almost same activity, selectivity of cycloadducts and regioselectivity of  $p/m$  to the homogeneous Lewis acid of  $\text{ZnCl}_2$  due to the similar active sites (entry 6). Comparing with the physical mixture of  $\text{ZnCl}_2/\text{NaY}$  catalyst, the selectivity of

Table 1

Comparison of  $\text{ZnCl}_2/\text{NaY}$  catalysts prepared by different methods in the Diels–Alder reaction<sup>a</sup>

	Catalyst	$\text{ZnCl}_2$ loading (mmol/g)	Preparation method	Conversion (mol%) <sup>b</sup>	Selectivity (%) <sup>c</sup>	Regioselectivity ( $p/m$ ) <sup>d</sup>
1	None	–	–	6.6	98.8	72:28
2	$\text{NaY}$	0	–	6.7	97.8	72:28
3	$\text{HY}$	0	Ion exchange in solution	23.2	92.3	81:19
4	$\text{ZnNaY}^e$	0.62	Ion exchange in solution	13.8	96.2	77:23
5	$\text{ZnCl}_2$	2.75	[10]	89.9	76.7	92:8
6	$\text{ZnCl}_2/\text{NaY}$	2.75	Physical mixture	90.2	77.2	92:8
7	$\text{ZnCl}_2/\text{NaY}$	2.75	Heated at 473 K for 1 h	90.6	87.5	93:7
8	$\text{ZnCl}_2/\text{NaY}$	2.75	Microwave irradiation	89.8	92.6	93:7
9	$\text{ZnCl}_2/\text{HY}$	2.75	Microwave irradiation	95.8	50.1	92:8

<sup>a</sup> The reaction was performed in  $\text{CH}_2\text{Cl}_2$  solvent at  $30^\circ\text{C}$  for 6 h.

<sup>b</sup> Conversion of myrcene.

<sup>c</sup> Selectivity for cycloadducts

<sup>d</sup>  $p/m$ : *para/meta*.

<sup>e</sup> The  $\text{Zn}^{2+}$  content was determined by AAS.

cycloadducts increase somewhat over the  $\text{ZnCl}_2/\text{NaY}$  catalyst prepared by heat treatment (entry 7). It is noticeable that  $\text{ZnCl}_2/\text{NaY}$  catalyst prepared by microwave irradiation shows the best selectivity of cycloadducts, high regioselectivity of  $p/m$  and similar activity of homogeneous  $\text{ZnCl}_2$  (entry 8). These observations should be attributed to the completely dispersed  $\text{ZnCl}_2$  on the surface of NaY zeolite, and also some of dispersed  $\text{ZnCl}_2$  react with surface oxygen ions to form new Lewis acid sites of  $-\text{O}-\text{Zn}-\text{Cl}$ , which is in good agreement with the discussion of XRD patterns of Fig. 1(c) and the IR spectra of Fig. 2(a). The catalyst prepared by microwave irradiation can be interpreted as heating method. Significantly, the use of microwave technologies to prepare  $\text{ZnCl}_2/\text{NaY}$  catalyst shows the advantages of not only reducing time and also without contamination during catalyst preparation as compared to the conventional heating method. However, when HY zeolite used as a support to prepare the catalyst under microwave irradiation, the selectivity of cycloadducts decreases apparently (entry 9). Whittington reported that zeolites in the H form adsorbed little energy of microwave irradiation [34]. In this case, the active sites should be from the homogenous  $\text{ZnCl}_2$  and the Brønsted acid sites of HY zeolite. The decrease of the selectivity for cycloadducts is due to the subsequent cyclization of the cycloadducts of myrac aldehyde and oligomerization of myrcene by Brønsted acid sites [8].

Overall, the suitable Lewis acid sites and the mid-acid strength of the catalysts are responsible for the high regioselective Diels–Alder reaction of myrcene and acrolein. The preparation of  $\text{ZnCl}_2/\text{NaY}$  catalyst by solid-state interaction of  $\text{ZnCl}_2$  and NaY zeolite under microwave irradiation is developed the best method among them.

Table 2 shows the effect of adsorbed water in NaY zeolite on the  $\text{ZnCl}_2/\text{NaY}$  catalysts prepared by different methods for the Diels–Alder reaction. The results indicate that the activity, selectivity of cycloadducts and regioselectivity of  $p/m$  over the physical mixture of  $\text{ZnCl}_2$  and hydrated NaY zeolite are less significantly than that of  $\text{ZnCl}_2/\text{NaY}$  catalysts prepared by heat and microwave treatment. The existence of water in the catalyst of physical mixture of  $\text{ZnCl}_2/\text{NaY}$  leads to the ability of zinc ions to enhance the Brønsted

acidity of catalyst by polarization of their solvating water molecules and to reduce the Lewis acid sites. It is known that microwave energy can be used to remove the water retained in sodium form zeolite. The catalyst prepared by microwave irradiation still exhibits the best catalytic behavior among the three catalysts preparation methods. However, Some loss of activity and selectivity in the  $\text{ZnCl}_2/\text{NaY}$  catalyst prepared by microwave irradiation comparing with in Table 1 (entry 8) are due to the water retained in NaY zeolite not to be removed completely.

### 3.3. Effect of $\text{ZnCl}_2$ loading on the catalytic properties

A series of experiments is carried out using the  $\text{ZnCl}_2/\text{NaY}$  catalyst prepared by microwave irradiation for the Diels–Alder reaction to examine the effect of  $\text{ZnCl}_2$  loading on the catalytic properties. The results are listed in Table 3. It can be seen that the catalytic activity and selectivity of cycloadducts remain almost unchanged with an increase of the  $\text{ZnCl}_2$  loading from 0.46 to 0.92  $\text{mmol g}^{-1}$ , which are very similar to that of  $\text{ZnNaY}$  catalyst prepared by the conventional ion exchange in solution. The results suggest that the dispersed  $\text{ZnCl}_2$  onto the NaY zeolite under microwave irradiation take place mainly solid-state ion exchange between  $\text{Zn}^{2+}$  with  $\text{Na}^+$  in NaY zeolite, but the acidic strength of this type of  $\text{Zn}^{2+}$  species is too weak to catalyze efficiently the Diels–Alder reaction. With an increase of  $\text{ZnCl}_2$  loading up to 1.84  $\text{mmol g}^{-1}$ , the activity and regioselectivity increase markedly. In this case, the dispersed  $\text{ZnCl}_2$  bonded on the surface of NaY zeolite plays great role in the high regioselective synthesis of myrac aldehyde and shows excellent activity. The catalytic mechanism is proposed by the coordination of Lewis acid site of  $\text{Zn}^{2+}$  with the carbonyl of acrolein, which is described in detail in our early studies [10]. The activity and regioselectivity of  $p/m$  increase slightly with an increase of  $\text{ZnCl}_2$  loading from 1.84 up to 2.75  $\text{mmol g}^{-1}$ . The decrease of the

Table 2  
Effect of adsorbed water in NaY zeolite on the  $\text{ZnCl}_2/\text{NaY}$  catalysts prepared by different methods in the Diels–Alder reaction<sup>a</sup>

Preparation method	Conversion (mol%) <sup>b</sup>	Selectivity (%) <sup>c</sup>	Regioselectivity ( $p/m$ ) <sup>d</sup>
Physical mixture	34.9	70.8	86:14
Heated at 473 K for 1 h	75.2	81.6	92:8
Microwave irradiation	84.8	84.0	93:7

<sup>a</sup> Same to Table 1.  $\text{ZnCl}_2$  loading is 2.75  $\text{mmol/g}$ , NaY was treated in the humidistat at constant temperature of 25 °C for 96 h and the weight of adsorbed water of NaY zeolite is 12.8  $\text{mmol/g}$ .

<sup>b</sup> Same as in Table 1.

<sup>c</sup> Same as in Table 1.

<sup>d</sup> Same as in Table 1.

Table 3  
Effect of  $\text{ZnCl}_2$  loading on the Diels–Alder reaction<sup>a</sup>

$\text{ZnCl}_2$ loading (mmol/g)	Conversion (mol%) <sup>b</sup>	Selectivity (%) <sup>c</sup>	Regioselectivity ( $p/m$ ) <sup>d</sup>
0	6.6	98.8	72:28
0.46	12.6 (18.6) <sup>f</sup>	96.6 (92.4)	77:23 (79:21)
0.62 <sup>e</sup>	13.8	96.2	77:23
0.92	15.2 (34.1)	96.5 (89.1)	83:17 (83:17)
1.84	63.7 (64.6)	93.1 (84.7)	92:8 (91:9)
2.75	89.8 (89.9)	92.6 (77.8)	93:7 (92:8)
3.24	93.7(94.8)	84.5 (71.3)	92:8 (92:8)

<sup>a</sup> Same as in Table 1.

<sup>b</sup> Same as in Table 1.

<sup>c</sup> Same as in Table 1.

<sup>d</sup> Same as in Table 1.

<sup>e</sup> The catalyst of  $\text{ZnNaY}$  is prepared by the conventional solution ion exchange method,  $\text{Zn}^{2+}$  content was determined by AAS.

<sup>f</sup> The value in the parentheses is the result of the same amount of only  $\text{ZnCl}_2$  used as a catalyst.

Table 4  
The catalytic performance of ZnCl<sub>2</sub>/NaY treated with different method<sup>a</sup>

	Catalyst	Catalyst treatment method	Conversion (mol%) <sup>b</sup>	Selectivity (%) <sup>c</sup>	Regioselectivity ( <i>p/m</i> ) <sup>d</sup>
1	None	–	6.6	98.8	72:28
2	ZnNaY <sup>e</sup>	Ion exchange in solution	13.8	96.2	77:23
3	ZnCl <sub>2</sub> /NaY <sup>f</sup>	No other treatment	12.6	96.6	77:23
4	ZnCl <sub>2</sub> /NaY <sup>f</sup>	Water washing, dried and calcined at 773 K for 3 h	12.5	96.6	77:23
5	ZnCl <sub>2</sub> /NaY <sup>f</sup>	Leaching with a mixture solvent of acrolein and CH <sub>2</sub> Cl <sub>2</sub>	12.7	96.1	77:23
6	ZnCl <sub>2</sub> /NaY <sup>g</sup>	Leaching with a mixture solvent of acrolein and CH <sub>2</sub> Cl <sub>2</sub>	86.8	93.6	93:7
7	ZnCl <sub>2</sub> /NaZSM-5 <sup>h</sup>	Prepared by microwave irradiation	13.7	96.5	79:21

<sup>a</sup> Same as in Table 1. The amount of catalyst in every experiment is 1 g.

<sup>b</sup> Same as in Table 1. The amount of catalyst in every experiment is 1 g.

<sup>c</sup> Same as in Table 1. The amount of catalyst in every experiment is 1 g.

<sup>d</sup> Same as in Table 1. The amount of catalyst in every experiment is 1 g.

<sup>e</sup> Same as in Table 1. The amount of catalyst in every experiment is 1 g.

<sup>f</sup> ZnCl<sub>2</sub>/NaY was the catalyst prepared by microwave irradiation before treatment and ZnCl<sub>2</sub> loading is 0.46 mmol g<sup>-1</sup>.

<sup>g</sup> ZnCl<sub>2</sub>/NaY was the catalyst prepared by microwave irradiation before leaching and ZnCl<sub>2</sub> loading is 2.75 mmol g<sup>-1</sup>.

<sup>h</sup> ZnCl<sub>2</sub> loading is 2.75 mmol g<sup>-1</sup>.

selectivity of cycloadducts with increasing of ZnCl<sub>2</sub> loading is supposed to be the oligomerization of myrcene at a high ZnCl<sub>2</sub> loading.

#### 3.4. The status of ZnCl<sub>2</sub> onto NaY zeolite under microwave irradiation

The XRD results and the effect of ZnCl<sub>2</sub> loading on the catalytic performances indicated that ZnCl<sub>2</sub>/NaY catalysts prepared by solid-state interaction between ZnCl<sub>2</sub> and NaY zeolite under microwave irradiation can lead to ZnCl<sub>2</sub> disperse completely onto the surface of NaY zeolite at ZnCl<sub>2</sub> loading less than 2.75 mmol g<sup>-1</sup>. What's the status of ZnCl<sub>2</sub> on the surface of NaY zeolite thus becomes interesting. In order to study the status of ZnCl<sub>2</sub> depended on loading, a further set of experiments is designed to investigate the solid-state interaction between anhydrous ZnCl<sub>2</sub> and NaY zeolite under microwave irradiation by testing their catalytic performances in the reaction, which is shown in Table 4. If the sample of ZnCl<sub>2</sub>/NaY at the ZnCl<sub>2</sub> loading of 0.46 mmol g<sup>-1</sup> prepared by microwave irradiation is washed chloride free with deionised water, and then dried and calcined at 773 K for 3 h, there is no change of the catalytic performances over the treated ZnCl<sub>2</sub>/NaY catalyst (entry 4) compared with that over the fresh prepared ZnCl<sub>2</sub>/NaY catalyst without any treatment (entry 3). The result indicates that the dispersed Zn<sup>2+</sup> can not be washed out of NaY zeolite by water. We would like to know if the dispersed ZnCl<sub>2</sub> could be leached out by the solvent and the dienophile or not. Another experiment is performed to leach the catalyst (1 g) after microwave treatment with a mixture of solvent of acrolein (5 ml) and dichloromethane (5 ml) at the reaction conditions for 1 h, and then filtrated. The resulted solid was used as a catalyst again in the reaction (entry 5). No change of catalytic performance is also observed, which suggest that ZnCl<sub>2</sub> onto the surface of NaY zeolite can not also be leached by the solvent and acrolein. All of the catalytic behaviors (entries 3–5) are similar to that of ZnNaY catalyst

prepared by the conventional ion exchange in solution (entry 2). These features suggest that microwave irradiation only accelerate the solid-state ion exchange between ZnCl<sub>2</sub> and NaY zeolite at a low ZnCl<sub>2</sub> loading, and also the exchanged Zn<sup>2+</sup> in the zeolite can not be leached by water, reactant and solvent.

In the case of a high ZnCl<sub>2</sub> loading, the catalytic activity and regioselectivity of *p/m* keep almost same even the ZnCl<sub>2</sub>/NaY catalyst is leached with a mixture solvent of acrolein and dichloromethane for 1 h at the reaction conditions (entry 6). The observation indicates that the dispersed ZnCl<sub>2</sub> can be immobilized onto the surface of NaY zeolite by forming the bond of –O–Zn–Cl used as a effective heterogeneous catalyst. This type of zinc species also can be explained by the catalytic behaviors of the Diels–Alder reaction over the catalyst of ZnCl<sub>2</sub>/Na-ZSM-5 (entry 7). It is found that the catalytic activity and the regioselectivity of *p/m* over the ZnCl<sub>2</sub>/Na-ZSM-5 catalyst is far less than that over ZnCl<sub>2</sub>/NaY catalyst even at the same ZnCl<sub>2</sub> loading of 2.75 mmol g<sup>-1</sup>. The loss of activity is attributed to the larger dynamic molecule size of the cycloadduct of myrac aldehyde blocking them to diffuse out of the channel of ZSM-5 zeolite. The dispersed ZnCl<sub>2</sub> onto the internal surface of ZSM-5 also can not dissolve in the reactants and solvent. The catalytic activity is expected from the ZnCl<sub>2</sub> dispersed on the external surface of ZSM-5 zeolite. This example gives us a further explanation that microwave irradiation can make anhydrous ZnCl<sub>2</sub> immobilize on the surface of NaY zeolite.

#### 4. Conclusion

The solid-state interaction between ZnCl<sub>2</sub> and NaY zeolite for preparation of ZnCl<sub>2</sub>/NaY catalysts by the treatment of different methods is compared. XRD patterns indicate that ZnCl<sub>2</sub> can disperse completely on the surface of NaY zeolite under microwave irradiation. The ZnCl<sub>2</sub>/NaY catalysts

treated by microwave irradiation are proved to be effective heterogeneous catalysts for high regioselective Diels–Alder reaction of myrcene and acrolein. The catalytic activity and regioselectivity strongly depend on the nature and the acid strength of the solid catalysts. Brønsted acid sites easily leads to decrease of selectivity and regioselectivity due to the subsequent cyclization for the cycloadducts of myrac aldehyde at high concentration and oligomerization of myrcene. The characteristic IR bands indicated that the active species are Lewis acid sites, which are responsible for the Diels–Alder reaction. The Lewis acid strength is also an important factor for catalyst to have a high activity and regioselectivity. If the  $\text{ZnCl}_2$  loading less than of  $0.92 \text{ mmol g}^{-1}$ , the activity and selectivity is not high due to the dispersed  $\text{ZnCl}_2$  mainly takes place solid-state ion exchange. This type of zinc species is not too strong enough for the Diels–Alder reaction. The catalytic activity and regioselectivity increase markedly when  $\text{ZnCl}_2$  loading increases from  $0.92$  to  $1.84 \text{ mmol g}^{-1}$ , which are attributed to the dispersed  $\text{ZnCl}_2$  leads to formation of new Lewis acid sites of  $-\text{O}-\text{Zn}-\text{Cl}$ . The mid-strength Lewis acid sites show the high regioselective in the synthesis of ‘para’ myrac aldehyde for the Diels–Alder reaction. The best catalytic activity (myrcene conversion of 89.8%) and regioselectivity ( $p/m = 93 : 7$ ) are achieved over  $\text{ZnCl}_2/\text{NaY}$  catalyst at the optimum  $\text{ZnCl}_2$  loading of  $2.75 \text{ mmol g}^{-1}$ . The active sites in the catalyst can not be leached from acrolein and solvent, which suggest that the preparation of  $\text{ZnCl}_2/\text{NaY}$  catalyst by solid-state interaction under microwave irradiation is a promising method for developing environment friendly alternative catalyst for the Diels–Alder reaction.

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