

Liquid phase acylation of 2-methylnaphthalene catalyzed by H-beta zeolite

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Abstract

Liquid phase Friedel–Crafts acylation of 2-methylnaphthalene (2-MN) has been investigated over zeolite catalyst. The influence of zeolite structures, substituents on naphthalene, acylating agents and solvents on the acylation has been discussed. 2-Methyl-6-butyrylnaphthalene (2,6-BMN), a promising precursor of 2,6-naphthalenedicarboxylic acid (2,6-NDCA), has been synthesized by the acylation of 2-MN using butyric anhydride (BA) as an acylating agent and H-beta zeolite as a catalyst. The influence of the preparative methods and dosage of H-beta zeolite, the molar ratio of reactants, the reaction temperature and reaction time on the catalytic butyrylation was also studied. The H-beta zeolite exchanged for four times and calcined at 550 °C possessed relatively better catalytic performance. Under the optimized condition, the conversion of BA reached 78.3% and the selectivity for 2,6-BMN was 53.1%.

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Keywords: H-beta zeolite; 2-Methylnaphthalene; Acylation; 2-Methyl-6-butyrylnaphthalene; 2,6-Naphthalenedicarboxylic acid

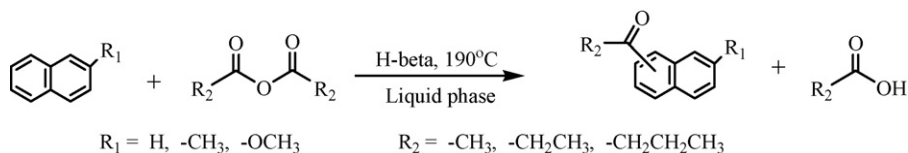
1. Introduction

2,6-Naphthalenedicarboxylic acid (2,6-NDCA) is the key monomer of the high-performance polyester polyethylene naphthalate (PEN) [1,2]. In addition, it is an important intermediate for the synthesis of liquid crystals, pharmaceuticals, agricultural chemicals, dyes and fluorsceners [3]. 2,6-NDCA can be produced by the Henkel process [4,5], or by the oxidation of 2,6-dialkylnaphthalene (2,6-DAN) [6–8] and 2-methyl-6-acylnaphthalene (2,6-AMN) [9]. Henkel process turns out not to be a good method in the industry due to its well-known shortcomings such as pollution, corrosion and poor reproducibility, and the oxidation of 2,6-DAN is currently the preferable method for the preparation of 2,6-NDCA. The key issue of the latter method lies in the availability of 2,6-DAN, which is generally acquired via alkylation catalyzed by zeolite at the present time [10–12]. However, due to the poor selectivity of alkylation, the tedious separation and purification of 2,6-DAN make this method less

desirable [13,14]. As a result, the Friedel–Crafts acylation of 2-methylnaphthalene (2-MN), which affords 2,6-AMN, is considered to be the most promising way for the preparation of 2,6-NDCA, thanks to less side reactions.

The MGC Company in Japan first reported the high-yielding production of 2,6-AMN with 2-MN as starting material and HF/BF₃ as catalyst [15]. In addition, CF₃SO₃H and AlCl₃ have also been used as catalysts in the synthesis of 2,6-AMN with good yield and selectivity [16]. However, all the catalysts mentioned above were employed in homogenous system and suffered from many drawbacks and disadvantages such as pollution, corrosion and difficulties in recycle. For developing environmental friendly catalytic process, solid acids have been used as catalysts instead of conventional liquid acid catalysts in Friedel–Crafts acylation, wherein zeolite gained a great deal of attention due to its adjustable, shape-selective and returnable performances [17–21]. Acylation of 2-methoxynaphthalene (2-MON) and naphthalene catalyzed by zeolite had been previously reported [22–30]. Herein we wish to report the acylation of 2-MN for the preparation of 2,6-AMN with zeolite as a catalyst. H-beta zeolite was found to be effective for the acylation of 2-MN (Scheme 1). Butyrylation of 2-MN with butyric anhy-

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Scheme 1.

dride (BA) over H-beta zeolite in the absence of any solvent was studied in detail. 2-Methyl-6-butyrylnaphthalene, the target product, was synthesized and separated from its' isomers by simple recrystallization. The relationship between acidic properties and H-beta zeolite ion-exchange times, calcination temperatures were investigated. The effect of reaction parameters such as dosage of the catalyst, molar ratio of the reactants, reaction temperature and time was discussed. The reuse and recovery performances of H-beta-4 zeolite in the acylation of 2-MN with BA under the optimum conditions were tested to study the reasons of deactivation.

2. Experimental

Commercially available HUSY and NaY zeolites were purchased from Changling Catalyst Supplies Co. Na-beta, NaZSM-5 and NaM zeolites were synthesized in the department of industrial catalysis in Dalian University of Technology. For Na-beta and NaZSM-5 zeolites, the removal of organic materials from zeolite networks was done by a temperature program-controlled calcination from 250 to 550 °C. All Na-zeolites were exchanged in an aqueous solution of ammonium nitrate (1.0 mol/L, 8 mL/g zeolite) at 90–100 °C for 1 h, followed by filtering and washing with deionized water to get rid of any residual ions which might occupy the zeolite pores. Then they were dried at 120 °C for 12 h and ulteriorly calcined at 540 °C for 5 h. The same processing was repeated to get the different ion-exchange times zeolite catalysts (named as H-zeolite-1, H-zeolite-2, and so on). Reused H-beta-4 zeolite catalyst was obtained after reaction by multiple washing then drying at 120 °C for 12 h. The reused catalyst was ulteriorly disposed by temperature programming calcination to attain regenerated catalyst.

NH₃-TPD was performed on a conventional set-up equipped with a thermal conductivity detector (TCD). 0.2 g catalyst sample (20–60 mesh) was first flushed with helium gas (30 mL/min) at 700 °C for 3 h, then cooled to 150 °C and saturated with NH₃ until equilibrium, flushed with helium gas again until the integrator baseline was stable. The processing of NH₃-TPD promptly started from 150 to 700 °C at a heating rate of 15 °C/min. All NH₃-TPD profiles were deconvoluted by means of a Gaussian and Lorentzian curve-fitting method. SRS 3400 X-ray fluorescence spectra instrument made by Bruker Company in Germany was used to determine the SiO₂/Al₂O₃ ratios and Na⁺-exchange degrees of the H-beta zeolites. ZETASIZER 1000 granulometer made by Malvern Company was used to determine the grain size of H-beta zeolite.

The liquid phase acylation over zeolite was carried out in a three-necked flask equipped with a condenser, a drying tube with

CaCl₂ and a thermometer. The temperature of the reaction vessel was maintained using an oil bath. All the materials and solvents were distilled and dried before use. In a typical run, 0.1 mol 2-MN and 2.0 g activated H-beta zeolite were charged to the flask and heated to melt, then 0.1 mol acylated agent BA was added and the mixture was heated to 190 °C, reacted for 10 h with vigorous stirring. After cooling, the catalyst was removed by filtration then the filtrate was analyzed by GC (HP 6890, equipped with HP-5 column, 30 nm × 0.32 mm × 0.25 μm; FID detector) and GC-MS (HP 5973 mass selective detector, HP-5MS column, 30 nm × 0.25 mm × 0.25 μm). The crude BMN products were obtained via vacuum distillation at 199–202 °C/0.5 kPa. Whereafter, colorless prismatic crystal of 2,6-BMN, whose melting point was 41.6–42.5 °C, was gained via recrystallization with absolute ethyl alcohol. The structure of refined product was determined by ¹H, ¹³C and several two dimensions NMR (Varian INOVA 400 MHz). The filtrate was concentrated and recrystallized again to give white squamose crystal of 2,7-BMN, whose melting point was 70.7–71.5 °C.

3. Results and discussion

3.1. Acetylation of 2-MN catalyzed by different zeolites

Five H-zeolites, H-beta (SiO₂/Al₂O₃ = 47, crystallite size is about 226 nm), HY (SiO₂/Al₂O₃ = 5), HZSM-5 (SiO₂/Al₂O₃ = 30), HM (SiO₂/Al₂O₃ = 10), HUSY (SiO₂/Al₂O₃ = 10) were used in the acetylation of 2-MN with acetic anhydride (AA) under the same reaction conditions (0.05 mol 2-MN, 0.05 mol AA and 2 g zeolite reacted in 5 g decalin at 140 °C for 10 h). Unfortunately, it was found only the microcrystalline H-beta zeolite showed a low catalytic activity with a 2.4% conversion of AA. Since both the natures of acid sites and pore structures work on the catalytic performance of zeolite, it could be deduced that the suitable pore mouth size (0.72 nm × 0.62 nm) and expedite tridirectional structure of H-beta zeolite may account for the catalytic activity. However, the HY and HUSY zeolites possessing tridirectional large pores (0.75 nm) with a large cavity of 1.3 nm did not exhibit any catalytic activity under the above condition, which could be due to their incongruous natures of acid sites. Fig. 1 presents the NH₃-TPD results of these five zeolites and shows that H-beta and HZSM-5 zeolites, which possess of less total acid amount considering their high SiO₂/Al₂O₃ ratios, reveal similar desorption profiles. Excessive strong acid sites on HM, HY and HUSY zeolites would chemisorb reactants and corresponding complex compounds intensely, then deactivate rapidly [31]. Accordingly, no acylated products were detected by GC when the catalysts were the above zeolites. The microcrystalline H-beta zeolite could minimize the activity attenuation

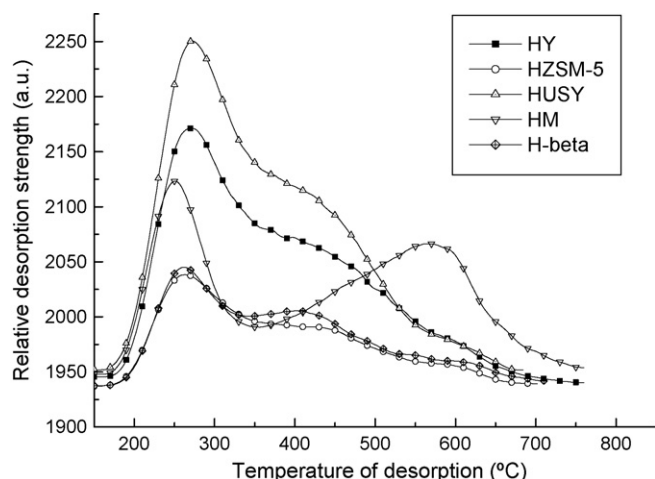


Fig. 1. NH_3 -TPD profiles of five zeolites.

and consequently exhibited comparative catalytic activity [31]. Besides, there is an obvious moderate-strong acid sites peak at about 400 °C in the NH_3 -TPD profile of H-beta zeolite, which differentiates H-beta zeolite from other zeolites and may constitute another reason for the H-beta zeolite to have the catalytic activity. In the reaction catalyzed by H-beta zeolite, three acylated isomers were detected by GC-MS, wherein the selectivity for 2,6-, 2,7- and 1,2-AMN were 57.1%, 29.6% and 13.3%, respectively. It is well known that the electrophilic substitution of naphthalene compound generally occurs at more active α -position. Besides, the electron donating methyl in 2-MN should facilitate the acylation at ortho α -position [32]. However, the shape-selective catalysis of H-beta zeolite made the sterically less bulky 2,6- and 2,7-AMN isomers to be formed with priority. Moreover, the critical diameter of 2,6-isomer was slightly smaller than that of 2,7-isomer [33]. Both the above reasons determined that 2,6-AMN was the major product.

3.2. Acetylation of naphthalene compounds with different substituents over H-beta zeolite

Červený et al. [30] and Čejka et al. [29] reported the acetylation of naphthalene with AA in the presence of zeolites with 35% yield of acetylnaphthalene (AN). However, the catalytic activity of zeolite on the acetylation of 2-MN was very low according to our research, which seemed to be in contradiction with the law of electrophilic substitution on aromatics. For this reason, acetylations of naphthalene, 1-MN, 2-MN and 2-MON over H-beta zeolite were studied under the same conditions (see Table 1). The

acylated results and isomers distributions of naphthalene and 2-MON accorded with the references reported previously on the whole [22–30]. Acylating agent was chemisorbed onto the active acid sites of zeolite to generate corresponding acylium cations, which attacked the aromatic rings to form activated complexes. The large steric hindrance of methyl groups in 2- and 1-MN blocked the acylium cations to attack the ortho-position C-atom with larger electron density, which accounted for the low activities of 2- and 1-MN. Moreover, the shape-selective catalysis of H-beta zeolite limited the formation of those bulky activated complexes. As a result, 2,6- and 2,7-isomers with filiform molecular structures, whose activated complexes could form, desorb and diffuse out of the zeolite channels easily, became the major acylated products of 2-MN. Wherein the high activity of 2-MON was attribute to the strong electron donating ability of methoxyl group. Besides, the steric hindrance of methoxyl group was smaller than that of methyl on naphthalene ring, therefore more acylation occurred on ortho-position of the same ring over the external surface of the H-beta zeolite [24,28].

3.3. Acylation of 2-MN over H-beta zeolite with different acylating agents

Various acylating agents (including short-chain acyl chloride, carboxylic acid and acid anhydride) were employed in the acylation of 2-MN catalyzed by H-beta zeolite (the results are shown in Table 2). Reaction temperatures were the reflux temperatures of these acylating agents respectively while other reaction conditions were kept identical. From Table 2, short-chain acyl chloride and carboxylic acid were found not to be the effective acylating agents for 2-MN in the presence of H-beta zeolite. Only acid anhydride possessed considerable reaction activity, which increased with the lengthening of the carbon chain. Generally, the activity order of acylating agents is acyl halide > acid anhydride > carboxylic acid. Nevertheless, under the experimental conditions here, only acid anhydride was active. The reason may be that the activation energy for 2-MN acylation catalyzed by zeolite is high but the relatively lower boiling points of short-chain acyl chlorides afford lower temperatures and cannot supply sufficient activation energy. Acid anhydrides possess higher boiling points, which can make the acylation occur at higher temperatures. With the increase of acid anhydride chain, the boiling point became higher, and at the same time acylation activity increased. Taking the cost and source of feedstocks into account, BA was chosen as the acylating agent for the acylation of 2-MN catalyzed by H-beta zeolite. In addition, an equimolar of carboxylic acid would form inevitably when acid anhydride

Table 1
Acetylation of four naphthalene substrates^a

Entry	Substrates	Conversion of AA (wt %)	Products distribution (wt %)
1	Naphthalene	12.9	2-AN: 75.4 1-AN: 24.6
2	1-Methylnaphthalene	0	0
3	2-Methylnaphthalene	4.8	2,6-AMN: 64.9 2,7-AMN: 35.1
4	2-Methoxynaphthalene	52.5	2,6-AMON ^b : 43.6 2,1-AMON: 53.1; 2,8-AMON: 3.3

^a Reaction conditions: 0.1 mol substrates, 0.05 mol AA and 2 g H-beta zeolite reacted in 10 g decalin at 140 °C for 10 h.

^b Methoxyacetylnaphthalene.

Table 2
Effect of acylating agents on the acylation of 2-MN over H-beta zeolite^a

Entry	Acylating agents	Reaction temperature (°C)	Conversion of acylating agent (wt %)	Product distribution (wt %)		
				2,6-AMN	2,7-AMN	Others
1	Acetyl chloride	50	0	0	0	0
2	Propionyl chloride	80	0	0	0	0
3	Acetic acid	120	0	0	0	0
4	Propanoic acid	140	0	0	0	0
5	<i>n</i> -Butyric acid	165	0	0	0	0
6	Acetic anhydride	140	0.9	100	0	0
7	Propionic anhydride	170	1.4	60.2	39.8	0
8	Butyric anhydride	190	5.1	59.8	40.2	0

^a Reaction conditions: 0.1 mol 2-MN, 0.1 mol acylating agent and 2 g H-beta zeolite reacted in 10 g decalin for 10 h.

Table 3
Effect of solvents on the butyrylation of 2-MN over H-beta zeolite^a

Entry	Solvents	Reaction temperature (°C)	Conversion of BA (wt %)	Product distribution (wt %)		
				2,6-BMN	2,7-BMN	Others
1	None	190	11.6	55.7	37.0	7.3
2	Nitrobenzene	190	8.6	54.9	39.1	6.1
3	Decalin	190	5.1	59.8	40.2	0
4	Sulfolane	190	9.0	50.3	44.2	5.5
5	Dimethyl sulfoxide	190	15.2	9.7	3.4	86.9
6	Chlorobenzene	130	5.8	59.4	40.6	0

^a Reaction conditions: 0.1 mol 2-MN, 0.1 mol BA and 2 g H-beta zeolite reacted in 10 g solvents for 10 h.

was used as the acylating agent. Carboxylic acid, as mentioned above, could not react with 2-MN over H-beta zeolite. What is more, they would undergo competitive adsorption with anhydride and consequently lead to the deactivation of zeolite [34].

3.4. Influence of solvents on butyrylation of 2-MN in the presence of H-beta zeolite

Several polar (sulfolane [30], dimethyl sulfoxide, nitrobenzene and chlorobenzene) and nonpolar (decalin [29,30]) solvents with high-boiling points were used in the butyrylation of 2-MN on H-beta zeolite. The results contrasted with that of solvent-

free condition were presented in Table 3. It can be seen that reactions in polar solvents were more active than that in non-polar solvent. The conversion of BA was the greatest when dimethyl sulfoxide acted as a solvent. But most of the products were α -position products in this case, the selectivity for 2-methyl-6-butyrylnaphthalene (2,6-BMN) was only 9.7% and a little 2-MN underwent disproportionating reaction. Other solvents made the reaction activities decrease compared with that of solvent-free condition. It was deduced that solvent molecules might compete with reactants to be absorbed on the activated acid sites of zeolite, therefore decrease the reaction activity of the acylation to some extent. Based on the above consideration, solvent-free condition was selected for the further study.

3.5. Influence of preparative conditions of zeolite on butyrylation of 2-MN

Preparative conditions such as ion-exchange degree and calcination temperature were investigated to adjust the acid properties and consequently the catalytic performance of H-beta zeolite.

3.5.1. Influence of H-beta zeolite calcination temperature

The catalytic performances of H-beta zeolites (exchanged for one time) calcined at different temperatures were studied and the acylation results of 2-MN with BA were summarized in Table 4. Fig. 2 presented the NH₃-TPD results of these H-beta zeolites with different calcination temperatures. Since higher concentration of acid sites would favor rapid deactivation of zeolite [29], it has been shown that, the total acid amounts of

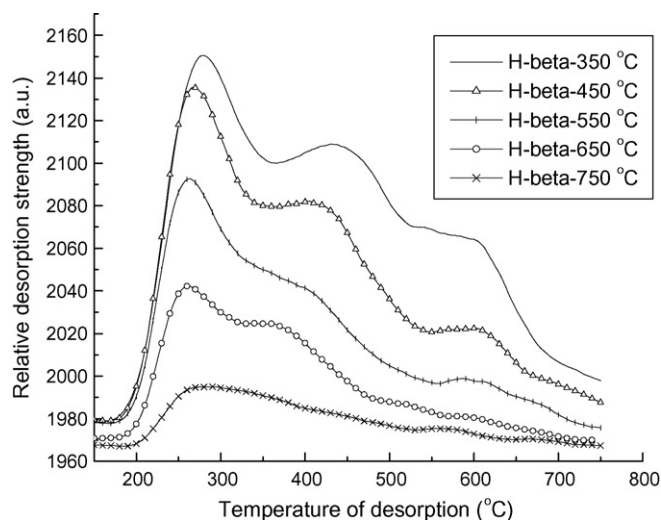


Fig. 2. NH₃-TPD profiles of H-beta zeolites calcined at different temperatures.

Table 4
Effect of H-beta zeolite calcination temperature on reaction performance^a

Entry	Calcination temperature (°C)	Relative crystallinity (%)	Conversion of BA (wt %)	Product distribution (wt %)		
				2,6-BMN	2,7-BMN	Other isomers
1	350	100	2.7	44.6	21.6	33.8
2	450	97.2	2.3	47.3	21.9	30.8
3	550	93.0	5.8	50.9	34.1	15.0
4	650	88.9	5.3	39.6	41.9	18.5
5	750	82.4	3.5	36.9	39.9	23.3

^a Reaction conditions: 0.05 mol 2-MN, 0.05 mol BA and 1 g H-beta-1 zeolite reacting at 190 °C for 10 h.

Table 5
Effect of ion-exchange times of H-beta zeolite on reaction performance^a

Entry	Zeolites	Na ⁺ -exchange degree (%)	SiO ₂ /Al ₂ O ₃ molar ratio	Conversion of BA (wt %)	Product distribution (wt %)		
					2,6-BMN	2,7-BMN	Other isomers
1	Na-beta	0	27.3	–	–	–	–
2	H-beta-1	68.3	29.6	5.8	50.9	34.1	15.0
3	H-beta-2	100	39.3	7.9	54.6	39.0	6.4
4	H-beta-3	100	47.0	8.1	54.6	39.4	6.0
5	H-beta-4	100	54.5	11.6	55.7	37.0	7.3
6	H-beta-5	100	55.3	9.5	56.3	36.5	7.2

^a Reaction conditions: 0.05 mol 2-MN, 0.05 mol BA and 1 g H-beta zeolite calcined at 550 °C reacting at 190 °C for 10 h.

H-beta zeolite decreased obviously with the increase of calcination temperature, especially for strong acid sites (desorption temperature was about 600 °C), as a result, the conversion of acylation and the selectivity for 2,6- and 2,7-BMN increased. As can be seen from Fig. 2, the strong acid sites were removed gradually when calcination temperature was raised, which was beneficial for the acylation. On the other hand, further decrease in the concentration of acid sites for H-beta zeolite would go against the catalytic performance [29]. Moreover, excessively high calcination temperature would cause dealuminization of the framework [35], make the relative crystallinity of the microcrystalline zeolite declined (see the results in Table 4) then go against the catalytic acylation. Accordingly, the highest activity and selectivity for 2,6-BMN was obtained when H-beta zeolite was calcined at 550 °C. Over this temperature the conversion of BA and selectivity for 2,6-BMN decreased. Above-mentioned factors determined that 550 °C was a proper calcination temperature of H-beta zeolite for the acylation.

3.5.2. Influence of ion-exchange times of H-beta zeolite

There are many factors to affect the ion-exchange degree of zeolite, and multiple exchanges and calcinations were used in this work to enhance the ion-exchange degree and catalytic performance. Table 5 presents the Na⁺-exchange degree, SiO₂/Al₂O₃ ratio and catalytic performance in butyrylation of 2-MN with identical conditions of H-beta zeolites with different exchange times. As shown in Table 5, the sodium ions in beta zeolite structure were easily exchanged by ammonium ions and the Na⁺-exchange degree reached 100% after two time exchanges and calcinations. Dealuminization occurred when Na-beta zeolite (SiO₂/Al₂O₃ = 27.3) underwent exchanges and calcinations, which led SiO₂/Al₂O₃ ratio to increase with the prolonged ion-exchange times. The catalytic performance mea-

sured by the conversion of BA and the selectivity for 2,6-BMN increased correspondingly and reached maximum respectively in the presence of H-beta-4 (SiO₂/Al₂O₃ = 54.5). Then they decreased when the reaction was catalyzed by H-beta-5. Fig. 3 gives NH₃-TPD results from H-beta-1 to H-beta-5 zeolite and shows that moderate-strong acid sites (desorption temperature was about 400 °C) increased significantly with the increase of exchange time, especially for the H-beta-4 in contrast to H-beta-3 zeolite. Together with Table 5, the above results proved the key contribution of moderate-strong acid sites about 400 °C for the catalytic butyrylation of 2-MN over H-beta zeolite. For H-beta-5 zeolite, excessive moderate-strong acid sites also would result in deactivation. Therefore, H-beta-4 zeolite was considered to be the best catalyst due to its high activity.

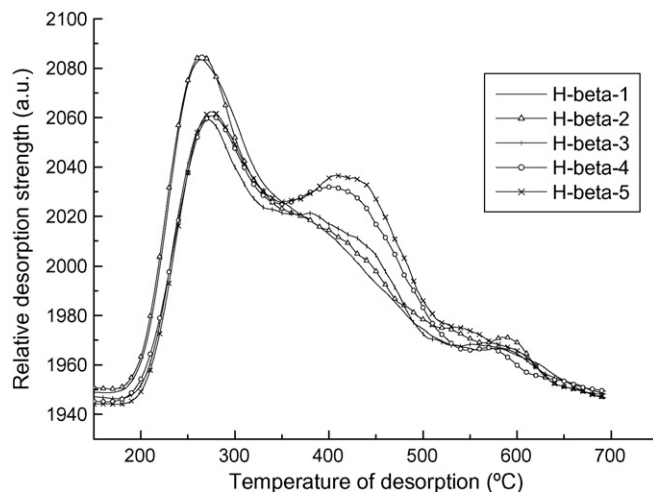


Fig. 3. NH₃-TPD profiles of H-beta zeolites with different exchange times.

Table 6
Effect of the dosage of H-beta zeolite on reaction performance^a

Entry	Dosage of zeolite (g)	Conversion of BA (wt %)	Product distribution (wt %)		BMN distribution (wt %)		
			Monoacylation	Diacylation	2,6-BMN	2,7-BMN	Others
1	0.2	0	0	0	0	0	0
2	0.5	4.5	100	0	57.0	30.6	12.4
3	1	11.6	100	0	55.7	37.0	7.3
4	1.5	13.6	97.0	3.0	53.2	36.7	10.1
5	2	29.4	92.5	7.5	42.0	47.9	10.1
6	2.5	42.2	93.6	6.4	43.2	48.6	8.2
7	3	48.6	96.4	3.6	42.8	50.6	6.6
8	3.5	54.1	96.0	4.0	41.8	52.9	5.3
9	4	56.2	95.5	4.5	40.2	54.9	4.9

^a Reaction conditions: 0.05 mol 2-MN, 0.05 mol BA and H-beta-4 zeolite calcined at 550 °C reacting at 190 °C for 10 h.

Table 7
Effect of the molar ratio of BA to 2-MN on reaction performance^a

Entry	Ratio	Conversion of BA (wt %)	Product distribution (wt %)			MBN distribution (wt %)		
			Monoacylation	Diacylation	Others	2,6-	2,7-	Others
1	0.2	51.0	92.7	0	7.3	53.6	46.4	0
2	0.5	76.4	100	0	0	53.1	40.6	6.3
3	1	54.1	96.0	4.0	0	41.8	52.9	5.3
4	1.5	34.7	89.9	10.1	0	43.3	47.4	9.3
5	2	31.4	89.6	10.4	0	49.8	40.3	9.9
6	2.5	35.0	90.4	9.6	0	50.1	40.4	9.5
7	3	33.9	90.5	9.5	0	51.2	39.0	9.8

^a Reaction conditions: 0.05 mol 2-MN, relevant mol BA and 3.5 g H-beta-4 zeolite calcined at 550 °C reacting at 190 °C for 10 h.

3.6. Optimization of reaction conditions in butyrylation of 2-MN catalyzed by H-beta zeolite

3.6.1. Influence of catalyst amount on butyrylation

Influence of the amount of catalyst on the conversion of BA and product distribution was summarized in Table 6, which indicated that the catalytic reaction could not proceed with as low as 0.2 g catalyst loading and the conversion of BA increased steadily from 0% to 61.2% as the dosage of zeolite was raised from 0.2 to 4.0 g. Whereas, diacylates emerged when the catalyst amount was higher than 1.5 g. In addition, a slight decrease of the selectivity for 2,6-BMN but increase of it for 2,7-BMN was observed with the increase in H-beta zeolite amount, and the content of other isomers reduced simultaneously. Therefore, 3.5 g H-beta zeolite was the proper dosage in view of the conversion and selectivity at the same time.

3.6.2. Influence of the molar ratio of BA to 2-MN on butyrylation

Influence of BA to 2-MN molar ratio on butyrylation over H-beta zeolite was studied by keeping the amount of 2-MN constant (Table 7). The conversion of BA exhibited higher when 2-MN was excess and reached as high as 76.4% at the ratio of 0.5. No diacylated product appeared and the selectivity for 2,6-BMN was also high at this ratio. However, when too excessive BA was used, excess acyl carbonium formed. As a result, consecutive reaction occurred then diacylated products emerged. The bulky diacylated products blocked the channels of H-beta zeolite to a certain extent, which resulted in the decrease of the BA con-

version. On the other hand, when the ratio was 0.2, even though no diacylation occurred, a little amount of 2-MN isomerized to 1-MN. Therefore, the proper ratio of BA to 2-MN was 0.5.

3.6.3. Influence of reaction temperature on butyrylation

Fig. 4 showed the influence of reaction temperature on butyrylation catalyzed by H-beta zeolite. The conversion of BA increased steadily from 55.3% to 83.2% as the temperature was raised from 140 to 200 °C. A bit of heavy products, which would

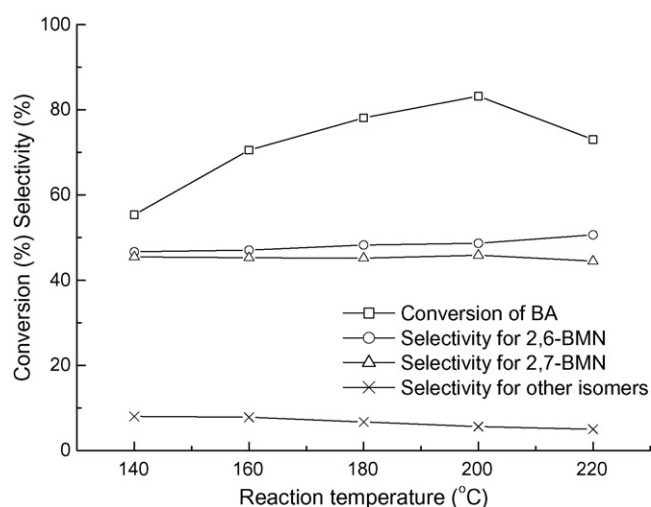


Fig. 4. Effect of reaction temperature on the butyrylation with 0.05 mol 2-MN, 0.025 mol BA and 3.5 g H-beta-4 zeolite calcined at 550 °C reacting for 10 h.

block the zeolite channels, were detected by GC when the acylation was conducted above 200 °C. It was likely to account for the drop of conversion. Reaction temperature had a slight effect on the selectivity for 2,6- and 2,7-BMN. The conversion of BA and selectivity for 2,6-BMN all obtained high values when the butyrylation was conducted at 200 °C.

3.6.4. Influence of reaction time on butyrylation

Influence of reaction time on butyrylation catalyzed by H-beta zeolite was described in Fig. 5. It was found that the conversion of BA reached a high level (64.7%) after 1 h. With the increase of reaction time, the competing adsorption between reactants and products as well as the emergence of heavy products brought on the deactivation of H-beta. As a result, the conversion of BA increased relaxedly after 1 h and leveled off after 8 h (about 78%). A slight improvement of the selectivity for 2,6- and 2,7-BMN was observed when the reaction time went up and no other isomers were detected after 24 h. It was likely to attribute to the deacylation of other isomers (with 1,2-BMN as main) [36] and the thermodynamic stability of 2,6- and 2,7-isomers [33].

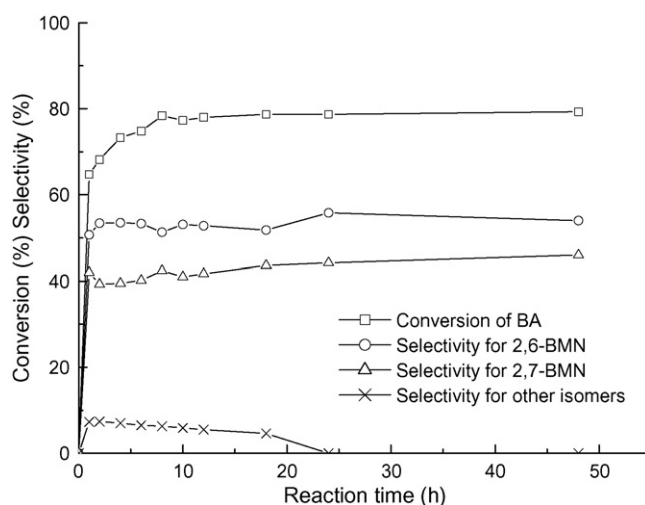
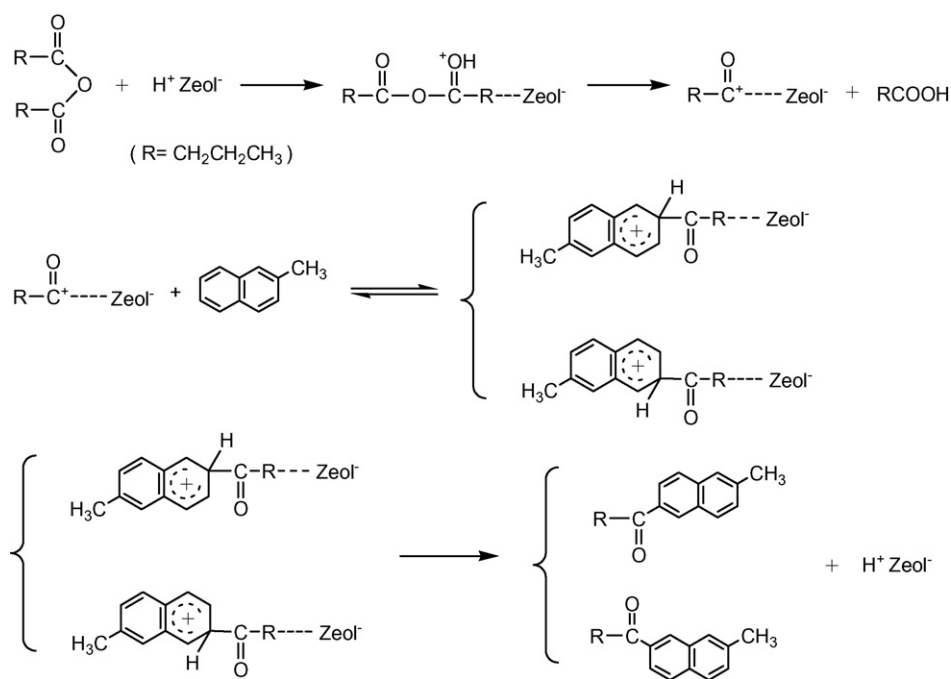
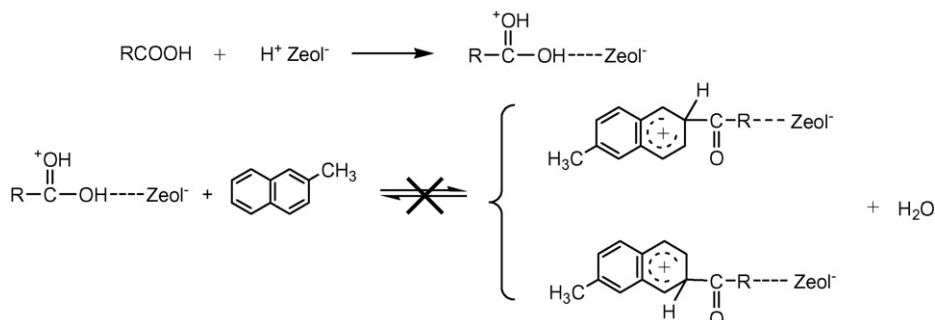


Fig. 5. Effect of reaction time on the butyrylation with 0.05 mol 2-MN, 0.025 mol BA and 3.5 g H-beta-4 zeolite calcined at 550 °C reacting at 200 °C.



Scheme 2.



Scheme 3.

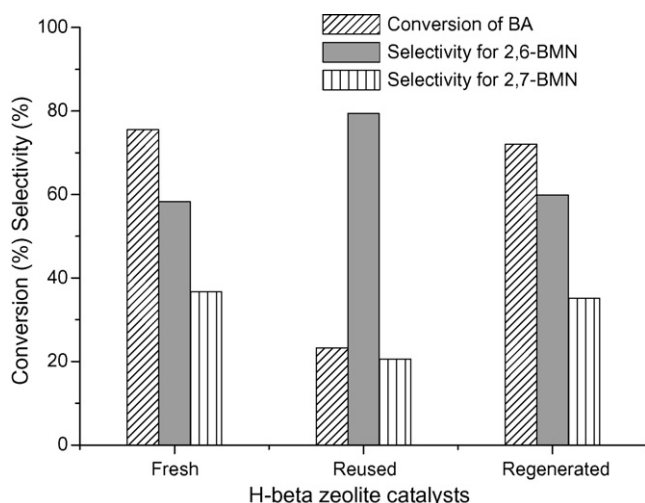


Fig. 6. The reuse and recovery performance of H-beta zeolite in the acylation of 2-MN with BA.

3.7. Mechanism of butyrylation of 2-MN with BA on H-beta zeolite catalyst

According to the experimental results and discussion, the performance of butyrylation depends not only on the electrophilic substitution of 2-MN but also on the shape-selective catalysis of H-beta zeolite. The moderate-strong acid sites (desorption temperature was about 400 °C) on H-beta zeolite made a key contribution to the catalytic butyrylation of 2-MN. A plausible reaction mechanism of butyrylation of 2-MN with BA over H-beta zeolite was proposed in Scheme 2. During the process of catalytic acylation, H-beta zeolite exhibited shape-selectivity of transition state, which was propitious to desorption and diffusion of the activated complexes towards 2,6- or 2,7-BMN with linear structures.

The equimolar by-product butyric acid, which was formed inevitably during the butyrylation of 2-MN with BA as the acylating agent, may undergo competitive adsorption with BA on the catalyst but not attack and react with 2-MN and consequently lead to the deactivation of H-beta zeolite (figured in Scheme 3). This deduction is consisted with the influence of reaction time on butyrylation activity (see Fig. 5) and the reuse performance of H-beta zeolite (presented in Fig. 6). Further, dealuminization of zeolite framework conducted by the by-product butyric acid would reduce acidity consequently as well. The notable decline in the conversion of BA over reused catalyst was due to the dealuminization of zeolite framework as well as the adsorption of butyric acid and other products. Just thanks to the narrower channels led by the adsorption and coke of products, the selectivity for 2,6-BMN increased (about 79.4%, Fig. 6). And that, the active differentia between fresh and regenerated catalyst recovered by temperature programming calcinations was ascribed to the framework dealuminization caused by butyric acid.

4. Conclusion

H-beta zeolite was employed as a catalyst in the liquid phase Friedel–Crafts acylation of 2-MN with anhydride and 2-methyl-

6-acynaphthalene was prepared successfully. In contrast, HY, HUSY, HM and HZSM-5 Zeolite showed no catalytic activity to the above reaction. The acetylation activities of four naphthalene substrates were in the order 2-MON > naphthalene > 2-MN > 1-MN. H-beta zeolite showed shape-selective catalysis in the acylation of 2-MN. Only acid anhydrides were effective acylating agents while the acylation activity increased with the lengthening of carbon chain under the conditions. No diacylation, isomerization and disproportionation occurred when the acylation proceeded under solvent-free condition. Preparative methods such as H-beta zeolite ion-exchange times and calcination temperature exerted influences on the catalytic butyrylation to some extent. H-beta-4 zeolite calcined at 550 °C possessed relatively better catalytic performance. Under optimized reaction conditions, only acylated isomers were formed and the conversion of BA and selectivity for 2,6-BMN was 78.3% and 53.1%, respectively.

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