

# The regioselective acylation of 2-methoxynaphthalene to 2-acetyl-6-methoxynaphthalene over zeolite beta

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## Abstract

The liquid phase acylation of 2-methoxynaphthalene (2-MON) with acetic anhydride over various solid acid catalysts was investigated under controlled reaction conditions. Only zeolite beta exhibited good regioselectivities to desired 2-acetyl-6-methoxynaphthalene (2,6-AMON). Characterization studies of zeolite beta samples indicated that acidity affected catalytic activity but not regioselectivity of 2,6-AMON. The secondary structure of zeolite beta particles was found to be an important factor for the selectivity probably because of its effect on diffusion process of reactants into internal pores. When the mole of acetic anhydride used as acylating agent was increased, the selectivity of desired 2,6-AMON product became worse. 1,2-Dichloroethane and dichloromethane were found to be effective solvents giving good regioselectivities of 2,6-AMON. Protiodeacylation took place not only for 1-acetyl-2-methoxynaphthalene (1,2-AMON) but also for 2,6-AMON. © 2000 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Friedel–Crafts acylation of aromatics is one of the most important reactions to produce aromatic ketones, which are useful intermediates for the synthesis of a number of fine chemicals such as pharmaceuticals, fragrances and dye

stuffs [1,2]. The conventional processes for the preparation of these aromatic ketones employ metal halides (AlCl<sub>3</sub>, FeCl<sub>3</sub>, etc.) or mineral acids (HF or polyphosphoric acid) as homogeneous catalysts [3]. Such processes, however, consume near stoichiometric quantities of catalysts, and the recovery of products from reaction mixture is difficult. Most of these catalysts cannot be recycled and pose serious waste disposal problems. Owing to these problems, many research groups have tried to develop environmentally benign acylation processes using solid

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acid catalysts [4–10]. In the acylation of 2-methoxynaphthalene (2-MON), one of the major products is 2-acetyl-6-methoxynaphthalene (2,6-AMON), the intermediate for an important antiinflammatory drug, (S)-(+)-6-methoxy- $\alpha$ -methyl-2-naphthaleneacetic acid, known as Naproxen. Harber et al. [11,12] reported that zeolite beta was the most effective catalyst among various zeolites in the acylation of 2-MON. According to their results, the external surface area played an important role in the catalytic activity. Gunnewegh et al. [13] studied the same reaction catalyzed by mesoporous molecular sieve such as MCM-41. They concluded that at reaction temperatures up to 100°C over H-MCM-41, the selectivity to 1-acetyl-2-methoxynaphthalene (1,2-AMON) was practically 100%. Increased reaction temperature led to a slight decrease in the selectivity of 1,2-AMON and formed small amount of undefined high molecular weight products. A similar result was reported by Choudary et al. [14] over cation-exchanged K10 montmorillonite.

Examination of these previous results indicates that Friedel–Crafts acylation of aromatic compounds could be successfully carried out over solid acid catalysts. These studies, however, have been conducted under widely different reaction conditions which could be crucial factors in determining the performance of catalysts in addition to known parameters such as the nature of catalysts, substrates and acylating agents. In the present study, we have studied the effects of reaction parameters such as solvents, reaction temperatures, concentration of reactants, and different ratios of reactants on the regioselective acylation of 2-MON with acetic anhydride to 2,6-AMON over zeolite beta which was chosen as the best catalyst in a catalyst screening study. The effects of post-treatment of zeolite beta have also been investigated. To investigate the characteristics of zeolite beta catalysts, chemical analysis, N<sub>2</sub> adsorption isotherms, FTIR, NH<sub>3</sub>-stepwise temperature programmed desorption (STPD), and SEM were used.

## 2. Experimental

### 2.1. Materials

The following zeolites were used in this study; zeolite Y of different Si/Al ratios (CBV-550, CBV-712, CBV-740, CBV-780) and beta (CP814B-25), both supplied by PQ, and the other form of beta (HSZ-930NHA) and mordenite (HSZ-620HOA) provided by Tosoh. Sulfated zirconia with 2 wt.% sulfur, a known solid superacid, was synthesized by a method reported in the literature [16]. A sample of 13% Nafion<sup>®</sup> resin/silica was provided by Dupont. The chemicals, 2-MON (Aldrich, 98%) and 2,6-AMON (Aldrich, 98%) were used without further purification. The acylating agent, acetic anhydride (Aldrich, 99%), and solvents, cyclohexane (Mallinckrodt, 99%), dichloromethane (Mallinckrodt, 99%), 1,2-dichloroethane (J.T. Baker, 99%), sulfolane (Aldrich, 99%), and nitromethane (Acros, 95%) were dried by means of molecular sieve 4A.

### 2.2. Post-treatment of zeolite beta

A zeolite beta, supplied by PQ, was converted to the active H-form by calcination in flowing air (30 ml/min) at 500°C for 4 h and denoted as H-beta. The other zeolite beta, provided by Tosoh, underwent the same treatment and was named H-beta(T). The dealuminated zeolite beta samples (DAB-0.5, 1.0, 2.0, and 10.0) were prepared by treating the parent zeolite beta (supplied by PQ) with a controlled concentration of HNO<sub>3</sub> of 0.5, 1.0, 2.0, and 10.0 M, respectively. The dealumination with 20 ml of acid solution per gram of catalyst took place in a 1-l three-necked flask under reflux at 80°C for 4 h followed by thorough washing with distilled water several times. The same treatment applied to Tosoh zeolite beta with 1.0 M HNO<sub>3</sub> and was named DAB-1.0(T). Steam-treated zeolite beta (STB-550) was prepared according to the procedure described in U.S. Pat. No. 5,522,984 [15]. Briefly, STB-550 was

obtained by steaming of the parent PQ zeolite beta at 550°C for about 2 h followed by a stabilization treatment of STB-550 without steam at 550°C for additional 2 h. DASTB-550 was prepared by stirring STB-550 in a mixture of 0.5 M HNO<sub>3</sub> and 1.5 M NH<sub>4</sub>NO<sub>3</sub> solutions at 80°C for 1 h and washing the obtained cake with distilled water several times. The silica-coated zeolite beta samples, SCB and SCB(T), were prepared by treating H-beta and H-beta(T) with the tetraethyl orthosilicate (TEOS) in hexane for 2 h according to the procedure described by Kunkeler et al. [24]. In order to convert these catalysts into the active H-forms, all the modified zeolite beta samples were treated in flowing N<sub>2</sub> (22 μmol/s) at 450°C for 2 h.

### 2.3. Reaction procedures

The acylation of 2-MON and the deacylation of 1,2-AMON and 2,6-AMON were performed at controlled reaction temperatures (PID temperature controller) in a 100 ml Autoclave batch reactor under the condition that the external mass transfer limitation was absent. Prior to adding the catalyst, the reactants were dissolved in solvent and then poured into the reactor vessel. When zeolites were used as catalysts,

they were converted to the active H-forms according to the procedure described above and then rapidly transferred to the reactor vessel just before the start of the reaction in order to minimize the time for which they were exposed to atmosphere. As-synthesized sulfated zirconia and 13% Nafion<sup>®</sup> resin/silica were stored in a desiccator until they were used for the reaction. The system was subsequently purged with dry N<sub>2</sub> before heating to flush air and moisture in the system. Samples were taken out periodically during the reaction and analyzed by GC (HP5890).

### 2.4. Synthesis of 1,2-AMON

In order to test deacylation of 1,2-AMON we prepared 1,2-AMON by a conventional Friedel–Crafts acylation with AlCl<sub>3</sub> catalyst [17,18]. The acetyl chloride (0.50 mol) was added slowly in 5 min at –20°C to a stirred suspension of AlCl<sub>3</sub> (0.55 mol) and 2-MON (0.49 mol) in dichloromethane (150 ml) under N<sub>2</sub>. At the end of the addition, the reaction mixtures were poured into 0.1 N HCl (1500 ml), cooled to 0°C and extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 1000 ml). The combined organic phase was dried over Na<sub>2</sub>SO<sub>4</sub> and molecular sieves 4A.

Table 1  
Physico-chemical properties of modified zeolite beta catalysts

Catalysts	Bulk Si/Al <sup>a</sup>	Surface area (m <sup>2</sup> /g)	Micropore <sup>b</sup> volume (ml/g)	ESA <sup>c</sup> (m <sup>2</sup> /g)	# Al sites/g <sup>a</sup>	Relative concentration (%) of acid sites <sup>d</sup>				
						Peak I	Peak II	Peak III	Peak IV	Peak V
H-beta	16	606	0.17	240	5.536 × 10 <sup>20</sup>	12.5	26.4	35.3	13.1	12.8
H-beta(T)	13	626	0.16	282	6.014 × 10 <sup>20</sup>	11.6	27.1	43.4	8.5	9.4
SCB	18	563	0.16	221	5.246 × 10 <sup>20</sup>	13.6	30.4	35.5	10.1	10.3
SCB(T)	16	663	0.18	277	5.557 × 10 <sup>20</sup>	14.4	22.6	47.0	9.7	6.3
DAB-0.5	70	630	0.18	246	1.339 × 10 <sup>20</sup>	4.6	25.0	29.9	12.1	28.4
DAB-1.0	78	635	0.18	248	1.228 × 10 <sup>20</sup>	5.9	21.4	33.4	11.8	27.5
DAB-1.0(T)	18	733	0.19	320	5.234 × 10 <sup>20</sup>	10.9	28.1	47.4	8.6	5.1
DAB-2.0	86	622	0.18	242	1.094 × 10 <sup>20</sup>	2.9	22.5	27.6	11.9	35.0
DAB-10.0	121	662	0.19	254	7.813 × 10 <sup>19</sup>	2.1	15.7	22.1	14.5	45.5
STB-550	16	557	0.16	215	5.635 × 10 <sup>20</sup>	16.5	37.4	31.6	6.8	7.7
DASTB-550	39	581	0.16	235	2.351 × 10 <sup>20</sup>	11.0	26.9	36.2	10.6	15.3

<sup>a</sup>By wet chemical analysis and ICP-atomic emission spectroscopy.

<sup>b,c</sup>The data were obtained from the slope of the t-plot of N<sub>2</sub> isotherm.

<sup>c</sup>ESA, external surface area.

<sup>d</sup>Acid sites distribution as determined from the NH<sub>3</sub>-stepwise temperature programmed desorption experiments (referred in Fig. 7).

After filtration, the solvent was removed in vacuo to give a residue. Recrystallization of the obtained powder in petroleum ether (50 ml) gave pure 1,2-AMON as confirmed by  $^1\text{H}$  NMR (300 MHz, Bruker).

### 2.5. Characterization of modified beta catalysts

Si/Al ratios for zeolite beta samples were determined by wet chemical analysis and ICP-atomic emission spectroscopy. BET areas and pore volume were obtained by  $\text{N}_2$  adsorption isotherms measured at the liquid  $\text{N}_2$  temperature using a constant volume adsorption system (Micromeritics ASAP 2010). All the analytical data for zeolite beta samples are shown in Table 1.

In order to compare the acid properties of each zeolite beta samples, the FTIR spectroscopy (Perkin Elmer 1800) and  $\text{NH}_3$ -STPD have been used. A self-supporting wafer (ca. 10  $\text{mg}/\text{cm}^2$ ) was placed in a glass sample holder inside a Pyrex IR cell with KBr windows, and heated to 450°C at a rate of 5°C/min under vacuum ( $5 \times 10^{-5}$  Torr), and then cooled to ambient temperature for recording IR spectra of hydroxyl vibration regions [19,20].  $\text{NH}_3$ -STPD was performed according to a procedure reported by Robb et al. [21], except that a sample

size of 20 mg was chosen for minimal readsorption of  $\text{NH}_3$ , and desorbed  $\text{NH}_3$  was analyzed by GC-MS (HP-5972 MSD). The particle shape of zeolite beta was observed by SEM (Hitachi, FESEM S-4200) equipped with a field emission gun.

## 3. Results

### 3.1. Effects of reaction variables

#### 3.1.1. Effect of various solid acid catalysts

Table 2 shows the results of acylation of 2-MON at 120°C with acetic anhydride over various solid acid catalysts. Most of the catalysts produced 1,2-AMON as the major product. Zeolite beta, however, was unique in producing 2,6-AMON with a higher selectivity than that for 1,2-AMON. In the case of zeolite Y (H-Y) catalysts, the conversion of 2-MON increased as the ratios of Si/Al increased. The selectivity of 2,6-AMON was low in general, but showed a maximum at Si/Al of 20. Sulfated zirconia and 13% Nafion<sup>®</sup> resin/silica showed high conversions, but very low selectivities of 2,6-AMON. Mordenite (H-MOR) showed a low 2-MON conversion and a modest selectivity to 2,6-AMON.

Table 2  
The acylation of 2-MON with acetic anhydride over different types of solid acid catalysts<sup>a</sup>

Catalysts (Si/Al) <sup>b</sup>	Surface ( $\text{m}^2/\text{g}$ )	Conversion of 2-MON <sup>c</sup> (%)		Selectivity (%)			
		1 h	14 h	1,2-AMON <sup>c</sup>		2,6-AMON <sup>c</sup>	
				1 h	14 h	1 h	14 h
H-Y(3)	750	14.9	15.6	92.6	92.4	5.9	5.8
H-Y(6)	730	59.4	57.2	88.3	86.8	8.1	9.2
H-Y(20)	750	57.6	59.1	84.3	78.6	10.6	13.5
H-Y(40)	780	62.5	60.0	87.7	87.3	8.2	8.4
H-MOR(8)	400	11.0	17.7	71.6	73.5	27.6	25.7
H-beta(16) <sup>d</sup>	606	42.4	57.7	34.8	31.7	58.3	60.5
Sulfated zirconia	83	57.1	54.8	96.8	96.7	1.9	2.1
13% Nafion <sup>®</sup> resin/silica	150	48.6	46.8	92.8	94.0	5.0	4.6

<sup>a</sup>Reaction conditions: initial mole ratio of acetic anhydride to 2-MON, 2; amount of solvent, 50 ml of 1,2-dichloroethane; reaction temperature, 120°C; catalyst loading, 1.0 g.

<sup>b</sup>Si/Al ratios were obtained from the suppliers.

<sup>c</sup>2-MON, 2-methoxynaphthalene; 1,2-AMON, 1-acetyl-2-methoxynaphthalene; 2,6-AMON, 2-acetyl-6-methoxynaphthalene.

<sup>d</sup>The Si/Al ratio was determined by wet chemical analysis and ICP-atomic emission spectroscopy.

### 3.1.2. Solvents

The solvent employed for acylation of 2-MON exerted a significant effect on activity and selectivity of H-beta catalyst as shown in Table 3. 1,2-Dichloroethane and dichloromethane showed higher activity and selectivity to 2,6-AMON. A nonpolar solvent (cyclohexane) or a very polar solvent (nitromethane) showed slightly lower selectivity of 2,6-AMON compared with 1,2-dichloroethane and dichloromethane. Most of the solvents tested in this study gave the ratios of 1,2-AMON/2,6-AMON less than 1, except for sulfolane and acetic anhydride with the latter used as acylating agent and solvent. Sulfolane showed unusually high selectivity toward 1,2-AMON over H-beta. According to the previous study by Fang et al. [22], quantitative analysis of zeolite Y after the acylation of *m*-xylene with benzoylchloride in sulfolane showed a 20% reduction in aluminum content. They concluded that the extra-framework aluminum in zeolite Y formed a catalytically active homogenous species when the reaction was performed in sulfolane as solvent. But in our system, H-beta did not change its Si/Al ratio after acylation of 2-MON with acetic anhydride in both sulfolane and 1,2-dichloroethane solvents. Consequently, it was concluded that the low selectivity of 2,6-AMON in sulfolane was not due to the modified catalytic

species but due to the properties of the solvent itself.

### 3.1.3. Reaction temperature and initial mole ratio of reactants

The effects of reaction temperature were tested at 60, 90, 120 and 180°C as shown in Fig. 1. At the low reaction temperature of 60°C, the conversion was limited to less than ca. 14% and the selectivity of 2,6-AMON was less than that of 1,2-AMON. When the reaction temperature was increased to 120°C, the conversion of 2-MON and the selectivity of 2,6-AMON increased. The conversion increased rapidly to ca. 45% within an hour and then increased very slowly afterwards. At 180°C, the initial rate of 2-MON conversion became greater, yet the conversion decreased slowly during the further reaction time.

When the initial mole ratio of acetic anhydride to 2-MON was changed, the catalytic activity and the selectivity of 2,6-AMON were also varied as shown in Fig. 2. When the mole ratio of acetic anhydride/2-MON increased for the fixed amount of 2-MON, the conversion increased up to the ratio of 2. Further increase in the ratio resulted in no gain in the catalytic activity or the conversion decreased when acetic anhydride was employed as the solvent. The

Table 3

The acylation of 2-MON with acetic anhydride in various solvents over H-beta<sup>a</sup>

Solvents	Conversion of 2-MON <sup>b</sup> (%)		Selectivity (%)			
	1 h	14 h	1,2-AMON <sup>b</sup>		2,6-AMON <sup>b</sup>	
			1 h	14 h	1 h	14 h
Cyclohexane	21.8	26.1	39.9	41.4	51.4	50.2
1,2-Dichloroethane + cyclohexane <sup>c</sup>	22.5	29.5	39.6	37.3	52.9	54.2
Dichloromethane	33.2	52.7	35.5	31.9	57.5	60.3
1,2-Dichloroethane	42.4	57.7	34.8	31.7	58.3	60.5
Nitrobenzene	37.1	40.0	37.5	37.0	54.7	55.0
Sulfolane	32.6	53.0	81.6	81.1	16.0	16.0
Acetic anhydride	31.6	34.0	59.8	61.5	35.4	33.2
Nitromethane	20.7	22.5	46.9	47.1	45.9	46.2

<sup>a</sup>Reaction conditions: initial mole ratio of acetic anhydride to 2-MON, 2; amount of solvent, 50 ml; reaction temperature, 120°C; catalyst loading, 1.0 g of H-beta.

<sup>b</sup>2-MON, 2-methoxynaphthalene; 1,2-AMON, 1-acetyl-2-methoxynaphthalene; 2,6-AMON, 2-acetyl-6-methoxynaphthalene.

<sup>c</sup>Ratio of two solvents, 1:1 by volume.

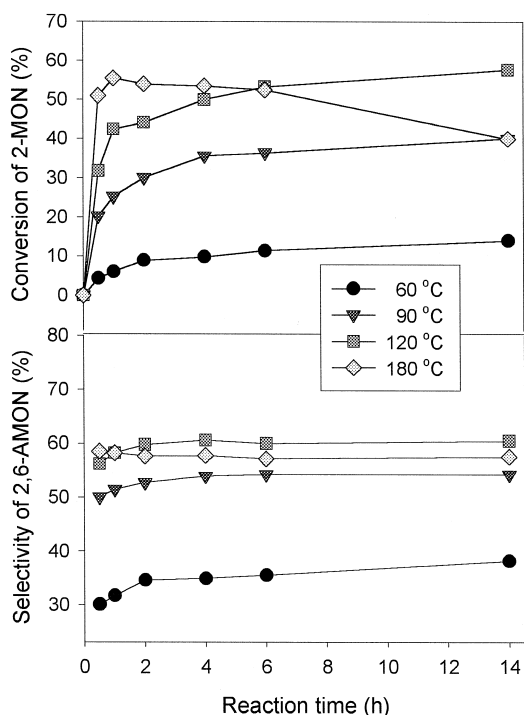


Fig. 1. Effect of the reaction temperature on the acylation of 2-MON with acetic anhydride over H-beta. Reaction conditions: initial mole ratio of acetic anhydride to 2-MON, 2; amount of solvent, 50 ml of 1,2-dichloroethane; catalyst loading, 1.0 g.

selectivity of 2,6-AMON decreased slightly with increasing the ratios and a very poor selectivity was obtained when acetic anhydride was used as the solvent. A selectivity of 2,6-AMON close to 75% was obtained at the acetic anhydride/2-MON ratio of 0.5.

### 3.1.4. Amounts of solvent and catalyst

Fig. 3 shows that the catalytic activity increases as the amount of solvent (1,2-dichloroethane) decreases or as the amount of catalyst (H-beta) increases. The selectivities to 2,6-AMON were similar in all cases except for the one which the larger amount of catalyst increased the selectivity of 2,6-AMON substantially. These results indicate that the more concentrated reaction system enhances the catalytic activity and the amount of catalyst affects the selectivity.

## 3.2. Deacylation reactions

The protideacylation of 1,2-AMON has been described in the literature [11,13]. In our experiments presented in Fig. 1, the conversion of 2-MON reached different saturated values with reaction time that depended on the reaction temperature; the higher saturated conversion at the higher temperature. At 180 °C, the conversion reached a maximum and decreased with time. The selectivity to 2,6-AMON also showed a strong dependence on the reaction temperature and the best selectivity was obtained at 120 °C. Furthermore, the calculated yield of 2,6-AMON (conversion of 2-MON multiplied by the selectivity to 2,6-AMON) also slightly decreased with time at 180 °C. To our best knowledge, the deacylation of 2,6-AMON, a thermodynamically stable substance, has not been reported.

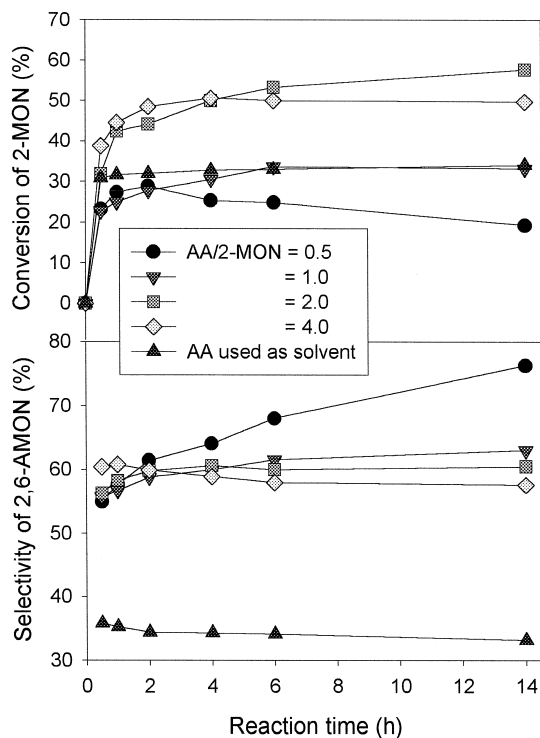


Fig. 2. Influence of acetic anhydride (AA)/2-MON mole ratios on the acylation of 2-MON over H-beta. Reaction conditions: initial mole of 2-MON, 10 mmol; reaction temperature, 120 °C; amount of solvent, 50 ml of 1,2-dichloroethane; catalyst loading, 1.0 g.

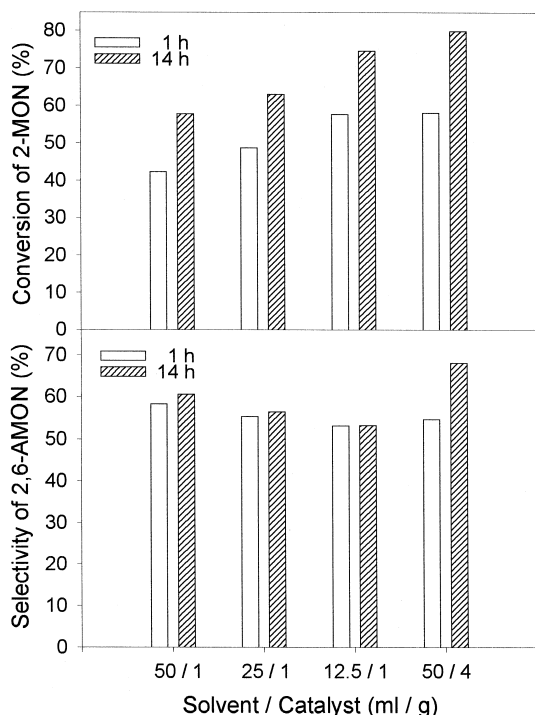


Fig. 3. Effect of the amounts of solvent (1,2-dichloroethane) and catalyst (H-beta) on the acylation of 2-MON. Reaction conditions: initial mole ratio of acetic anhydride to 2-MON, 2; reaction temperature, 120°C.

Hence, we tested the deacylation of both 1,2-AMON and 2,6-AMON over H-beta. The deacylation of 1,2-AMON at three reaction temperatures is presented in Fig. 4. Both deacylation to 2-MON and reacylation to 2,6-AMON occurred. As the reaction temperatures increased, the conversion of 1,2-AMON and the selectivity to 2,6-AMON were increased. The selectivity to 2,6-AMON at 180°C decreased slightly after 0.5 h of the reaction. Fig. 5 shows that the deacylation of 2,6-AMON indeed occurred at 180°C. But the reaction did not proceed at 120°C. The selectivity of 2-MON is ca. 32% and the rest was other products that did not include 1,2-AMON. These results account for plateaus in 2-MON conversions with reaction time shown in Fig. 1, indicating that the reaction temperatures must be optimized to develop a process of regioselective acylation of 2-MON over H-beta.

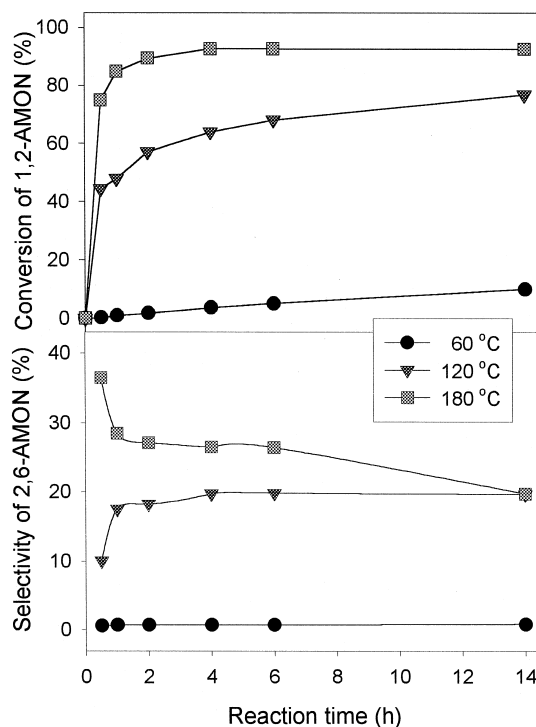


Fig. 4. Influence of reaction temperatures on the deacylation of 1,2-AMON over H-beta. Reaction conditions: initial mole of 1,2-AMON, 10 mmol; amount of solvent, 50 ml of 1,2-dichloroethane; catalyst loading, 1.0 g.

We also tested the deacylation of 1,2-AMON (10 mmol) in dichloroethane (50 ml) over sul-

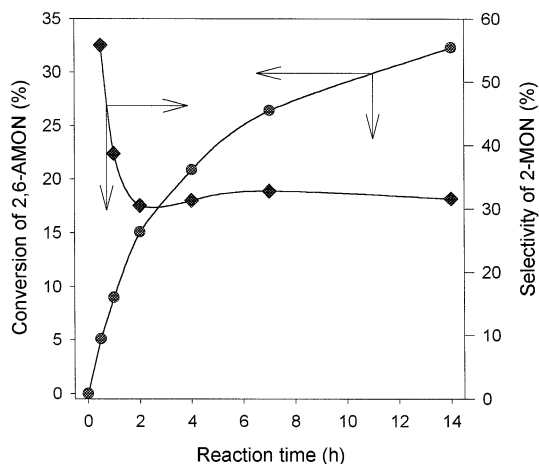


Fig. 5. The deacylation of 2,6-AMON over H-beta. Reaction conditions: initial mole of 2,6-AMON, 10 mmol; reaction temperature, 180°C; amount of solvent, 50 ml of 1,2-dichloroethane; catalyst loading, 1.0 g.

fated zirconia (1.0 g) at 120 and 180°C. In both cases, the major product was 2-MON without converting to 2,6-AMON, and the conversions were 58 and 79% after 14 h, respectively.

### 3.3. The acylation of 2-MON over modified beta catalysts

Table 4 shows the effects of different treatments of zeolite beta samples on the acylation of 2-MON. Surprisingly, there was a significant difference between H-beta and H-beta(T) in the selectivity of 2,6-AMON even though both catalysts had similar physico-chemical properties as shown in Table 1. At the similar level of conversion, 2,6-AMON was the major product over H-beta while 1,2-AMON was dominant over H-beta(T). These catalysts were treated with TEOS to obtain SCB and SCB(T) samples, although we were aware of the difficulty of a uniform silica-coating by the TEOS on the surface of zeolite beta microcrystalline size [24]. The conversion of 2-MON over these catalysts was slightly lower at the reaction time of 1 h, but after 14 h, they recovered the conversions of untreated catalysts. Both treated catalysts displayed slightly increased selectivity of 2,6-AMON compared with untreated ones.

Increasing the ratio of bulk Si/Al by acid treatment of parent H-beta with increasing concentrations of HNO<sub>3</sub> (DAB-0.5 to DAB-10.0) resulted in the substantial increase in the 2-MON conversion and decrease in the selectivity of 2,6-AMON. When excessive HNO<sub>3</sub> concentrations ( $\geq 2.0$  M) were employed, however, extremely high Si/Al ratios were observed and the catalytic activity decreased. Overall, the selectivity of 2,6-AMON was decreased slightly with increasing Si/Al ratios for the same parent zeolite beta catalyst. In case of steamed catalyst (STB-550), the bulk Si/Al ratios was not changed from its parent zeolite beta and the catalytic activity and selectivity were only slightly affected. When STB-550 was treated with 0.5 M HNO<sub>3</sub> (DASTB-550), the conversion increased and the selectivity of 2,6-AMON decreased slightly compared with STB-550 in line with the effects of the acid treatment observed for unsteamed catalysts.

### 3.4. Characterization of modified zeolite beta catalysts

It is well known that the properties and the catalytic activities of zeolite depend on the states of aluminum in zeolite itself. Observation of

Table 4  
The acylation of 2-MON with acetic anhydride over modified zeolite beta catalysts<sup>a</sup>

Catalysts	Conversion of 2-MON <sup>b</sup> (%)		Selectivity (%)			
	1 h	14 h	1,2-AMON <sup>b</sup>		2,6-AMON <sup>b</sup>	
			1 h	14 h	1 h	14 h
H-beta	42.4	57.7	34.8	31.7	58.3	60.5
H-beta(T)	46.8	58.8	74.7	71.5	20.5	22.2
SCB	36.2	56.2	34.1	29.7	59.1	62.5
SCB(T)	40.0	56.3	62.0	57.3	32.4	35.8
DAB-0.5	60.4	70.7	52.4	45.1	41.6	47.4
DAB-1.0	55.7	72.0	55.8	45.8	38.6	46.9
DAB-1.0(T)	60.7	62.6	73.3	72.0	19.5	22.1
DAB-2.0	50.8	62.4	55.8	49.4	38.6	43.8
DAB-10.0	24.6	26.6	58.0	55.3	37.5	39.7
STB-550	42.6	50.4	37.7	35.4	55.7	57.4
DASTB-550	52.4	57.6	45.5	41.5	48.4	51.7

<sup>a</sup>Reaction conditions: initial mole ratio of acetic anhydride to 2-MON, 2; amount of solvent, 50 ml of 1,2-dichloroethane; reaction temperature, 120°C; catalyst loading, 1.0 g.

<sup>b</sup>2-MON, 2-methoxynaphthalene; 1,2-AMON, 1-acetyl-2-methoxynaphthalene; 2,6-AMON, 2-acetyl-6-methoxynaphthalene.



hydroxyls absorption bands in zeolite beta using FTIR provides useful information concerning the states of aluminum [19,20,23]. Five types of hydroxyl groups are generally known; strongly acidic bridging hydroxyl groups (ca.  $3610\text{ cm}^{-1}$ ), hydroxyls bonded to extra-framework aluminum ( $3660\text{--}3680\text{ cm}^{-1}$ ), internal SiOH at framework defects (ca.  $3738\text{ cm}^{-1}$ ), terminal silanol groups (ca.  $3746\text{ cm}^{-1}$ ), and hydroxyls bonded to transient states of aluminum leaving the framework (ca.  $3782\text{ cm}^{-1}$ ). In our FTIR study, all these bands were confirmed although the band for the extra-framework aluminum was very weak or absent (Fig. 6). The differences

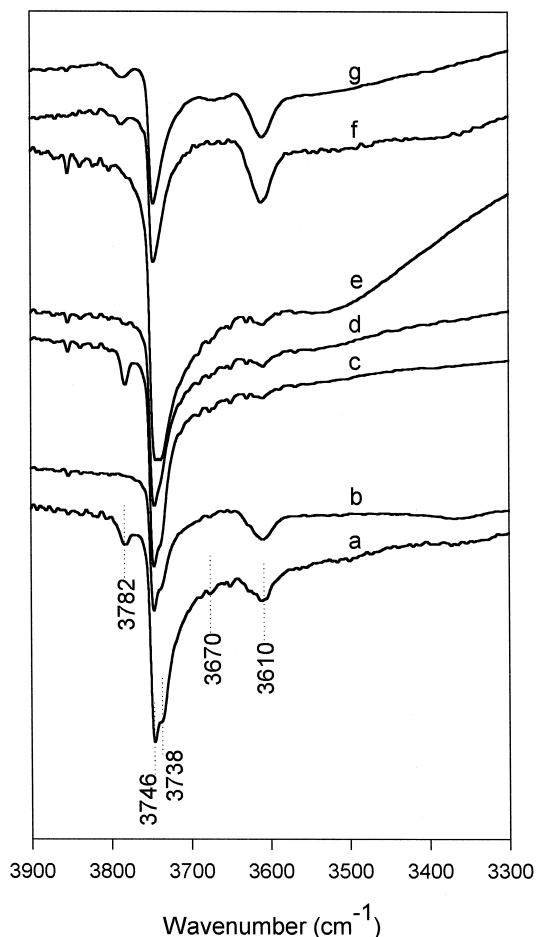


Fig. 6. FTIR spectra (hydroxyl vibration region) of zeolite beta catalysts. (a) H-beta, (b) SCB, (c) STB-550, (d) DASTB-550, (e) DAB-1.0, (f) H-beta(T), (g) SCB(T).

between H-beta and H-beta(T) used in this study (Fig. 6a,f) were the higher intensity for H-beta(T) of the band at  $3610\text{ cm}^{-1}$  due to bridging hydroxyls and the existence of internal SiOH at  $3738\text{ cm}^{-1}$  for H-beta due to framework defects. In the case of SCB (Fig. 6b), relative peak intensity was weakened and the band of AlOH associated with the transition state was disappeared compared to the spectrum of its parent beta (Fig. 6a). In the case of SCB(T) (Fig. 6g), however, there were no significant difference from the spectrum of its parent beta (Fig. 6f). The FTIR spectrum of STB-550 (Fig. 6c) displayed slightly intensified the band of AlOH associated with the transition state. Such band disappeared after mild acid treatment (Fig. 6d). When the Si/Al ratio increased by acid treatment to 78 in DAB-1.0, all bands concerning Al were weakened, but the band due to the internal SiOH at framework defects was strengthened in its FTIR spectrum (Fig. 6e). A feature shared by steam-treated or dealuminated beta zeolites is the drastic reduction in the intensity of bridging hydroxyls as shown in Fig. 6c–e.

To investigate the relative acidity of each zeolite beta samples, we conducted the  $\text{NH}_3$ -STPD experiments. The  $\text{NH}_3$ -STPD data of various modified zeolite beta catalysts were presented in Table 1 as relative concentration (%) of acid sites. In Fig. 7, two typical  $\text{NH}_3$ -STPD spectra for H-beta and H-beta(T) are displayed that show the five peaks, with their relative areas presented in Table 1, together with the program of temperature ramping employed. Robb et al. [21] found that the first two peak (peak I, II) in Fig. 7 corresponded to weak Lewis acid sites, while the last three (peak III, IV, and V) were assigned to Brønsted acid sites of increasing strength. Following their interpretation, H-beta and H-beta(T) possess the similar relative concentration (%) of Lewis acid sites, but H-beta(T) has more Brønsted acid sites (peak III) than H-beta. As the Si/Al ratio was increased by acid treatment (DAB-0.5 to DAB-10.0), the relative concentration (%) of stronger

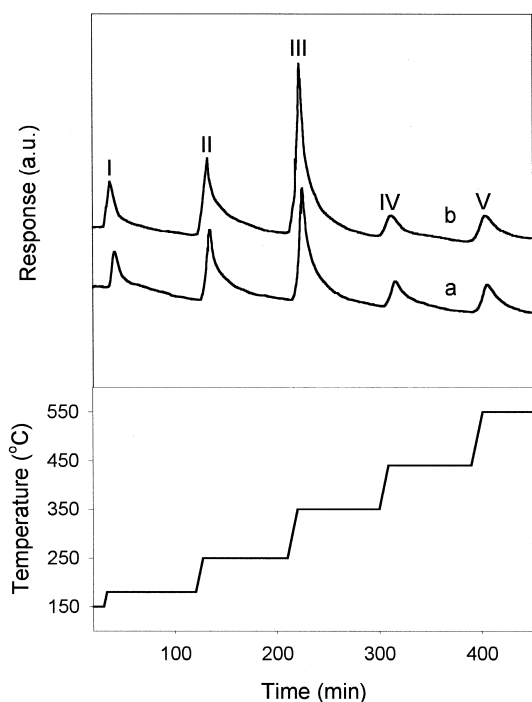


Fig. 7.  $\text{NH}_3$ -stepwise temperature programmed desorption ( $\text{NH}_3$ -STPD) of H-beta (a) and H-beta(T) (b).

Brønsted acid sites (peak V) was also increased, yet the selectivity of 2,6-AMON was decreased. In the case of steamed zeolite beta (STB-550), the FTIR band for AlOH groups associated with the transition states was strengthened and that of bridging hydroxyls decreased. The relative concentrations of Lewis acid sites (Peak I, II) were increased at the expense of Brønsted acid site concentrations (Peak III–V). On the other hand, the catalytic activity and the selectivity of 2,6-AMON were slightly decreased without significant change in bulk Si/Al ratio.

The scanning electron micrographs of H-beta, H-beta(T), SCB and SCB(T) are shown in Fig. 8. Both H-beta and H-beta(T) showed particle sizes less than 50 nm but their morphology was considerably different from each other. H-beta was in the form of small aggregates composed of several particles, while H-beta(T) formed large aggregates made of a great number of particles. There was no significant change of its shape in SCB as compared to H-beta. But the

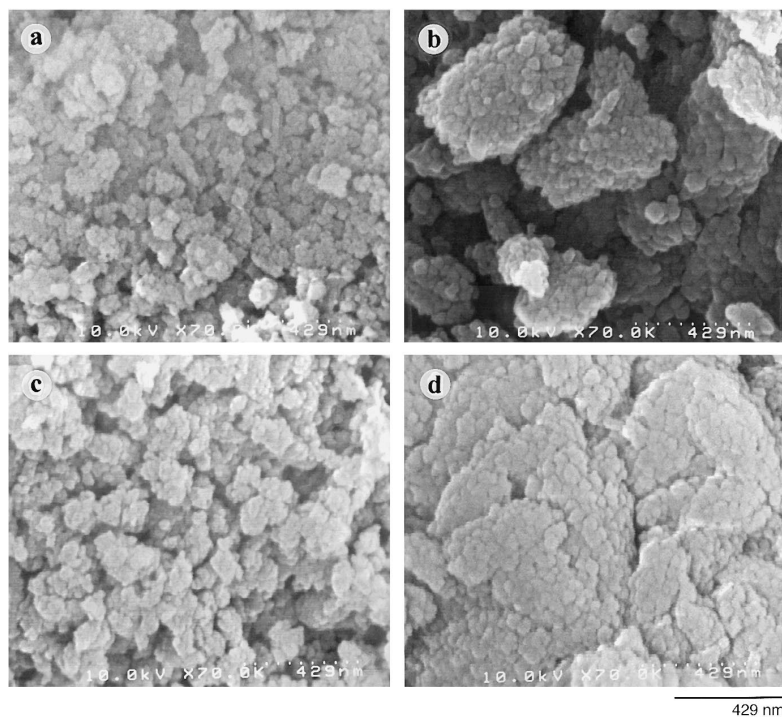


Fig. 8. SEM images of H-beta (a), H-beta(T) (b), SCB (c), and SCB(T) (d).

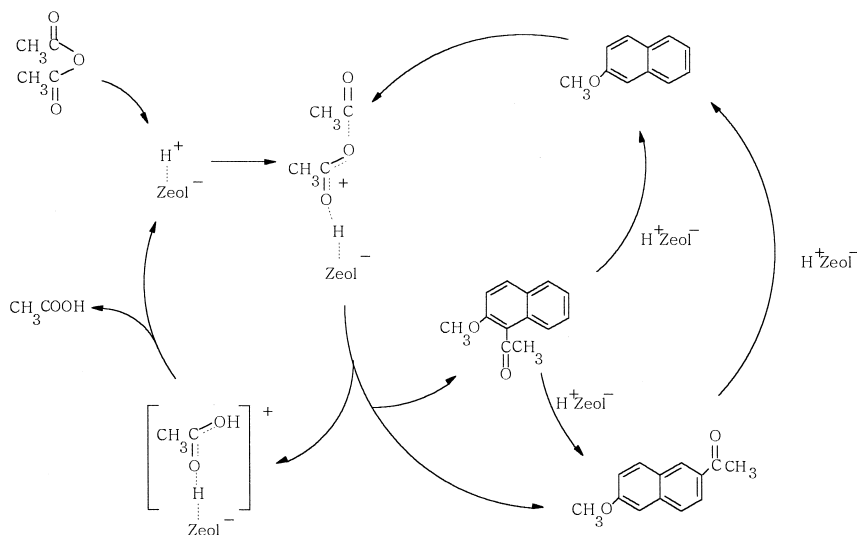
aggregation in SCB(T) was intensified compared to its parent H-beta(T).

#### 4. Discussion

In the Friedel–Crafts acylation of 2-MON, 1,2-AMON is a kinetic product and 2,6-AMON is a thermodynamic product. In homogenous catalytic system, the acylation of 2-MON gives to a mixture of 1,2-AMON and 2,6-AMON initially, and then 1,2-AMON is converted to 2,6-AMON in a long reaction time [3,17]. Because the homogeneous catalyst provides free catalytic sites, substituted acyl group at the sterically hindered 1-position migrates to the more stable 6-position. The result represents an isomerization of 1,2-AMON to 2,6-AMON with homogeneous catalyst system. In heterogeneous catalytic system, however, most of catalytic sites are fixed on external surfaces and inner pores, and the selectivity of the products will be changed according to the restriction imposed on the sites. Over fixed catalytic sites without a geometric restriction, formed 1,2-AMON converted back only to 2-MON at higher temperatures [13,14]. Indeed, we observed that the major product in the deacylation of 1,2-AMON

was 2-MON and no formation of 2,6-AMON even at 180°C when sulfated zirconia was used as catalyst. Over H-beta, by contrast, 1,2-AMON reacted to yield not only 2-MON but also 2,6-AMON.

The reactions occurring in acylation of 2-MON over H-beta could be summarized as in Scheme 1. Acetic anhydride is coordinated to a Brønsted acid site of the zeolite beta to form an electrophilic complex. The complex attacks an incoming 2-MON to produce aromatic ketones and another electrophilic complex. This other complex gives acetic acid as by-product and the catalytic acid site is recovered. Among aromatic ketones, only 1,2-AMON and 2,6-AMON are major products. They are produced in different ratios depending on the geometric restrictions imposed on the catalytic sites. Less stable 1,2-AMON undergoes further reactions of deacylation to 2-MON and isomerization to 2,6-AMON. These reactions may proceed in two steps. First, 1,2-AMON is easily deacylated to 2-MON, and gives acylium ions on the sites. In the next step, the attached acylium ion attacks the less sterically hindered position of 2-MON (6-position) to produce 2,6-AMON. The deacylation of thermodynamically stable 2,6-AMON also occurs over H-beta catalyst at high temperatures.



Scheme 1. A reaction pathway for the acylation of 2-MON catalyzed by H-beta.

The solvent has a significant effect on catalytic activity and selectivity in acylation of 2-MON over H-beta. The yield of 2,6-AMON reaches a maximum in 1,2-dichloroethane with an intermediate polarity. The cause of this interesting solvent effect is not clear at the moment.

It is not an easy task to exactly assign the characteristic bands of FTIR to peaks of  $\text{NH}_3$ -STPD. The band for bridging hydroxyls at framework is well known to be due to strong acid sites and could be assigned to the last three peaks of the  $\text{NH}_3$ -STPD with different acid strengths. These bridging hydroxyls at framework should be the main source of acid-catalyzed reactions. Indeed, the catalytic activity increased as Si/Al ratio increased in DAB-series catalysts and the  $\text{NH}_3$ -STPD peak areas of higher acid strengths also increased with Si/Al ratios until the loss of total active sites offset the gain in acid strength in DAB-10.0. However, the selectivity of 2,6-AMON decreased continuously as Si/Al ratio increased. This suggests that regioselectivity is controlled by the structure of the catalyst rather than its acidity. Thus, the acid treatment impairs the original structure of beta that was responsible for the high regioselectivity for 2,6-AMON. This could be seen in the intensified internal SiOH band at framework defects as presented in Fig. 6e. In the case of passivation by the TEOS of H-beta and H-beta(T), the reason for the lower catalytic activity after 1 h compared to their parent catalysts is probably due to silica coating of their surface active sites. There is an interesting result in Fig. 6 that shows a difference between two zeolite beta catalysts. The band due to AlOH groups associated with the transition state disappeared after the passivation for SCB but not for SCB(T). Thus, the passivation do not exert the same effect on H-beta and H-beta(T). Furthermore, the acid treatment with 1.0 M  $\text{HNO}_3$  resulted in great increase in Si/Al ratio for H-beta, but did not affect much for H-beta(T).

Zeolite beta has a three-dimensional intersecting, 12-membered ring channel system,  $0.76 \times 0.64$  nm for two straight channels and  $0.55 \times$

$0.55$  nm for a sinusoidal channel [25]. According to Harvey and Mader [11], only zeolite beta gives 2,6-AMON as the major product because it has a more restricted pore structure to the desired product. However, one interesting observation made in this study is the greatly different catalytic selectivity between H-beta and H-beta(T). As shown in Fig. 8, H-beta is in the form of aggregates consisting of only several particles while H-beta(T) forms large aggregates made up of lots of particles. Thus, 2-MON would need a longer average diffusion length in H-Beta(T) to reach internal pores of the zeolite. Zeolite beta in general possesses significant fractions active sites on its external surface as well as in its inner pores. Table 1 shows that the fraction of external surface area is greater than 40% for two H-beta catalysts and that H-beta(T) has a significantly greater external surface area. With these two considerations, one can expect that the contribution of internal sites to the reaction is greater for H-beta than H-beta(T). Since the only internal acid sites with restricted geometry can produce 2,6-AMON, the higher selectivity over H-beta could be accounted for. The presence of internal defects in H-beta could also have facilitated the diffusion of 2-MON into internal pores. The relative difficulty of reaching internal pores of H-beta(T) is also reflected in the absence of any significant changes upon passivation and dealumination treatments while marked changes are observed for H-beta.

## 5. Conclusion

There are many factors affecting the regioselective acylation of 2-MON. The pore structure of zeolite beta is the key to the selective formation of desired 2,6-AMON. Because of the importance of material transport through pores, and only internal pores of zeolite beta are responsible for the formation of 2,6-AMON, the secondary structure of zeolite particles are also important. This appears to be responsible for the

different selectivities between H-beta and H-beta(T). Furthermore, reaction conditions such as temperature, reactant ratio, and solvent should be optimized in order to enhance the selectivity to 2,6-AMON.

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