

Acylation of 2-Methoxynaphthalene and Isobutylbenzene over Zeolite Beta

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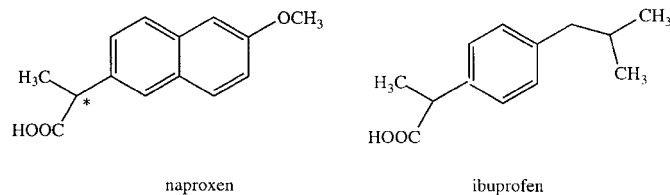
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The acylation of 2-methoxynaphthalene (2MN) with acetic anhydride is carried out in the liquid phase in the presence of zeolite beta. Two main products, 1-acetyl-2-methoxynaphthalene (1,2-AMN) and the desired 2-acetyl-6-methoxynaphthalene (2,6-AMN) are obtained. Variations of reaction temperature, the concentration of the acylating agent, and the weight of the catalyst are investigated to find reaction conditions sufficient to provide for good conversion of 2MN and limited deactivation. Surface-poisoning experiments show that the formation of 1,2-AMN occurs on the external surface of the zeolite. When the external surface of zeolite beta is passivated by coating with amorphous silica, a significant increase in the selectivity of 2,6-AMN is observed and this result is a clear example of shape-selective acylation with zeolite catalysts. The acylation of isobutylbenzene with acetic anhydride is investigated also. At conversions of around 10%, the selectivity to 4-isobutylacetophenone is excellent (>97%). For the acylation of isobutylbenzene, the external surface of the zeolite contributes significantly to the formation of 4-isobutylacetophenone, so the shape-selective properties of the zeolite are not utilized. © 2000 Academic Press

Key Words: shape-selective acylation; 2-methoxynaphthalene; naproxen; isobutylbenzene; ibuprofen; zeolites beta.

1. INTRODUCTION

Friedel Craft acylation is a useful step for the synthesis of pharmaceutical compounds such as (*S*)-naproxen and ibuprofen (1).

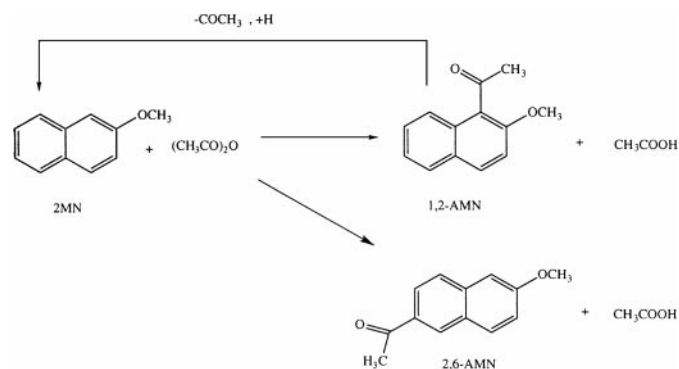


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The acylation of 2-methoxynaphthalene (2MN) by aluminum chloride was a step in the first large-scale synthesis of naproxen (2), and the acylation of isobutylbenzene with hydrogen fluoride is currently used in the synthesis of ibuprofen (3). Because of current environmental restrictions, replacement of conventional homogeneous catalysts with solid acid catalysts has great industrial importance. Zeolites, with their shape-selective properties and good regenerability, have been found to be viable alternatives to liquid acids in numerous cases (4–17). The first industrial application of a zeolite-promoted acylation for the production of an aromatic ketone was recently reported by researchers at Rhône-Poulenc (11).

The acetylation of 2MN has been investigated over MCM-41 (18), HY, ZSM-12 and *BEA (4, 16), and ZSM-5 and mordenite (5). Two products are usually obtained, 1-acetyl-2-methoxynaphthalene (1,2-AMN) and 2-acetyl-6-methoxynaphthalene (2,6-AMN), with the undesired 1,2-AMN product generally predominating. Indeed, the acylation generally occurs at the kinetically favored 1-position. However, the deacylation of the acyl group has been observed to give back 2MN (4). These data are consistent with the following reaction scheme:



The results from all previous investigations suggest that zeolite beta may be an interesting catalyst for the production of 2,6-AMN since it was speculated that its formation is favored inside the pores of *BEA (4). Moreover, molecular modeling has been investigated over mordenite, L, and

*BEA (19). It has been shown that the energy barrier for diffusion of 2,6-AMN is smaller than those of the other isomers in the case of zeolite beta, which is in agreement with observed catalytic properties (4). However, due to the contribution of acid sites on the external surface of the crystals, a large amount of 1,2-AMN product is formed (16). In fact, this reaction has been used as a model reaction to characterize the external surface of zeolite beta crystals (20). In contrast, the acylation of isobutylbenzene over zeolite beta has been reported by researchers at Rhône-Poulenc to be selective in the production of 4-isobutylacetophenone, the desired product (21).

Here, the acylation of 2MN and isobutylbenzene with zeolite beta is investigated. The goal of this work is to test whether the external surface sites can be eliminated to improve the performance of the catalyst to obtain a viable acylation catalyst for the formation of precursors to the nonsteroidal anti-inflammatory agents naproxen and ibuprofen.

2. EXPERIMENTAL SECTION

2.1. Materials

Numerous samples of zeolite beta with different Si/Al ratios and crystal sizes were used in this study for the acylation of 2MN and isobutylbenzene. The sample denoted BEA1 was obtained from PQ and was ion exchanged with a 1.0 M NH_4Cl solution for 24 h at $\sim 80^\circ\text{C}$ (repeated three times) with subsequent calcination to 550°C in air to generate the proton form. BEA2 and BEA3 were synthesized in fluoride media by modifying the method reported by Cambor *et al.* (22). Tetraethylammonium fluoride (12.13 g, 81.3 mmol, Aldrich) and aluminum nitrate nanohydrate (0.92 g, 2.45 mmol, Aldrich) were dissolved in water (13.58 g, 75.44 mmol). To this solution was added tetraethylorthosilicate (TEOS) (25.45 g, 122.2 mmol, Aldrich) dropwise with stirring. The solution was allowed to stir for 24 h, after which the alcohol generated by hydrolysis was removed *in vacuo*. Additional water was added and the evaporation procedure was repeated. The gel obtained and 50 mg of zeolite beta seed crystals were transferred to a Teflon-lined autoclave and heated under autogenous pressure at 140°C for 7 days in rotary mode (BEA2) or in static mode (BEA3). The samples were recovered by filtration, washed with water, and dried in air overnight at 100°C . The samples were calcined in air using the following temperature program: heat to 175°C at $1^\circ\text{C}/\text{min}$ and hold at 175°C for 2 h; heat to 550°C at $1^\circ\text{C}/\text{min}$ and hold at 550°C for 6 h.

2.2. Postsynthetic Modifications

Modifications of the zeolite beta crystals were performed using the following method: 0.25 g of HBEA (BEA1, BEA2, or BEA3) were stirred under an argon atmosphere

in 3 ml of hexane to which 0.1 ml of TEOS was added. Stirring was continued for 3 h, 1 h, or 30 min, after which the zeolite was recovered by filtration and washed with hexane. This method has been shown to coat the surface of zeolite beta with silica (23). The samples are identified by the letter "p" and followed by the time of coating, e.g., BEA1p(3h) denotes the BEA1 sample that was contacted with TEOS for 3 h.

2.3. Characterization

X-ray powder diffraction (XRD) patterns were collected on a Scintag XDS 2000 diffractometer using $\text{CuK}\alpha$ radiation. Nitrogen adsorption isotherms were obtained at 77 K using an Omnisorp 100 sorption apparatus. Adsorption capacities of vapor-phase cyclohexane were obtained on a McBain-Bakr balance. The micropore volume was determined at $P/P_0 = 0.25$. Prior to all adsorption experiments, the samples were degassed under vacuum at 250°C for 2 h. Scanning electron micrographs (SEM) were recorded on a Camscan Series 2-LV scanning electron microscope. X-ray photoelectron spectroscopy (XPS) experiments were conducted on a Kratos AXIS-HS spectrometer. The X-ray source was monochromatized $\text{AlK}\alpha$ at 1478 eV. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, TN. The increases in weight of the used catalysts were obtained on a Dupont Instruments 951 thermogravimetric analyzer (TGA). The samples were heated in air to 800°C and maintained for 1 h at 800°C . The extraction of the carbonaceous compounds deposited in the zeolite was carried out according to the procedure described by Guisnet and Magnoux (24).

2.4. Catalyst Testing

All chemicals were purchased from Aldrich Chemical Co. Only the acetic anhydride was purified (reflux in the presence of magnesium for 5 days and then distilled) before use.

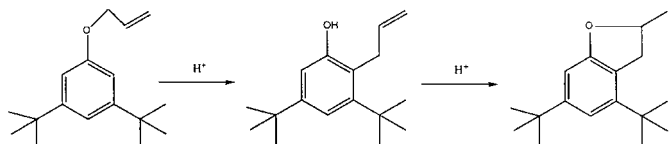
Acylation reactions were carried out in a sealed batch reactor under argon equipped with a magnetic stirrer (600 rpm) and heated under autogenous pressure in an oil bath at 100°C with acetic anhydride as the acylating reagent and 1,2-dichloroethane as the solvent. Prior to use, 0.10 g or 0.25 g of catalyst was calcined *in situ* in air to 550°C . 2MN or isobutylbenzene (1.1 mmol), acetic anhydride (1.1 mmol), and an internal standard (1,3,5-tri-*tert*-butylbenzene or dodecane) were dissolved in 0.860 ml of solvent and added to the vessel. Aliquots of the reaction mixture were sampled and analyzed by gas chromatography equipped with a FID detector (HP 5890 II) on a 30-m HP-5 column.

The products were identified by comparing their retention time to commercial (2,6-AMN) or synthesized (1,2-AMN) compounds or by GC-MS analysis (other acylated compounds, diacylated compounds). The error in

the experimental results was found to be in a range of ± 3 –4%.

At the end of the reaction, the sample was recovered by filtration, washed with dichloromethane, and dried at room temperature, *in vacuo*. Then, the sample was regenerated under dried air to 550°C or characterized by different methods.

The external surface activity of the zeolite was measured using the conversion of the bulky allyl 3,5-di-*tert*-butylphenyl ether (23, 25). This ether is too large to enter the pores of zeolite beta and is transformed into 2-allylphenol that is then cyclized into 2-methylidihydrobenzofuran:



The reaction was carried out in a batch reactor under argon at 100°C with 0.10 g of activated zeolite, 0.4 mmol of allyl 3,5-di-*tert*-butylphenyl ether, and 2 ml of 1,2-dichloroethane. Aliquots of the reaction mixture were sampled and analyzed by gas chromatography on a 30-m HP-5 column.

3. RESULTS AND DISCUSSION

3.1. Characterization of Zeolite Beta Samples

Table 1 lists the Si/Al ratio and the crystal size of the samples BEA1, BEA2, and BEA3. The materials synthesized in fluoride media, BEA2 and BEA3, have larger crystal sizes than the commercial sample. BEA2, obtained under stirred conditions, has a smaller crystal size than BEA3, which was prepared at static conditions. All of these samples have an XRD pattern typical of highly crystalline *BEA.

The micropore volume of the parent zeolites BEA1, BEA2, and BEA3 and the passivated samples BEA1p(3h), BEA2p(3h), and BEA3p(3h) are given in Table 2. Except for BEA1, the micropore volumes determined with nitrogen and cyclohexane are similar. From the nitrogen adsorp-

TABLE 1

Properties of Zeolite Beta Samples

Sample	Si/Al ^a	Crystal size (μm) ^b
BEA1	12	<1
BEA2	40	2.5
BEA3	40	9

^a As determined by elemental analysis.

^b As determined by SEM.

TABLE 2

Micropore Volume of Zeolite Beta Samples

Sample	Micropore volume (cm^3/g)	
	Nitrogen adsorption	Cyclohexane adsorption
BEA1	0.24	0.20
BEA2	0.19	0.21
BEA3	0.19	0.22
BEA1p(3h)	0.20	0.22
BEA2p(3h)	0.18	0.21
BEA3p(3h)	0.18	0.22

tion isotherm of small zeolite beta crystals it is impossible to know where the onset of extracrystalline adsorption occurs. Thus, for the case of BEA1, it is likely the volume determined with nitrogen is slightly overestimated as it also takes into account a part of the extracrystalline volume of this zeolite. Thus, the cyclohexane adsorption values are the most reliable and show that there are no decreases in the intrazeolitic pore spaces of the passivated zeolites as they have the same micropore volumes as their parent zeolites.

Figure 1 shows the total conversion of allyl 3,5-di-*tert*-butylphenyl ether over several zeolite beta samples. As previously shown (23, 25), the conversion of the probe molecule is significantly higher on zeolite BEA1 with small crystals than on BEA2 and BEA3 (BEA2 and BEA3 have larger crystals and thus less acid sites on the external surface than BEA1). Moreover, the conversion is lower on the passivated samples BEA2p(3h) and BEA3p(1h) than on the parent zeolites BEA2 and BEA3. These results show that the coating of zeolite with a medium crystal size and in particular a large crystal size is very efficient. Almost all of the acid sites on the external surface are passivated by the amorphous silica layer.

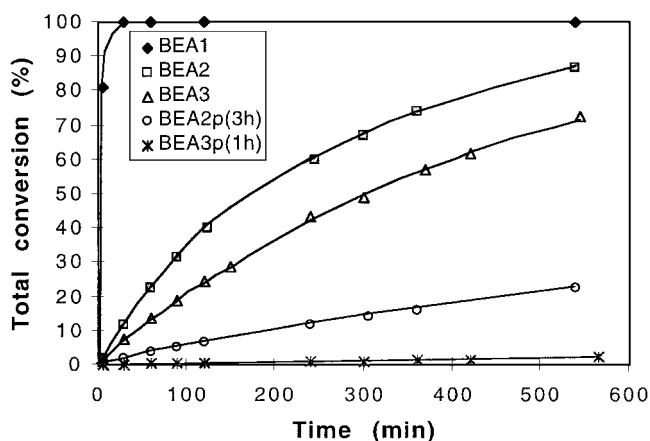


FIG. 1. Conversion of allyl 3,5-di-*tert*-butylphenyl ether versus reaction time over zeolite BEA1, BEA2, BEA3, BEA2p(3h), and BEA3p(1h) (0.10 g of catalyst, 100°C, 0.4 mmol of allyl 3,5-di-*tert*-butylphenyl ether, 2 ml of 1,2-dichloroethane).

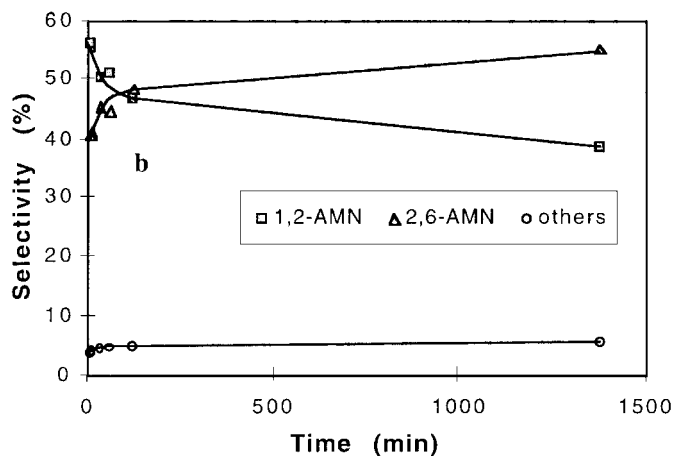
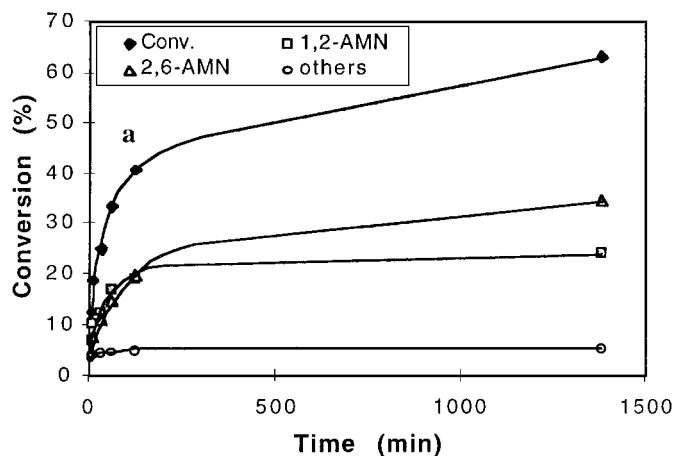


FIG. 2. Conversion of 2MN (a) and selectivity of acylated products (b) versus reaction time over zeolite BEA1 (0.10 g of catalyst, 100°C, 2MN : acetic anhydride, 1 : 1 and 1.1 mmol, 0.860 ml of solvent).

3.2. Acylation of 2MN with Acetic Anhydride over Zeolite Beta

3.2.1. Investigation of Reaction Conditions for the Formation of 2,6-AMN

Effect of reaction time. Figure 2a shows the total conversion of 2MN and the yield of reaction products versus reaction time over zeolite BEA1. 2MN is mainly transformed into 1,2-AMN and 2,6-AMN. Small amounts of the other monoacylated methoxynaphthalene isomers are produced. As the reaction progresses, traces of diacylated compounds are formed. The conversion of 2MN is 39% at 2 h and then slowly levels off to a final value of 62% at 24 h. Initially, 1,2-AMN is formed with a slight selectivity over 2,6-AMN. With longer reaction times, the opposite selectivity is observed (Fig. 2b).

Effect of catalyst weight. The reaction was conducted at four different weights of catalyst from 30 to 140 mg. The increases in conversion of 2MN and yields of 1,2-AMN and 2,6-AMN (at 4 min of reaction) are linear when the weight is increased from 30 to 100 mg (Fig. 3). Above this weight, the conversions no longer increase with catalyst mass (Fig. 3). Also, the initial selectivity for 2,6-AMN is higher when the zeolite weight decreases. However, after 24 h of reaction, the selectivity is independent of the weight of the catalyst.

Effect of reaction temperature. The reaction was investigated at 70, 100, and 120°C. The yield (Fig. 4a) and the selectivity of 2,6-AMN increase significantly when the temperature increases. The yield of 1,2-AMN increases when the temperature is elevated from 70 to 100°C. However, at 120°C, a decrease in the yield of 1,2-AMN is observed with reaction time and may be due to the protiodeacylation of the acyl group (4) (Fig. 4b). The increase in the temperature leads also to catalyst samples becoming darker in color after reaction and likely indicates increasing carbonaceous

residue contents. With the initial rate data from Fig. 4, the apparent activation energies are estimated to be 21 kJ/mol for 1,2-AMN and 45 kJ/mol for 2,6-AMN.

Effect of acetic anhydride (Ac_2O) to 2MN molar ratio. The ratio of acetic anhydride to 2MN was varied while a constant amount of 2MN and total reaction solution volume was maintained. At early reaction times, the concentration of the acylating agent has practically no influence on the conversion of 1,2-AMN and 2,6-AMN. Thus, the reaction order is close to zero order. At longer reaction time, the effect of the ratio of acetic anhydride to 2MN is different for the formation of 1,2-AMN and 2,6-AMN (Fig. 5). At longer reaction times, the kinetic product (1,2-AMN) is favored when the ratio of $Ac_2O/2MN$ increases and the conversion to 2,6-AMN is a maximum for a ratio equal to 2. Moreover, it must be noted that in the presence of excess acylating agent ($2MN/acetic\ anhydride > 1$), small amounts of

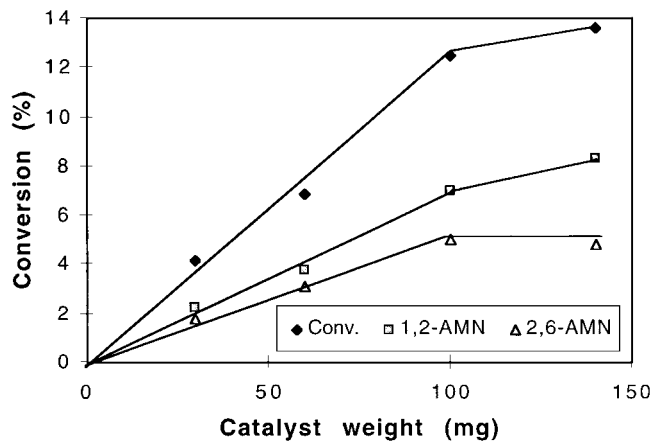


FIG. 3. Total conversion, yield of 1,2-AMN and yield of 2,6-AMN (at 4 min of reaction) versus weight of zeolite BEA1 (100°C, 2MN : acetic anhydride, 1 : 1 and 1.1 mmol, 0.860 ml of solvent).

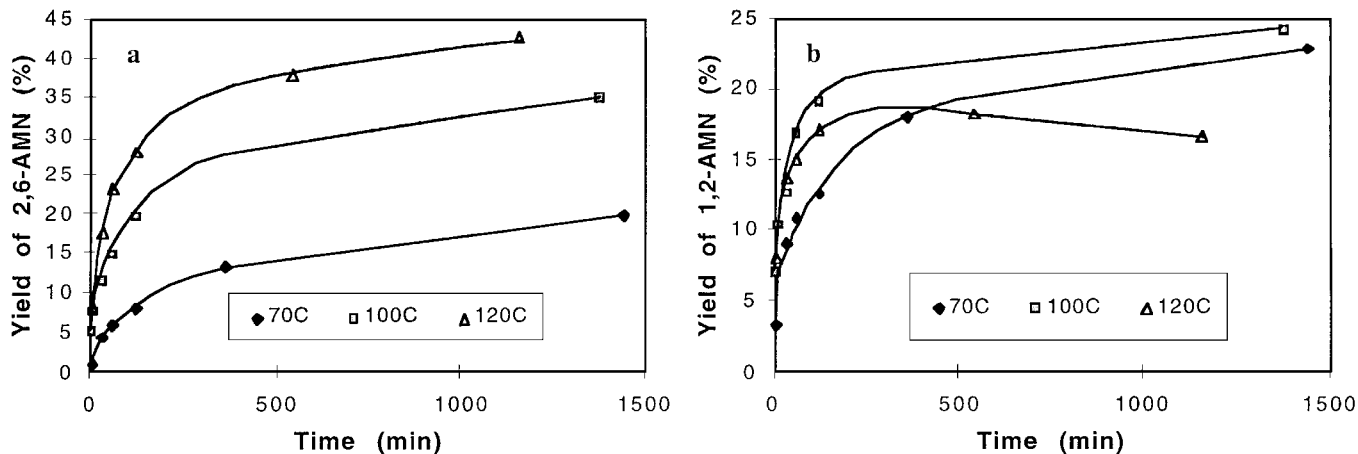


FIG. 4. Yield of 2,6-AMN (a) and 1,2-AMN (b) versus reaction time over zeolite BEA1 as a function of temperature (0.10 g of catalyst, 2MN : acetic anhydride, 1 : 1 and 1.1 mmol, 0.860 ml of solvent).

diacylated compounds are formed and the catalyst rapidly turns into a dark solid that is indicative of a large formation of heavy products (the increase in catalyst weight after 24 h of reaction is 11.7% as opposed to 7.6% at a ratio of 1). Additionally, dealumination of the zeolite is observed. The Si/Al ratio of BEA1 is 12, and after 24 h of reaction, the Si/Al ratio reaches 14.2 and 16.3 for a ratio of acetic anhydride to 2MN equal to 1 and 4, respectively. The increase in dealumination with the acetic anhydride/2MN ratio is likely due to the increased amounts of acetic acid formed from elevated conversions (acetic acid is known to dealuminate zeolite beta (26)).

Effect of presence of acetic acid. The addition of acetic acid (2MN/acetic anhydride/acetic acid = 1) leads to a significant decrease in the yield of 1,2-AMN and 2,6-AMN (Fig. 6) but a small increase in the selectivity of 2,6-AMN. Moreover, the increase in weight of the catalyst after 24 h of

reaction is higher in the presence of acetic acid (10.3% instead of 7.1%). This could be due to a strong adsorption of acetic acid on the internal and external sites of the zeolite.

Conversion of 1,2-AMN and 2,6-AMN. Deacylation experiments with 1,2-AMN and 2,6-AMN were carried out for 2 h at 100°C in dichloroethane in the presence of acetic acid (AMN/acetic acid = 1) (Table 3). The deacylation of 1,2-AMN leads to the formation of 2MN (19.2%) and 2,6-AMN (0.6%). However, the protideacylation of the acyl group at the 1-position is limited in the presence of acetic anhydride (1,2-AMN/acetic acid/acetic anhydride = 1). The deacylation reaction essentially does not occur with the thermodynamically more stable 2,6-AMN (Table 3).

Deacylation experiments with 1,2-AMN and 2,6-AMN in the absence of the acylating agent were also carried out at 100°C in dichloroethane. After 2 h, no reaction of 1,2-AMN is observed. However, after 24 h, 44% of 1,2-AMN

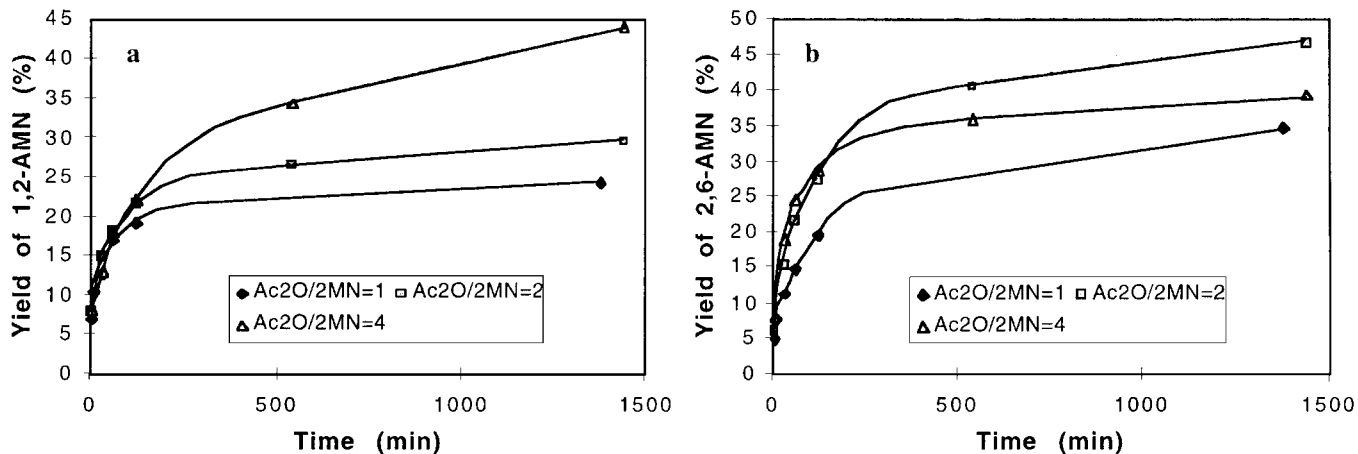


FIG. 5. Yield of 1,2-AMN (a) and 2,6-AMN (b) versus reaction time over zeolite BEA1 as a function of acetic anhydride to 2MN molar ratio (0.10 g of catalyst, 100°C, 2MN = 1.1 mmol).

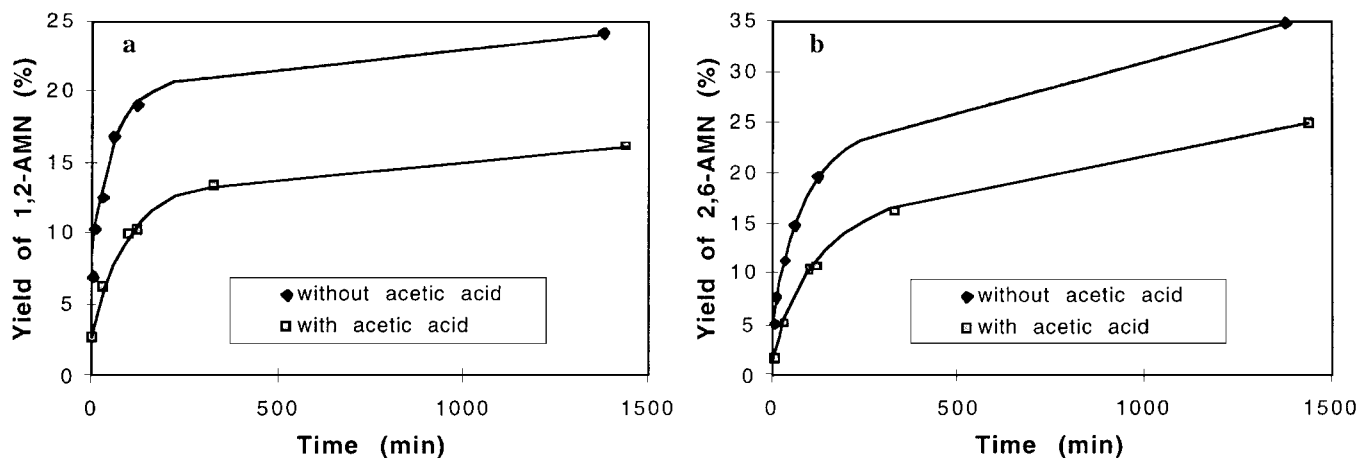


FIG. 6. Yield of 1,2-AMN (a) and 2,6-AMN (b) versus reaction time over zeolite BEA1. Without acetic acid, 0.10 g of catalyst, 100°C, 2MN : acetic anhydride, 1 : 1 and 1.1 mmol, 0.860 ml of solvent. With acetic acid, 0.10 g of catalyst, 100°C, 2MN : acetic anhydride : acetic acid, 1 : 1 : 1 and 1.1 mmol, 0.860 ml of solvent.

is transformed and gives 20.8% of 2MN and 19.2% of 2,6-AMN whereas no transformation of 2,6-AMN is observed at the same conditions.

These results are consistent with the reaction network proposed by various authors (4, 18). That is, 1,2-AMN is deacylated to give back 2MN that can then be acylated to form 2,6-AMN.

Composition of the organic compounds retained on the zeolite. The composition of carbonaceous residue from BEA1 was determined from a 400-mg sample exposed to the reaction at 100°C for 24 h. A large part of the retained compounds are extracted in methylene chloride by simple soxhlet treatment of the sample (5.6 wt% of the catalyst). The extract contains mainly 2,6-AMN and diacylated products that are not observed in the reaction solution (Table 4). Moreover, the 2,6-AMN-to-1,2-AMN ratio is higher in the extract (2.3) than in the reaction solution (1.5).

A less significant part of the retained compounds is not collected by extraction and can be recovered in a hydrofluoric acid solution that dissolves the zeolite. More than 95% of the compounds are diacylated molecules (Table 4) that may be formed by the acylation of 2,6-AMN.

TABLE 3

Conversion of 1,2-AMN and 2,6-AMN over Zeolite BEA1

Reactant	Conv. (%)	2MN (%)	1,2-AMN (%)	2,6-AMN (%)
1,2-AMN ^a	19.8	19.2	—	0.6
1,2-AMN ^b	5.1	4.2	—	0.5
2,6-AMN ^a	0.3	0.2	0.1	—

^a 0.10 g of catalyst, 100°C, 2 h, 1,2-AMN (or 2,6-AMN) : acetic acid, 1 : 1 and 1.1 mmol, 0.860 ml of solvent.

^b 0.10 g of catalyst, 100°C, 2 h, 1,2-AMN : acetic anhydride : acetic acid, 1 : 1 : 1 and 1.1 mmol, 0.860 ml of solvent.

3.2.2. Contribution of the External Surface

External surface-poisoning experiments. The transformation of 2MN was carried out in the presence of 2,4,6-tri-*tert*-butylpyridine (5 mol% of 2MN) or triphenylphosphine (5 wt% of catalyst) for 2 h with BEA1. These molecules are too large to enter the zeolite pores and can be adsorbed on the external acid sites. In the absence of poison, the total conversion is 39.2% and the selectivity to 2,6-AMN is 48%. In the presence of poison, a significant decrease in the total conversion occurs; e.g., the conversion is 7.5% in the presence of 2,4,6-tri-*tert*-butylpyridine and an increase in the selectivity of 2,6-AMN is observed, e.g., 75% in the presence of 2,4,6-tri-*tert*-butylpyridine. These data suggest that a large amount of 1,2-AMN is formed on the external surface and that the selective acylation of 2MN into 2,6-AMN occurs inside the zeolite pores.

Effect of crystal size. Three zeolite beta samples with varying crystal size were investigated for the acylation of 2MN to test for the effects of reaction at the external surface: BEA1 with a small crystal size, BEA2 with an intermediate crystal size, and BEA3 with a large crystal size.

TABLE 4

Composition of the Organic Compounds Retained on the Zeolite BEA1

wt% ^a	Distribution (wt%)				
	2MN	1,2-AMN	2,6-AMN	others AMN	di-AMN
5.6 ^b	9	18	41	4	28
0.7 ^c	—	—	trace	—	>95

^a Weight percentage of extract on the catalyst.

^b Before extraction.

^c After extraction.

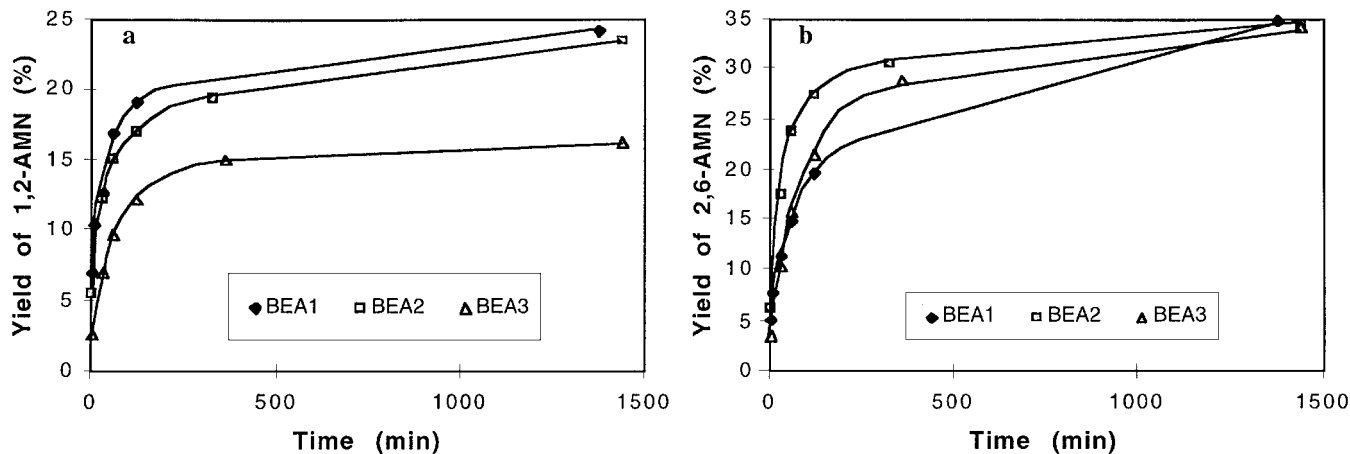


FIG. 7. Yield of 1,2-AMN (a) and 2,6-AMN (b) versus reaction time over zeolite BEA1, BEA2, and BEA3 (0.10 g of catalyst, 100°C, 2MN : acetic anhydride, 1 : 1 and 1.1 mmol, 0.860 ml of solvent).

BEA1 has a Si/Al ratio equal to 12 while BEA2 and BEA3 both have Si/Al = 40 (Table 1).

The total conversion of 2MN is nearly the same using BEA1, BEA2, and BEA3 (data not shown) and suggests that the reaction occurs close to the external surface of the zeolite. The yield of 1,2-AMN is higher for the zeolite with the lower Si/Al ratio and the smaller crystals (Fig. 7a) while the yield of 2,6-AMN is higher on the zeolites with a larger crystal size (BEA2 and BEA3, Fig. 7b). These results show that the shape-selective acylation at the 6-position occurs preferentially in the interior of the crystals as the relative number of external acid sites are decreased with increasing crystal size. To test further this premise, attempts to passivate the external crystal surfaces were explored.

Passivation of external surface. The activity and selectivity of the passivated zeolite beta samples BEA1p(3h), BEA2p(3h), and BEA3p(3h) are compared to those of the parent zeolites BEA1, BEA2, and BEA3 and the data are given in Table 5. Compared to the parent zeolites, the passivation of the external surface by coating the crystal with amorphous silica leads, after 2 h of reaction, to a decrease in the total conversion but an increase in the selectivity of 2,6-AMN (Table 5). This phenomena is more pronounced as the size of the crystal increases. Results from passivated and nonpassivated BEA2 and BEA3 at similar conversions are provided to compare selectivities. At near isoconversion, the yield of 2,6-AMN is higher on BEA3p(3h) (7.9%) than on BEA3 (3.4%) and the yield of 1,2-AMN is dramatically suppressed on the passivated sample (Table 5).

Kunkeler *et al.* (23) have shown that the coverage of the external surface by amorphous silica is significantly better on larger crystals and the reaction data shown in Fig. 1 confirm these results. Moreover, XPS analysis shows that the Si/Al ratio of BEA3 increases from 37 to 62 after the passivation treatment. Thus, it is clear that 1,2-AMN is formed on the external acid sites. Low rates of 2,6-AMN

formation are observed with BEA2p(3h) and, in particular, BEA3p(3h). Since the cyclohexane adsorption experiments show that the micropore volume is the same for BEA2, BEA2p(3h), BEA3, and BEA3p(3h), it is likely that the decrease in the rate of 2,6-AMN formation is due to the additional diffusional barrier imposed by the surface layer of amorphous silica.

To test further the effects of surface passivation, the time of coating of the largest crystals (BEA3) was decreased from 3 to 1 h (BEA3p(1h)) and to 30 min (BEA3p(30min)). The conversions to 1,2-AMN and 2,6-AMN on BEA3p(3h), BEA3p(1h), and BEA3p(30min) are compared to those from BEA3 in Fig. 8. The yield of 1,2-AMN is dramatically suppressed on the passivated zeolites and, in particular, on BEA3p(3h) with the largest external surface covering. However, the yield of 2,6-AMN is significantly higher for BEA3p(30min) and BEA3p(1h) than for BEA3p(3h)

TABLE 5

Acylation of 2MN Catalyzed by Zeolite Beta Samples (The Effect of Surface Modification on Reaction Behavior Are Given; 0.10 g of Catalyst, 100°C, 2 h, 2MN : Acetic Anhydride, 1 : 1 and 1.1 mmol, 0.860 ml of Solvent)

Sample	Conv. (%)	Yield of 1,2-AMN (%)	Yield of 2,6-AMN (%)	Yield of other AMN (%)	Selectivity of 2,6-AMN (%)
BEA1	39.2	18.5	18.8	1.9	48
BEA1p(3h)	36.8	15.7	19.2	1.9	52
BEA2	46.8	17	27.4	2.1	58
BEA2 ^a	30.9	12.2	17.4	1.2	56
BEA2p(3h)	23.6	5.7	16.8	1.1	71
BEA3	35.5	12.1	21.5	1.7	60
BEA3 ^b	6.3	2.6	3.4	0.2	55
BEA3p(3h)	8.5	0.4	7.9	0.2	92

^a At 30 min of reaction.

^b At 4 min of reaction.

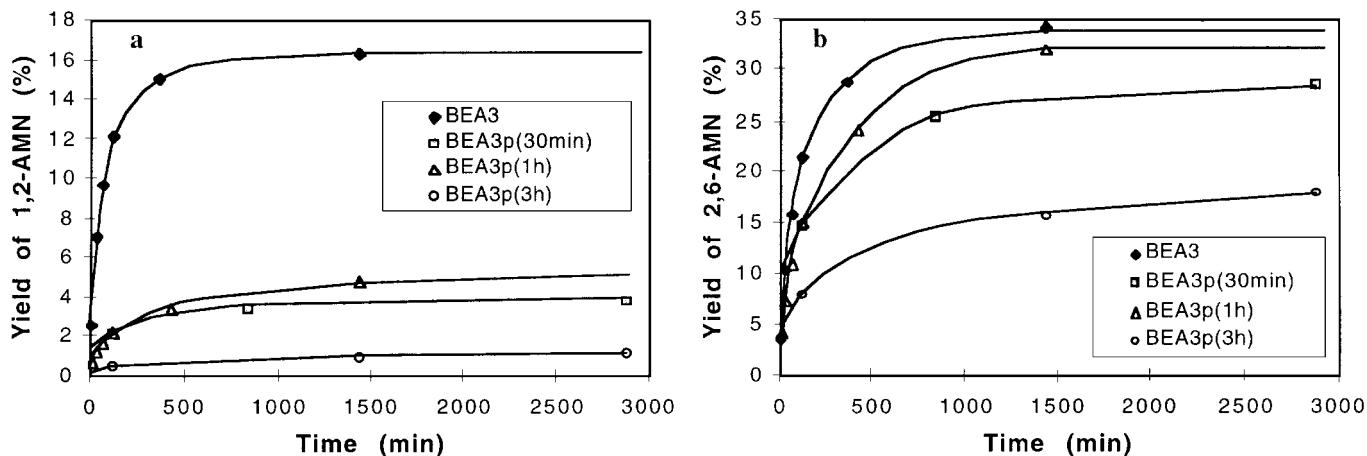


FIG. 8. Yield of 1,2-AMN (a) and 2,6-AMN (b) versus reaction time over zeolite BEA3, BEA3p(30 min), BEA3p(1 h), and BEA3p(3 h) (0.10 g of catalyst, 100°C, 2MN: acetic anhydride, 1:1 and 1.1 mmol, 0.860 ml of solvent).

and is consistent with enhanced diffusional limitations as the thickness of the amorphous layer is increased.

The regeneration of BEA3p(3h) was investigated. As can be seen from the data illustrated in Fig. 9a, the yield of 2,6-

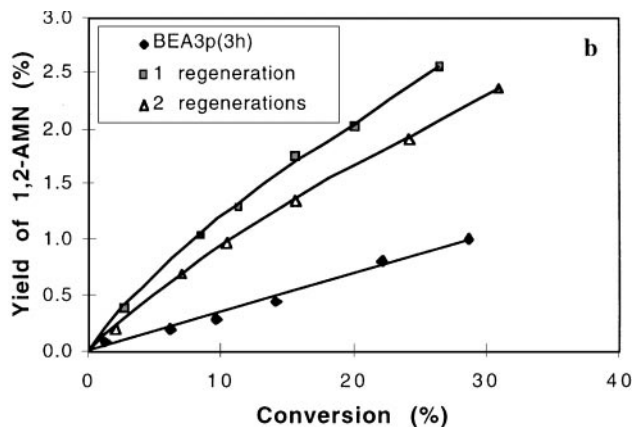
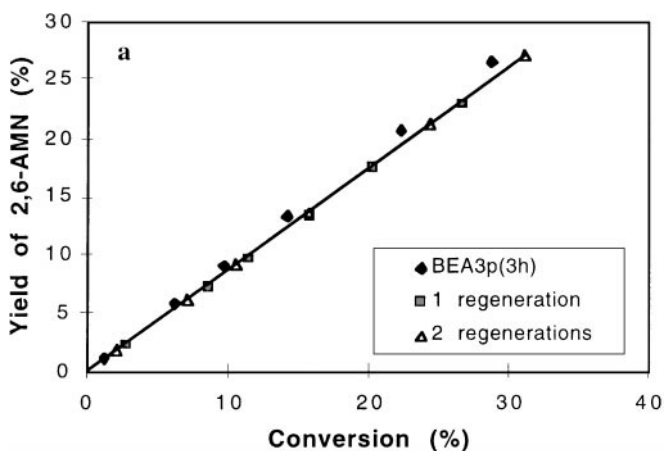


FIG. 9. Yield of 2,6-AMN (a) and 1,2-AMN (b) versus total conversion over zeolite BEA3p(3h) as a function of the number of regeneration (100°C, 2MN: acetic anhydride, 1:1).

AMN is similar on the fresh zeolite and on the regenerated samples. However, an increase in the selectivity to 1,2-AMN occurs when the catalyst is regenerated (Fig. 9b). The selectivities to 1,2-AMN from the regenerated samples correspond to the values obtained on BEA3p(1h). These data suggest that, on the sample passivated for 3 h (BEA3p(3h)), the amorphous silica is sintering during regeneration and making surface acid sites available.

3.3. Acylation of Isobutylbenzene with Acetic Anhydride over Zeolite Beta

Figure 10 shows the total conversion of isobutylbenzene and the yield of reaction products versus reaction time over BEA1. The major product is 4-isobutylacetophenone. A small amount of 2-isobutylacetophenone is observed. The selectivity of 4-isobutylacetophenone is excellent. However, the activity of the catalyst is low. The turnover number at 4 min of reaction is equal to 0.3 for the acylation of

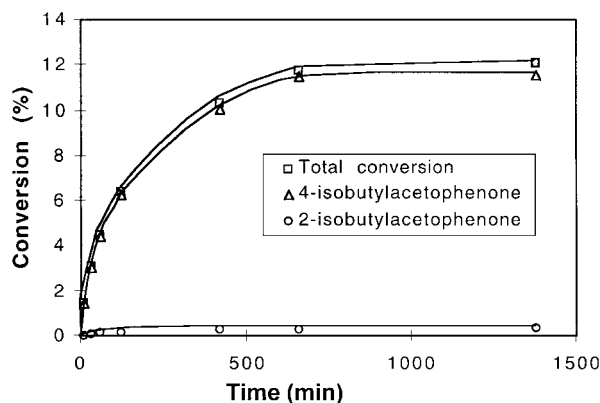


FIG. 10. Conversion of isobutylbenzene versus reaction time over zeolite BEA1 (0.10 g of catalyst, 100°C, isobutylbenzene: acetic anhydride, 1:1 and 0.8 mmol, 1 ml of solvent).

TABLE 6

Acylation of Isobutylbenzene Catalyzed by Zeolite Beta Samples (0.25 g of Catalyst, 100°C, 11 h, Isobutylbenzene:Acetic Anhydride, 1:1 and 1.1 mmol, 0.860 ml of Solvent)

Sample	Conv. (%)	Selectivity of 4-isobutylacetophenone (%)
BEA1	16.6	>99
BEA2	10	>99
BEA3	11	97

isobutylbenzene whereas it is equal to 15.8 for the acylation of 2MN.

The conversion of isobutylbenzene and the selectivity of 4-isobutylbenzene over BEA1, BEA2, and BEA3 are presented in Table 6. The zeolite with the lower Si/Al ratio and the smallest particle size is the more active zeolite for the transformation of isobutylbenzene into 4-isobutylacetophenone. In this case, a high external surface has no effect on the reaction selectivity as the acylation does not require the shape-selectivity properties of the zeolite. Moreover, small crystals, as in the case of BEA1, are preferable for obtaining a high number of exposed external sites and a shorter intracrystalline diffusion path length.

4. CONCLUSIONS

Zeolite beta is active for the acylation of 2MN but is not selective to the desired product (2,6-AMN). Mild operating conditions (temperature and concentration of acylating agent) can be used to obtain reasonable conversions and to limit the deactivation of the catalyst. Surface-poisoning experiments show that the formation of 1,2-AMN occurs on the external surface of the zeolite and that the formation of 2,6-AMN can take place inside the pores of the zeolite. Therefore, the selectivity to 2,6-AMN is improved on zeolite beta samples with a larger crystal size. On the large crystals, most of the acid sites can be passivated by coating of the crystals with a layer of amorphous silica. Upon reduction of surface acid sites, significant increases in the selectivity for 2,6-AMN are observed. The amount of surface coating on the large crystals determines the yield of 2,6-AMN and the selectivity to this product. These data are a clear example of shape-selective acylation with zeolites.

Isobutylbenzene is less reactive than 2MN but the desired product, 4-isobutylacetophenone, is always obtained since the isobutyl group provides for the para position being the preferred sites for acylation. For isobutylbenzene, the external surface of the zeolite contributes significantly to the formation of 4-isobutylacetophenone. Thus, zeolite beta with a small crystal size is the most desired catalyst for this reaction.

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