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Acetylation of 2-methoxynaphthalene with acetic anhydride over a series of dealuminated HBEA zeolites

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The liquid phase acylation of 2-methoxynaphthalene with acetic anhydride was carried out in a batch reactor at 120 °C over a series of HBEA zeolites resulting from dealumination of a commercial sample by treatment with chlorhydric acid or with ammonium hexafluorosilicate. Lewis acid sites which correspond to extraframework aluminium species and to transient-state species (aluminium atoms which are leaving the framework) were preferentially removed. With all the HBEA samples, acetylation of 2-methoxynaphthalene leads preferentially to 1-acetyl-2-methoxynaphtalene, this compound undergoing isomerization into 2-acetyl-6-methoxynaphthalene and 1-acetyl-7-methoxynaphthalene as well as deacylation. A maximum in acetylation and isomerization activities is found for a Si/Al ratio between 20 and 35. The low activity of the commercial sample can be related to limitations in the desorption of acetylated products from the zeolite micropores caused by the large amount of extraframework aluminium species present on this sample. Lewis acid sites were shown to be completely inactive for acetylation and isomerization reactions.

Keywords: 2-methoxynaphthalene acetylation, isomerization, dealuminated HBEA zeolites, acidity, activity, active sites

1. Introduction

Aromatic ketones are important intermediates in the production of fine chemicals and pharmaceuticals [1,2]. A typical example is the synthesis of the anti-rheumatic Naproxen which is produced by the Friedel–Crafts acylation of 2-methoxynaphthalene into 2-acetyl-6-methoxynaphthalene and subsequent Willgerodt–Kindler reaction [1]. Present industrial practice of aromatic acylation involves acid chlorides and over-stoichiometric amounts of metal chlorides (e.g., $AlCl_3$) as catalysts, which results in a substantial production of by-products (more than 4 moles of Cl^- per mole of ketone produced) and in corrosion problems. Therefore, the substitution of these corrosive and polluting catalysts by solid acid catalysts and of acid chlorides by anhydrides or acids is most attractive.

In a previous paper [3], we have shown that a high yield in 2-acetyl-6-methoxynaphthalene (II) could be obtained by acylation of 2-methoxynaphthalene (2MN) with acetic anhydride (AA) over a commercial HBEA zeolite. Actually, while 1-acetyl-2-methoxynaphthalene (I) was preferentially formed by direct acetylation of 2MN, this compound underwent isomerization into the desired 2-acetyl-6-methoxynaphthalene (II) and into low amounts of 1-acetyl-7-methoxynaphthalene (III). Isomers II and III were shown to be formed through an intermolecular mechanism involving transacylation of 2MN by I. From molecular modelling [4], it was also concluded that acetylation of 2MN and isomerization of I could occur inside the zeolite pores. Indeed, neither strong limitations in the diffusion of 2MN, I, II and III in the pores of the BEA zeolite nor significant steric constraints on the formation of the bulky bimolecular intermediates were found. Moreover, the analysis of the compounds present in the zeolite pores during isomerization of I suggests that acetylation and isomerization occurred mainly inside the zeolite pores [5]. A different conclusion had been previously drawn [6,7]. While the linear acetylation product II could be formed inside the zeolite pores, the bulky product I could not enter the micropores, hence would be formed only at the large outer surface of the HBEA crystallites.

In addition to its generally large outer surface related to the small size of its crystallites [6–10], the BEA zeolite has particular acid properties which are related to local defects, i.e., aluminium atoms which are not fully coordinated to the framework [10,11] or in other words which are leaving the framework [12]. These transient-state species, which are Lewis acid sites, would be the active sites in Meerwein–Ponndorf–Verley reactions [13,14]. Extraframework aluminium species which are also Lewis sites, were proposed to be active in acylation of 2-methoxynaphthalene over HBEA zeolites [7].

In this paper, acetylation of 2-methoxynaphthalene was carried out in a batch reactor over a series of HBEA zeolites resulting from dealumination of a commercial sample by acid treatment. One sample obtained by dealumination of the commercial sample by ammonium hexafluorosilicate according to the method developed by Breck et al. [15] was also used. The acidity of the samples was characterized by pyridine adsorption followed by IR spectroscopy.

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The aim is to determine the effect of dealumination on the rate and selectivity of formation of II, i.e., the precursor of Naproxen and to specify the nature of the active sites (Brønsted or Lewis).

2. Experimental

2.1. Preparation of dealuminated samples

The parent HBEA sample was supplied by PQ (CP 811 B25). Before acid treatment, this zeolite was calcined up to 550 °C following the procedure described by Corma et al. [16]. The acid treatment was carried out under stirring at temperatures of 30, 60 or 100 °C, with a HCl concentration of 0.1, 0.5, 1.0 and 1.5 N, and a ratio of acid solution and of zeolite of 10 $\mathrm{cm^3\,g^{-1}}$. After acid treatment, the zeolite samples were washed with a large amount of warm (70–80 °C) deionized water, recovered by centrifugation then put in an oven at 120 °C for 24 h.

The starting material for dealumination by ammonium hexafluorosilicate was the ammonium form of the parent BEA sample. 1 g of this NH_4BEA zeolite was preheated at 75 °C in 250 cm^3 of a 0.8 M aqueous solution of ammonium acetate. An aqueous solution of $(NH_4)_2SiF_6$ (0.5 M) was added dropwise at a rate of approximately 0.25 $\mathrm{cm^3\,min^{-1}}$ (final pH = 6.2) under stirring. The quantity of $(NH_4)_2SiF_6$ added corresponded to 0.75 times the stoichiometric amount required for the complete dealumination of the sample. The solution was then stirred for 3 h at 75 °C. The zeolite was recovered by filtration and repeatedly washed with warm water (about 80 °C, total amount about 600 cm^3) to eliminate completely the unreacted $(NH_4)_2SiF_6$, then dried for 3 h at 120 °C.

2.2. Physicochemical characterization of the HBEA samples

The position of the IR structure band (450–1250 cm^{-1}) was determined with wafers obtained by dilution of the zeolite samples in KBr (1/200). For IR characterization of the hydroxy groups and of adsorbed pyridine (Py) molecules, the zeolite samples were pressed into thin wafers: 4–8 $\mathrm{mg\,cm^{-2}}$ and activated *in situ* in the IR cell. The activation conditions were: heating in air flow (1 $\mathrm{cm^3\,s^{-1}}$) at 500 °C for 16 h and then in vacuum (10^{-6} Torr) at 400 °C for 1 h. The spectra were recorded with a Nicolet Magna IR 550 spectrometer.

The concentration of acid sites was determined in quantitative IR studies of pyridine sorption. Excess pyridine was sorbed at 420 K and physisorbed pyridine was desorbed by evacuation at the same temperature. The concentrations of Brønsted and Lewis acid sites were calculated from the integrated intensities of the PyH^+ and PyL bands (1545 and 1450 cm^{-1}) using the values of the molar extinction coefficients of these bands (1.13 and 1.28 $\mathrm{cm\,\mu mol^{-1}}$, respectively) determined in a previous study [17] by sorption of measured amounts of pyridine on H-mordenite (containing only Brønsted sites) and on alumina (containing only Lewis sites).

2.3. Acetylation of 2-methoxynaphthalene

The reactions were carried out in a flask equipped with a cooler and a magnetic stirrer (500 rpm). The conditions were the following: temperature of 120 °C, 500 mg of catalyst previously activated at 500 °C overnight under dry air flow, solution containing 35 mmol of 2MN ($C_{\mathrm{2MN}} = 3.43\ \mathrm{mol\,l^{-1}}$) and 7 mmol of AA ($C_{\mathrm{AA}} = 0.68\ \mathrm{mol\,l^{-1}}$) and 4 cm^3 of nitrobenzene solvent.

Time zero of the reaction was taken as the time of introduction of the zeolite in the reactant mixture heated at the reaction temperature. Small samples of the reaction mixture (0.1 cm^3) were taken periodically and analysed by GC on a capillary CP Sil 8 CB column. Identification of the products was carried out by using reference samples or by mass spectrometry.

The conversion of 2-methoxynaphthalene (2MN) into acetylated products (isomers I, II and III) is taken as

$$X_{\mathrm{2MN}} = \frac{\%\mathrm{I(II, III)}}{\%\mathrm{2MN} + \%\mathrm{I} + \%\mathrm{II} + \%\mathrm{III}} \times 100.$$

The yields into I, II or III were taken as the ratio between the conversion of 2MN into I, II, III and the maximum of conversion of 2MN into acetylated products.

3. Results and discussion

3.1. Characteristics of HBEA samples

The physicochemical characteristics of the acid dealuminated samples (table 1) are similar to those found for samples previously prepared under similar conditions [9]. The acid treatment causes only slight changes in the pore volume (table 1) but significant changes in the composition and in the acidity of the zeolite. For the dealuminated samples, the bulk Si/Al ratio determined by elemental analysis is close to the framework Si/Al ratio estimated from linear correlations established between the wavenumber of structure bands and N_{Al} the number of framework aluminium atoms per unit cell [9]. This indicates that the extraframework aluminium species are mainly eliminated before dealumination of the zeolite framework (table 1). The number of protonic sites and the one of Lewis sites, able to retain pyridine adsorbed at 150 °C, decrease with increasing dealumination. The number of protonic sites decreases regularly with N_{Al} (figure 1). On the other hand, the number of Lewis acid sites first decreases very sharply becoming very low and practically constant for $N_{\mathrm{Al}} \leqslant 1.5$ (framework Si/Al ratio $\geqslant 40$) (figure 1). The initial pronounced decrease in the number of Lewis acid sites can be related to the elimination of extraframework aluminium species and transient-state species.

Table 1
Physicochemical characteristics of HBEA samples.

Sample	$(Si/Al)_{bulk}$	$(Si/Al)_{fram.}$ [a]		V_{micro}	V_{meso}	Acidity (μmol g^{-1})	
		ν_1	ν_2	(cm^3 g^{-1})	(cm^3 g^{-1})	B	L
HBEA15	11.1	17.8	17.5	0.268	0.530	417	279
HBEA20	17.5	20.3	19.6	0.275	0.523	401	173
HBEA40	39	37	40	0.292	0.527	260	29
HBEA60	55	63		0.278	0.490	169	18
HBEA90	85	n.d.	n.d.	0.240	0.385	111	18
HBEA HFS	24	26	27	0.168	0.433	336	16

[a] Established from the wavenumber of the asymetric stretch band (ν_1) and of the ring-breathing band (ν_2).

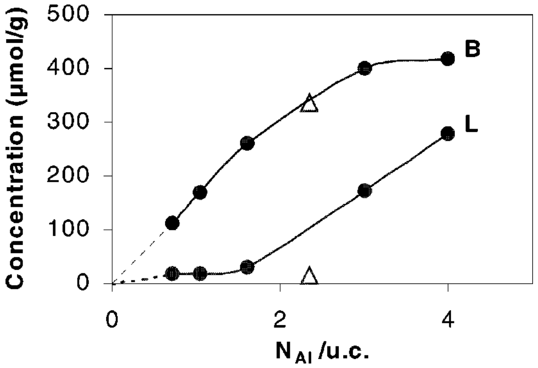


Figure 1. Concentrations of Brønsted (B) and Lewis (L) acid sites of a series of acid dealuminated HBEA samples (●) and of a sample dealuminated by ammonium hexafluorosilicate (△) as a function of N_{Al}, the number of framework aluminium atoms per unit cell.

On the other hand, the treatment with ammonium hexafluorosilicate causes a significant decrease in the micropore volume. This decrease can be ascribed to a blockage of the access of nitrogen to the micropores caused by silica deposits formed by hydrolysis of SiF_4 that results from decomposition of ammonium hexafluorosilicate [18,19]. This treatment of HBEA15 by ammonium hexafluorosilicate causes a slight decrease in the protonic acidity which can be related to a slight dealumination of the framework and to a partial blockage of the access of pyridine to the protonic sites. A very significant decrease in the number of Lewis acid sites is also observed, which can be related to the elimination of extraframework aluminium species.

All the changes in acidity could be expected. Indeed, HBEA15 is known to have a large amount of extraframework aluminium cationic species. These cationic species can be easily exchanged either by acids or by ammonium cations. This explains the rapid decrease with dealumination in the concentration of Lewis species and the slow initial decrease in the protonic acidity (figure 1). Indeed, the exchange causes an increase in the concentration of protonic sites which partially compensates the decrease in this concentration due to framework dealumination (and to pore blockage with HBEA HFS).

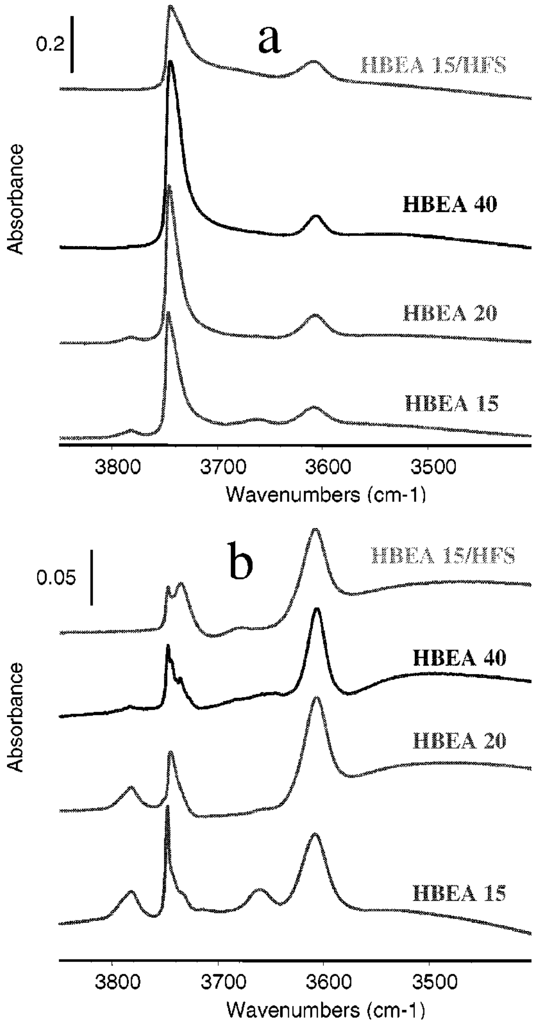
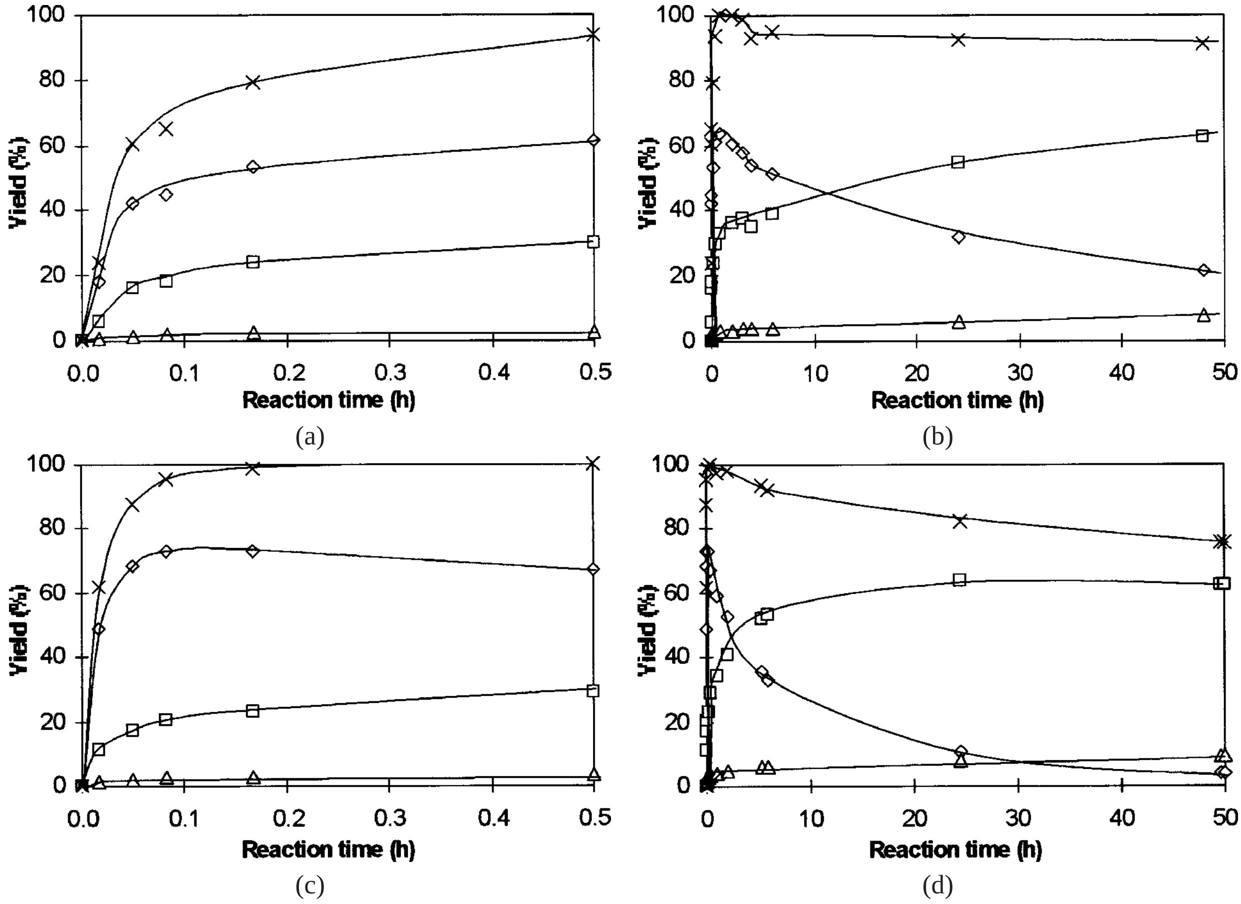


Figure 2. Spectra of all the hydroxyl groups of four HBEA samples (a) and of the acidic hydroxyl groups (b) (difference spectra between spectra (a) and spectra obtained upon pyridine sorption and desorption at 150 °C).

Five types of hydroxyl bands can be observed in the IR spectra of HBEA samples (figure 2(a)): at 3608 cm^{-1} due to strongly acidic bridging hydroxyl groups, at 3730 and 3745 cm^{-1} corresponding to internal and terminal silanol groups, at 3780 and 3660–3680 cm^{-1} corresponding to OH groups connected to aluminium atoms which are leaving the framework (transient-state species) and to extraframework aluminium species [11,12].

Sorption of pyridine results in the disappearance of all the OH bands, except those for silanol groups. However, part of the silanol groups interact with pyridine hence are acidic (figure 2(b)). Dealumination by chlorhydric acid or



(a) (b)

(c) (d)

Figure 3. Acetylation of 2-methoxynaphthalene over HBEA15 (a, b) and HBEA40 (c, d). Total yields (×) and yields in isomers I (◇), II (□) and III (△) versus reaction time.

by ammonium hexafluorosilicate decreases the bands corresponding to bridging OH groups (3608 cm^{-1}), to extraframework aluminium species and transient-state species (3660–3680 and 3780 cm^{-1}). However, these latter bands are preferentially removed: they are practically absent for the HBEA HFS sample and for acid-dealuminated samples with $Si/Al \geqslant 40$ (figure 2), in agreement with the previous conclusions.

3.2. Acetylation of 2-methoxynaphthalene (2MN) with acetic anhydride (AA)

3.2.1. Activity of fresh HBEA catalysts (initial activity)

Whatever the HBEA sample (see, for example, in figure 3 for HBEA15 and HBEA40), acetylation of 2MN leads to three isomers indicated I (1-acetyl-2-methoxynaphthalene), II (2-acetyl-6-methoxynaphthalene), III (1-acetyl-7-methoxynaphthalene) in low amount and to acetic acid. For the series of acid-dealuminated samples, the initial activity for acetylation passes through a maximum for a number of framework aluminium atoms per unit cell N_{Al} between 1.5 and 2.0 (Si/Al ratio between 30 and 40). The mode of dealumination has only a slight effect on the catalyst activity. The activity of HBEA HFS is slightly lower (figure 4), most likely because of pore blockage by silica deposits. The turnover frequency (TOF) increases with dealumination passing from 420 h^{-1} with HBEA15 to 2650 h^{-1} with HBEA90 (table 2).

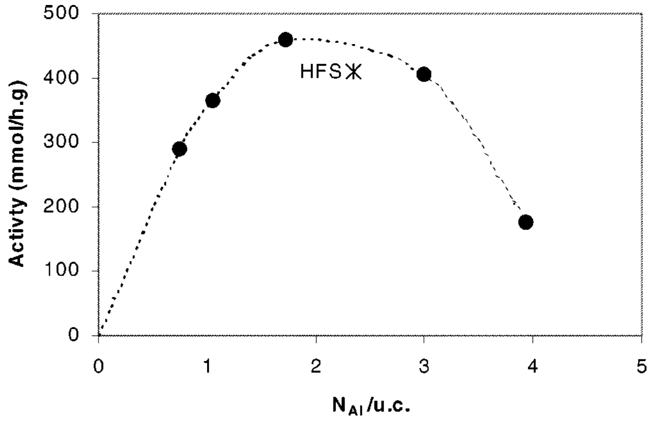


Figure 4. 2-methoxynaphthalene acetylation on a series of acid dealuminated HBEA samples. Initial activity versus N_{Al}, the number of framework aluminium atoms per unit cell. *HFS: sample dealuminated by ammonium hexafluorosilicate.

The shape of the activity curve (figure 4) is the one generally found for reactions over zeolite catalysts. Indeed, whereas dealumination decreases the number of acidic sites, it causes also an increase in their strength, isolated protonic sites having the maximum strength, hence the maximum

Table 2
Acetylation of 2-methoxynaphthalene with acetic anhydride over various HBEA zeolites. Initial rates (r_0) of formation of acetyl-methoxynaphthalene isomers I, II, III and rate ratios.

Catalyst	r_0 (mmol h^{-1} g^{-1})				$r_0(\text{I})/r_0(\text{II})$	TOF
	I + II + III	I	II	III		(h^{-1})
HBEA15	175	130	41.2	3.8	3.15	420
HBEA20	407.6	317	81.3	9.3	3.9	1020
HBEA40	428.5	340.5	78.2	9.8	4.35	1650
HBEA60	384.3	308.7	67.3	8.3	4.6	2260
HBEA90	295	240.9	48.2	5.7	5	2650
HBEA HFS	402.5	340.1	62.2	7.2	5.45	1220

activity [20,21]. However, the number of framework aluminium atoms per unit cell is not the only parameter which determines the catalyst activity. Aluminium extraframework species (EFAL) and transient state species can also play a role. Indeed these Lewis sites could be active sites as furthermore proposed in acetylation [7]. Moreover, they could interact with framework protonic sites, increasing their acid strength, hence their activity [22]. On the other hand, the EFAL species can have a negative effect on activity causing either limitation or blockage of the access to the micropores or neutralisation of the protonic sites (when these EFAL are cationic).

The comparison of figures 1 and 4 demonstrates that Lewis sites cannot be the active sites in acetylation. Indeed, four samples which have practically no Lewis sites (no EFAL and no transient state species) are however very active in acetylation, moreover HBEA15, which has the greater concentration in Lewis sites, is the less active sample. Therefore, either Lewis sites have no effect on activity (which would depend only on N_{Al}) or they play a negative role. This latter proposal seems most likely, the maximum in acid strength, hence in activity, being expected at a higher value of N_{Al} [21]. As was proposed above, the negative effect is partly due to the exchange of protonic sites by cationic EFAL species. However, it could also be related to limitations in the desorption of the bulky product molecules from the zeolite micropores.

It should be emphasized that for a similar series of HBEA samples, the initial activities for the acylation of phenol by phenylacetate (production of *para*-hydroxyacetophenone) changed with N_{Al} exactly in the same way as 2MN acetylation: low activity value for HBEA15 and maximum activity for a framework Si/Al ratio of 35–40. The low activity of HBEA15 was attributed to limitations by EFAL species of the desorption of the polar products from the zeolite micropores [23].

In agreement with this proposal, a different behaviour is found for m-xylene transformation [24] for which diffusion limitations are most unlikely. The activity of the fresh HBEA samples is practically proportional to N_{Al} (or to the number of protonic sites), HBEA15 being therefore the most active sample.

3.2.2. Selectivity of HBEA samples

Firstly, it should be noticed that high yields in II, the precursor of Naproxen, can be obtained at long time with most of the samples (table 3). The highest yields are observed with HBEA20 and HBEA40 (65–70%). As previously found with HBEA15 [5], even higher yields should be obtained by operating at higher temperatures ($\geqslant 170\,^{\circ}\text{C}$).

The initial selectivity (obtained by extrapolation at time zero) is slightly affected by dealumination. Thus, the ratio between the rates of formation of isomers I and II passes from 3.3 with HBEA15 to 5.1 with HBEA90, the highest value of this ratio being obtained with HBEA HFS (5.75). The increase of this ratio with acid dealumination can be explained by the elimination of extraframework species, hence by an easier desorption of the bulkier isomer I from the micropores. Another explanation could be that acid dealumination causes a change in the ratio between the number of inner and of outer sites, the former being only responsible for the formation of the linear isomer I, the latter for both formations of I and II [6,7]. However, molecular modelling shows that isomer I can easily lodge in the micropores of the HBEA zeolite (maximum interaction energy of -27.4 kcal mol^{-1}) [4]. Along the straight channel of HBEA the interaction energy is always negative (barrier of diffusion of approximately 10 kcal mol^{-1}), which suggests that the molecules of I can diffuse inside the pores and desorb from the pores. Moreover, adsorption experiments with I under the operating conditions of acetylation confirmed that isomer I can enter in, hence can desorb from the HBEA micropores [5]. The high value of I/II ratio found with the sample dealuminated by ammonium hexafluorosilicate can also be explained by an easier desorption of I from the micropores in which the extraframework cationic species were eliminated by exchange with ammonium hexafluorosilicate without deposition of silica.

With all HBEA samples, a complete conversion of AA and 100% yield in isomers I, II and III can be obtained after 30 to 70 min reaction. At longer times a decrease in this yield is observed (table 3), which indicates a deacylation of the acetylmethoxynaphthalene isomers. However, deacylation is accompanied by a faster isomerization of I into II and III: whatever the catalyst, the percentage of I in the I, II and III mixture decreases significantly whereas those of II and III increase. It should be remarked that part of the decrease in the percentage of I could be due to the preferential deacylation of this product: deacylation of I was found to be twice faster than deacylation of II [3].

The percentage of deacylation of acetylmethoxynaphthalene (I + II + III) can be taken as the decrease in the total yield in (I + II + III) after total conversion of AA (i.e., 100% yield in I + II + III). With most of the samples, deacylation is very fast during the first hours of reaction, then practically negligible. However, with HBEA20, deacylation increases regularly with reaction time. Therefore, after approximately 50 h reaction the percentage of deacylation is maximum with HBEA20 (37.3%). It is very low with

Table 3
Acetylation of 2-methoxynaphthalene with acetic anhydride. Distribution of acetyl-methoxynaphthalene isomers (I, II and III), total yield, yield in I and II + III as a function of reaction time.

Catalyst	Reaction time (h)	Distribution (%) I	II	III	Yield (%) Total	I	(II + III)
HBEA15	0	75.5	22.5	2.0	0	0	0
	0.75	63.6	33.2	3.2	100	63.6	36.4
	25	34.3	59.4	6.3	91.9	31.5	60.4
	50	23.4	68.4	8.2	90.9	21.3	69.6
HBEA20	0	79	19	2	0	0	0
	0.5	68.4	28.4	3.2	100	68.4	31.6
	24	16.7	73.2	10	88.7	14.8	73.9
	49	6.7	81.2	12.1	63.7	4.3	59.4
HBEA40	0	80.5	17.5	2	0	0	0
	0.5	67.4	29.2	3.4	100	67.4	32.6
	24.5	12.9	77.3	9.8	82.3	10.6	71.7
	49.5	5.4	82.8	11.8	75.8	4.1	71.7
HBEA60	0	81.5	16.5	2	0	0	0
	0.5	70.1	26.7	3.2	100	70.1	29.9
	24	23	68.6	8.4	85	19.5	65.5
	48	14.6	75.6	9.9	82.5	12	70.5
HBEA90	0	82	16	2	0	0	0
	1	70.9	26.2	2.9	100	70.9	29.1
	23	35.9	58	6.1	87.1	31.3	55.8
	48	23.8	68.6	7.6	87.5	21.8	65.7
HBEA HFS	0	83.5	14.5	2	0	0	0
	1.17	72.9	24.5	2.7	100	72.9	27.1
	24	45.8	48.8	5.4	91.7	42	49.7
	40	39.3	54.5	6.2	85	33	52

HBEA15 (9%): for the other samples, the higher the Si/Al ratio, the lower the deacylation (table 3).

On the other hand, the isomerization of I into II and III, taken as the increase in the yields of II plus III after total conversion of AA (i.e., by supposing that only I undergoes deacylation) increases with time, up to a quasi complete disappearance of isomer I. HBEA20 and 40 have practically the same activity, slightly greater than that of HBEA60 and greater than those of the other samples. Therefore the activity curve versus N_{Al} is similar to the one found for acetylation (figure 4). It can therefore be concluded that this reaction occurs, like acetylation, in the zeolite micropores and that the Lewis acid sites mainly present in HBEA15 are inactive.

4. Conclusion

Dealumination of a commercial HBEA sample by acid treatment or by ammonium hexafluorosilicate removes preferentially the Lewis acid sites which consist of extraframework aluminium species and of aluminium atoms which are leaving the framework (transient-state species). A significant decrease in Brønsted acidity corresponding to the dealumination of the zeolite framework occurs only for severe acid treatment.

With all the HBEA samples, acetylation of 2-methoxynaphthalene leads preferentially to 1-acetyl-2-methoxynaphthalene (I), this compound undergoing isomerization into 2-acetyl-6-methoxynaphthalene (II) and deacylation. Despite this latter reaction, II, which is a precursor of the anti-inflammatory Naproxen, can be obtained with a high yield (65–70%). As previously found with HBEA15 [5], higher yields should be obtained by operating at higher temperatures ($\geqslant 170\,^{\circ}\mathrm{C}$).

The activities for acetylation and for the subsequent isomerization step pass through a maximum for a framework Si/Al ratio of the HBEA zeolite between 20 and 40. This maximum in activity which is not found for m-xylene transformation can be explained by the opposite effect of the decrease in the number of protonic sites and of the increase in their strength caused by dealumination and more especially by an easier desorption of the bulky acetylation products from the micropores of dealuminated samples.

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