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Acetylation of 2-methoxynaphthalene in the presence of beta zeolites: influence of reaction conditions and textural properties of the catalysts

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The Friedel–Crafts acetylation of 2-methoxynaphthalene (2-MN) in the liquid phase has been studied over three H-beta zeolite catalysts, featuring the same composition and acidity, but exhibiting different textural characteristics. The various catalysts led to significantly different yields of acetylated products, 1-acetyl-2-methoxynaphthalene (1-Ac-2-MN) and 2-acetyl-6-methoxynaphthalene (2-Ac-6-MN). On the basis of the relationship between the product yields and the textural characteristics of the samples, the formation of the two acetylated products has been assumed to occur at different locations: inside the micropores in the case of 2-Ac-6-MN and on the outer surface of the crystals in the case of 1-Ac-2-MN.

The influences of the temperature of the reaction and of the polarity of the solvent have been also examined. Under our conditions, products were formed via parallel reactions whatever the temperature and no consecutive and secondary reactions occurred. An increase of the solvent polarity led to a decrease of both catalytic activity and 2-Ac-6-MN/1-Ac-2-MN yield ratio. Such a result has been explained by a competitive adsorption between solvent and reactants on the active sites, which is more pronounced in the micropores.

KEY WORDS: Friedel–Crafts acetylation; zeolite beta; 2-methoxynaphthalene; textural properties; interparticle voids; solvent polarity.

1. Introduction

The Friedel–Crafts acylation of aromatic compounds is a convenient method for the synthesis of aromatic ketones, which are often used as intermediates for the production of fine and pharmaceutical chemicals [1]. The most common way of preparation of these arylketones is the acylation reaction catalysed by Lewis acids such as $AlCl_3$. However, because of current environmental restrictions, the replacement of conventional homogeneous catalysts with solid acid catalysts has great industrial importance. Due to their easy handling and their shape-selective properties, zeolites have been found to be suitable alternatives for aromatic electrophilic substitution reactions [2–5]. The first industrial application of a zeolite-promoted acylation for the production of aromatic ketones, 4-methoxyacetophenone and $3',4'$-dimethoxyacetophenone, was recently introduced by Rhône-Poulenc (now Rhodia) [6].

Acetylation at the 6-position of 2-methoxynaphthalene is of particular interest, as it produces 2-acetyl-6-methoxynaphthalene (2-Ac-6-MN), which is a precursor of the anti-inflammatory drug Naproxen [7,8]. This reaction has been carried out over various acidic zeolites [9–20], mesoporous molecular sieves [21,22], clays [23] and sulfated zirconia [24]. Acylation of 2-methoxynaphthalene generally occurs at the kinetically controlled 1-position, leading selectively to 1-acetyl-2-methoxynaphthalene (1-Ac-2-MN). However, over acidic zeolites, different product distributions were obtained depending on the type of framework [9]. These differences were interpreted by shape-selective effects: for instance the preferential formation of the linear 2-Ac-6-MN over H beta zeolites (HBEA) as compared to H faujasite (HY) was interpreted in terms of steric constraints inside the narrow pores of the HBEA framework. Moreover, Harvey and Mäder [9] observed a secondary reaction of 1-Ac-2-MN over HBEA: deacylation to give back 2-methoxynaphthalene. This phenomenon was suggested to be a protiodeacylation mechanism. Further studies of the same reaction over HBEA suggested that 2-Ac-6-MN could be formed inside the micropores of the zeolite whereas 1-Ac-2-MN would be formed only on the outer surface of the crystals [10].

Due to the unique behavior of HBEA zeolites, several groups recently reported results of the study of the acetylation reaction of 2-methoxynaphthalene over such catalysts. The effects of various parameters such as pre-treatment of the catalyst [11,12,14,17], crystal size [18,19], solvent polarity [12,16,17] or excess of reactants [15] on the catalytic activity and the product distribution have been examined. However, these contributions led to different and sometimes contradictory results and conclusions, which could be explained, at least in part, by different experimental conditions

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from one study to another. For instance, after treatment of HBEA zeolite at high temperature, Heinichen and Hölderich [11] showed that a higher 2-Ac-6-MN selectivity could be obtained. This result was related to the formation of extra-framework species in the micropores of the zeolites, i.e. to a reduction of the internal void space which would limit formation of the sterically hindered 1-Ac-2-MN. This interpretation was based on the assumption that 1-Ac-2-MN could be formed inside the micropores of the zeolite. On the contrary, an increase of the 1-Ac-2-MN selectivity upon decreasing the crystal size of the catalysts [18,19] has also been reported, which seems to confirm the proposal of Harvey *et al.* [10] that 1-Ac-2-MN formation occurs on the outer surface of HBEA crystals. With regards to possible reaction pathways, authors such as Harvey and Mäder [9] and Fromentin *et al.* [15,16] observed deacylation and also isomerization of 1-Ac-2-MN to give, respectively, 2-methoxynaphthalene and 2-Ac-6-MN. However, secondary reactions of 1-Ac-2-MN were not observed by Casagrande *et al.* [17], Kim *et al.* [12] or Das and Cheng [13] over similar catalysts.

In view of the differing conclusions reported on the catalytic behavior of HBEA zeolites for this reaction, the main objective of this work has been to investigate in detail the influence of some parameters of this catalytic system, such as the textural properties of the zeolite catalysts, the reaction temperature and the solvent polarity, on the activity and the product yields. For this purpose, we have selected samples of zeolite beta with the same composition and acidity, but featuring quite different textural characteristics.

2. Experimental

2.1. Catalysts and reactants

The three zeolites selected had the same Si/Al molar ratio of 12.5, and were obtained in the H-form (residual Na < 0.02 wt%) from PQ Corporation (now Zeolyst Int.). They are denoted hereafter HBEA1, HBEA2 and HBEA3, and result from three different batches CP810B25, CP811BL25 and CP814E, respectively. Before catalytic measurements and characterization the samples were calcined at 773 K for 6 h (heating rate = 60 K h^{-1}) in a flow of dry air.

2-Methoxynaphthalene, acetic anhydride, nitrobenzene and undecane (external standards, 99%) were commercially available from Aldrich. Chlorobenzene and sulfolane, pure analytical grade from Aldrich, were used after drying over molecular sieves.

2.2. Catalytic experiments and analytical methods

The reactions were performed under atmospheric pressure in a 100 mL round-bottomed flask equipped with a condenser. A typical reaction was carried out as follows. A solution of 1.90 mL (20 mmol, 0.4 mol L^{-1}) of acetic anhydride in 40 mL of chlorobenzene was introduced in the flask and magnetically stirred at 1000 rpm under nitrogen atmosphere. The freshly activated catalyst (0.5 g) was added and the mixture was allowed to heat up to 353 K. An amount of 1.58 g of 2-methoxynaphthalene (10 mmol, 0.2 mol L^{-1}) in 10 mL of chlorobenzene was then added and the reaction mixture was stirred. Samples were periodically collected and analyzed by gas chromatography (Hewlett-Packard 5890 Series II gas chromatograph equipped with a flame ionization detector, capillary column HP-1, 25 m $\times$ 0.2 mm, 0.33 μm thickness, carrier gas hydrogen). When sulfolane was used as the solvent, the reactants were introduced prior to the solvent. After homogenization of the solution, the catalyst was added and the reaction mixture was allowed to heat up to the reaction temperature. The 2-methoxynaphthalene conversions, which are given for reaction times of 4 or 9 h respectively, correspond to a plateau reached after 1–2 h, as previously evidenced over HY zeolite [20].

2.3. Characterization

The acidity of the samples was characterized by ammonia thermodesorption [25]. The desorption profiles and amounts of base dosed ($1.14 \pm 0.03 \times 10^{-3}$ mol g^{-1}) were nearly identical for the three samples.

The morphology of the three zeolites was determined using scanning electron microscopy (SEM) images collected using a Hitashi S 4500 microscope. The samples appeared to be constituted of particles in the range 0.3–1 μm, consisting of loose aggregates of small elementary crystals 30–50 nm in size. The particles were agglomerated in grains of 8–20 μm in size (figures 1–3). The SEM images revealed differences in the density of the grains of these materials, originating, most probably, from different preparation conditions. Nitrogen adsorption/desorption isotherms were measured at 77 K using

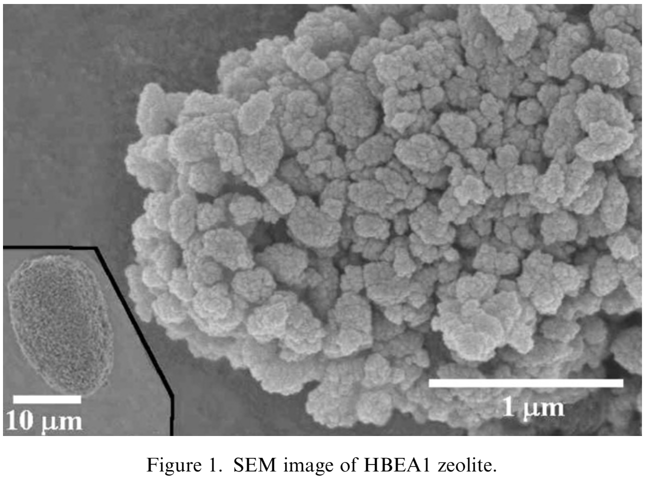

Figure 1. SEM image of HBEA1 zeolite.

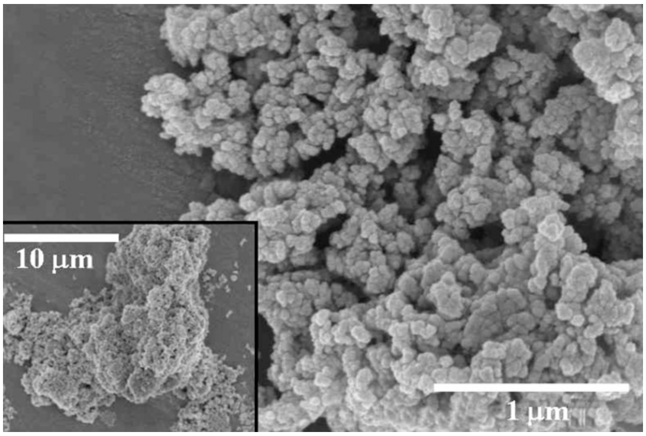

Figure 2. SEM image of HBEA2 zeolite.

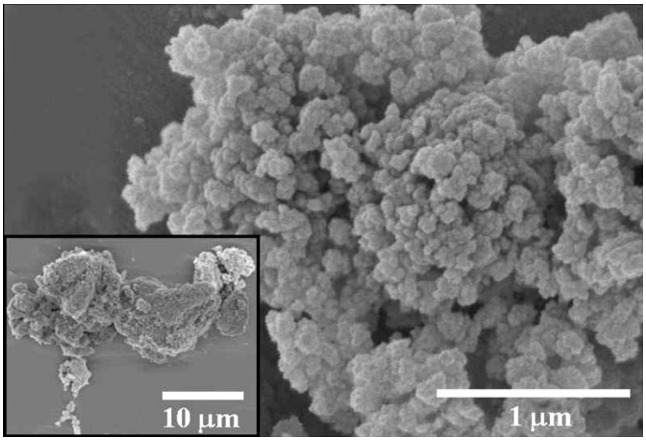

Figure 3. SEM image of HBEA3 zeolite.

an ASAP 2010 Micromeritics apparatus. Prior to use, the samples (100 mg) were outgassed under vacuum at 523 K for 10 h. External surfaces areas (S_{EXT}) were calculated from the t-plot curves for relative pressures p/p^{o} in the range 0.1–0.3, using a non-porous silica as reference. Micropore volumes were determined from the intercept at the origin of the t-plot curve. Total pore volumes were derived from the desorption branch of the isotherm, at $p/p^{\mathrm{o}} = 0.96$. They corresponded to the filling of pores up to 50 nm in diameter.

3. Results and discussion

3.1. *Influence of the textural properties on catalytic behavior*

Under the experimental conditions described above, after 4 h of reaction 1-Ac-2-MN and 2-Ac-6-MN were formed as major (>99%) products. The reaction was therefore highly selective toward acetylation over the three catalysts. However, both the conversion of 2-MN and the yields (conversion × selectivity) of products varied significantly from sample to sample as shown by the figures reported in the right-hand columns of table 1. More precisely, a constant yield ($6.3 \pm 0.4\%$) in 2-Ac-6-MN was obtained on the three catalyst whereas that of 1-Ac-2-MN varied by a factor of almost 5. Since the three zeolites feature identical acidic properties and micropore volumes, such a behavior points to a significant contribution of the external surface of the crystals in catalysis, as already reported by Harvey *et al.* [10]. Such a statement is evident from figure 4 where the yields of the two isomers are plotted as a function of the external surface area of the zeolite catalysts. The figure strongly supports the hypothesis of a definite contribution of the acid sites located on the external surface of the grains to the production of 1-Ac-2-MN, whereas 2-Ac-6-MN would be formed inside the zeolite micropores.

In order to get a better insight into the origin of the different behaviors of the catalysts, the textural characteristics—more precisely the non-structural, secondary porosity—of the three samples were analyzed in more detail. The distribution of mesopore volumes was differentiated as a function of pore diameter range. Mesopore volumes associated with pore diameters in the range 2–15 nm and corresponding roughly to the filling of the voids between the elementary crystals (interparticle voids) were obtained by integrating the volumes sorbed in the range $0.19 < p/p^{\mathrm{o}} < 0.86$. Mesopore volumes contained in pores with diameters in the range 15–50 nm (intergrain voids) were calculated from the portion of the isotherm $0.86 < p/p^{\mathrm{o}} < 0.96$ (table 1). It turns out that the formation of 1-Ac-2-MN is

Table 1
Textural characteristics, 2-methoxynaphthalene conversion and product yields for the HBEA samples ($[\text{2-MN}]_{\mathrm{o}} = 0.2\,\mathrm{mol\,L^{-1}}$; $[\mathrm{Ac_2O}]_{\mathrm{o}} = 0.4\,\mathrm{mol\,L^{-1}}$; catalyst = 0.5 g; solvent = chlorobenzene, 50 mL; $T = 353$ K)

Sample	S_{EXT} ($\mathrm{m^2\,g^{-1}}$)	Total pore volume ($\mathrm{mL\,g^{-1}}$)	$V_{\mathrm{micropores}}$ ($\mathrm{mL\,g^{-1}}$)	$V_{\mathrm{mesopores}}$ for $2 < \mathrm{dp} < 15\,\mathrm{nm}$ ($\mathrm{mL\,g^{-1}}$)	$V_{\mathrm{mesopores}}$ for $15 < \mathrm{dp} < 50\,\mathrm{nm}$ ($\mathrm{mL\,g^{-1}}$)	Conversion [a] (%)	Product yield [b] (%)	
							1-Ac	2-Ac
HBEA1	245	0.638	0.19	0.306	0.142	15	8.5	6.0
HBEA2	269	0.871	0.189	0.385	0.297	27	19.7	6.2
HBEA3	210	0.937	0.181	0.227	0.529	12	4.8	6.7

[a] Conversion after 4 h reaction.

[b] In each case, 1-acetyl-7-methoxynaphthalene is also obtained (0.27–0.48%).

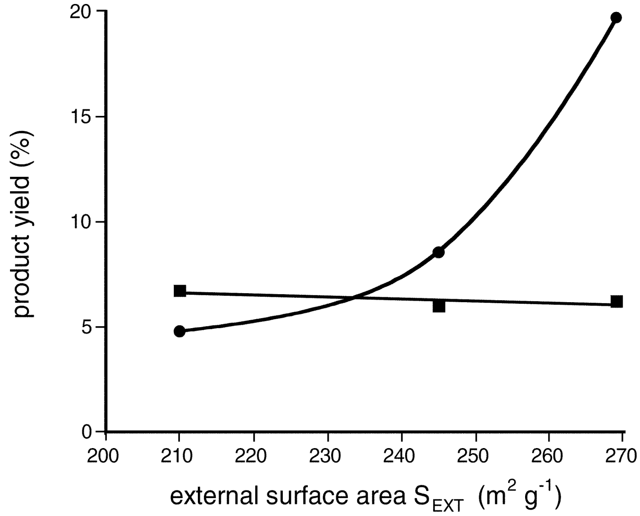

Figure 4. Product yield versus external surface area (S_{EXT}) of the samples: ●, 1-Ac-2-MN; ■, 2-Ac-6-MN ($[2\text{-MN}]_o = 0.2\,\text{mol}\,L^{-1}$; $[Ac_2O]_o = 0.4\,\text{mol}\,L^{-1}$; catalyst = 0.5 g; solvent = chlorobenzene, 50 mL; $T = 353$ K).

enhanced for HBEA2, which exhibits the higher interparticle porosity. Since the secondary porosity of solid oxides, among them zeolites, is strongly dependent on their preparation procedure [26], particularly the washing and drying conditions, our results could provide a straightforward rationale to the difference in behavior of zeolite beta catalysts reported in previous publications.

3.2. *Influence of the reaction temperature and of the solvent polarity*

The influence of the polarity of the solvent was studied over HBEA3, at different reaction temperatures. Two solvents, characterized by different Reichardt parameters E_T [27], were used: chlorobenzene ($E_T = 0.188$) and sulfolane ($E_T = 0.410$). Reactions were carried out in the temperature ranges 353–453 K and 373–448 K in chlorobenzene and sulfolane, respectively. The results are presented in table 2. It has been verified that both activity and yields of products were identical for initial acetic anhydride concentrations equal to 0.2 and $0.4\,\text{mol}\,L^{-1}$ in sulfolane. Therefore, results obtained using the two solvents can be compared. Table 2 shows that 2-methoxynaphthalene conversions and yields of products increase logically with the reaction temperature. However, the most important result is that both 2-methoxynaphthalene conversion and 2-Ac/1-Ac yield ratio decrease when sulfolane is substituted for chlorobenzene. Indeed, the 2-Ac/1-Ac yield ratio, which is around 2 in chlorobenzene, becomes less than 1 in sulfolane. Similar results have already been reported in the literature [12,16,17], and are related to a competitive adsorption between solvent and reactants on the active sites which increases with increasing solvent polarity. This competitive adsorption induces a reduction of the catalytic activity when a more polar solvent is used. Furthermore, the decrease of the yield of 2-Ac-6-MN is much more important than that of the 1-acetyl isomer when the solvent polarity increases (table 2). This phenomenon could be readily explained by an enhanced solvent adsorption in the confined space of the zeolite pores and provides support to the hypothesis that 2-Ac-6-MN is essentially formed within the micropores. A similar reduction of the catalytic activity inside the micropores has been reported by Guisnet *et al.* [16] when sulfolane is substituted for a less polar solvent (1,2-dichlorobenzene). Our results are also in agreement with those of Jacobs *et al.* [28], who demonstrated that solvents with intermediate polarity, like chlorobenzene in our case, favor the catalytic activity and are generally the best solvents.

Figure 5 shows the evolution of product yield versus 2-methoxynaphthalene conversion at 398 K, using chlorobenzene (solid line) and sulfolane (dotted line) as solvents. The linear increase of product yield and the constant isomer ratio with conversion observed for the two solvents at 398 K (and also for lower and higher reaction temperatures) clearly indicate that the products

Table 2
Influence of the reaction temperature on 2-methoxynaphthalene conversion and the product yield, using chlorobenzene or sulfolane as solvent ($[2\text{-MN}]_o = 0.2\,\text{mol}\,L^{-1}$; $[Ac_2O]_o = 0.2$ (in sulfolane) or $0.4\,\text{mol}\,L^{-1}$ (in chlorobenzene); HBEA3 = 0.5 g; solvent = 50 mL; $T = 353$–453 K and 373–448 K)

Temperature (K)	Conversion[a] (%)		Product yield (%)				2-Ac/1-Ac	
	(a)	(b)	1-Ac-2-MN		2-Ac-6-MN		(a)	(b)
			(a)	(b)	(a)	(b)		
353	12		4.8		6.7		1.40	
373		4.5		2.3		2.2		0.95
398	25	12	8.5	6.0	15.5	5.7	1.82	0.95
423	32	19	10.4	9.5	20.6	9.1	1.98	0.96
448		23		11.3		11.1		0.98
453	36		11.9		21.9		1.84	

[a] Conversion after 4 h reaction. (a) In chlorobenzene; (b) in sulfolane.

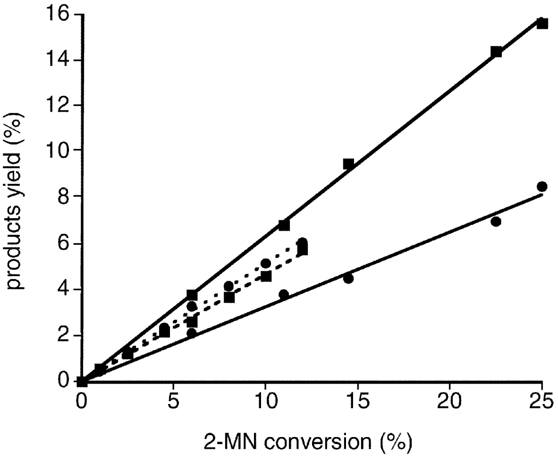

Figure 5. Yields of products versus 2-methoxynaphthalene conversion in chlorobenzene (solid line) and sulfolane (dotted line): ●, 1-Ac-2-MN; ■, 2-Ac-6-MN ($[\text{2-MN}]_o = 0.2\,\text{mol L}^{-1}$; $[\text{Ac}_2\text{O}]_o = 0.2$ (in sulfolane) or $0.4\,\text{mol L}^{-1}$ (in chlorobenzene); HBEA3 = 0.5 g; solvent = 50 mL; $T = 398$ K).

are formed via parallel reactions and that no secondary reactions occur, at least in this conversion range. Such a conclusion is consistent with the report of Casagrande *et al.* [17] who investigated the acylation reaction using diluted solutions of 2-MN, as in our case ($0.2\,\text{mol L}^{-1}$).

On the contrary, consecutive reactions of 1-Ac-2-MN have been observed by Harvey and Mäder [9] and Fromentin *et al.* [15] who performed their studies using more concentrated media, 2 and $3.4\,\text{mol L}^{-1}$, respectively. For instance, deacylation and isomerization reactions of 1-Ac-2-MN have been observed by Fromentin *et al.* [15] over HBEA zeolites. These authors have suggested, moreover, that 1-Ac-2-MN isomerization proceeds via an intermolecular transacylation mechanism. If this statement is correct, the occurrence of secondary isomerization reactions could well be related to a higher dependence on 2-MN concentration of the rate of 1-Ac-2-MN isomerization and deacylation than acetylation.

4. Conclusions

The selectivity of the Friedel–Crafts acetylation of 2-MN in the liquid phase in the presence of acidic zeolites is highly dependent on the experimental conditions used and, above all, on the textural characteristics of the solid catalyst. This has been demonstrated in this work by using three H-beta zeolite catalysts, featuring the same composition, acidity and size of the individual crystals but different secondary porosities resulting from different modes of aggregation of the particles. On the basis of the relationship between the product yields and the textural characteristics of the samples, the formation of the two main acetylated products has been assumed to occur at different locations: inside the micropores in the case of 2-Ac-6-MN and on the outer surface of the crystals in the case of 1-Ac-2-MN. The two isomers are produced via parallel pathways, the contributions of which to the overall process are dramatically influenced by solvent and concentration effects.

Our results could provide the basis for clarifying the conflicting conclusions reached in previous literature reports by different research groups.

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