

Acetylation of aromatics over acid zeolites: Seeking a viable alternative to Friedel–Crafts catalysts*

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Abstract: Three acid zeolites (H-BEA, H-FAU, and H-MWW) were used as catalysts for acetylation in batch reactors with acetic anhydride of five aromatic compounds (benzenic and naphthalenic derivatives). The substrate reactivity is mainly governed by electronic factors (the nature of the substituents and degree of ring activation), but steric effects also play a relevant role when the reaction takes place in a narrow micropore system. In general, H-FAU was the most active catalyst, whereas with H-BEA remarkable steric constraints were observed. H-MWW showed good stability toward deactivation and an interesting activity of the sites located on the external surface.

Keywords: zeolites; acetylation; acetic anhydride; H-BEA; H-FAU; H-MWW; aromatic ketones; heterogeneous catalysis.

INTRODUCTION

Aromatic ketones are useful intermediates for the synthesis of a wide range of compounds used in the fine and specialty chemical industry. The acylation reactions are generally carried out in batch reactors over corrosive conventional Friedel–Crafts catalysts, whose usage implies several environmental and economical drawbacks. In particular, the use of over-stoichiometric amounts of metal halide “catalyst” is no longer considered acceptable and alternative recyclable solids are preferred [1]. Acid zeolites (in their protonic form) are shown to be a suitable catalytic system for the acetylation of aromatic ethers (anisole and veratrole), and the zeolite-based process has been operated at industrial scale by Rhodia [2–4]. Replacing the classic AlCl_3 -based system with a zeolite-based one gave rise to several benefits from an economic, environmental, and safety point of view. Nevertheless, only a limited number of substrates were deeply investigated and systematic comparative studies on the performance of the catalysts over different aromatics under the same reaction conditions are not frequent [5].

We have recently shown that an acid beta zeolite (H-BEA; $\text{Si}/\text{Al} = 15$) can be used as a catalyst for the acetylation with acetic anhydride of arenes with different characteristics and that the electronic factors, affected by the nature of the substituents on the aromatic ring, are the primary factors governing the reactivity of the substrate [6]. However, some diffusion limitations were evidenced by the differences in the acetylation rates passing from monocyclic to bicyclic aromatics. For this reason, in this

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report, we present the data obtained in the liquid-phase acetylation with acetic anhydride of a series of variously substituted aromatic compounds (both mono- and bicyclic ones) over three zeolites of different morphologies: (i) a beta zeolite (BEA) with a bimodal channel system (0.76×0.64 nm and 0.55×0.55 nm), (ii) a Y zeolite (FAU) with pore openings of 0.74×0.74 nm, and (iii) a MCM-22 zeolite (MWW) with independent pore systems (large supercages of $1.82 \times 0.71 \times 0.71$ nm connected by openings of 0.40×0.55 nm; sinusoidal channels of 0.41×0.51 nm; large external cups of $0.70 \times 0.71 \times 0.71$ nm). All three zeolites were employed in their protonic form.

EXPERIMENTAL

H-BEA (CP811B25; total Si/Al ratio = 15) and H-FAU (CBV720; total Si/Al ratio = 15) zeolites were provided by PQ Zeolites. The acidic form of MCM-22 zeolite (H-MWW) was synthesized as previously described [7]. The physicochemical characteristics of the three catalysts are summarized in Table 1. The concentrations of Brønsted and Lewis acid sites were determined by pyridine adsorption at 423 K followed by IR spectroscopy, according to the methodology reported in ref. [8]. Sample porosity was measured by nitrogen adsorption at 77 K with a Micromeritics Tristar apparatus. Before adsorption, the samples were pretreated at 623 K in vacuo for 12 h.

Table 1 Physicochemical characteristics of the acidic zeolites.

Material	Si/Al ratio	V_{TOT} (cm ³ g ⁻¹)	V_{micro} (cm ³ g ⁻¹)	V_{meso} (cm ³ g ⁻¹)	C_{B} (μmol g ⁻¹)	C_{L} (μmol g ⁻¹)
H-BEA	15	0.787	0.282	0.505	345	372
H-FAU	15	0.498	0.325	0.173	270	109
H-MWW	17	0.487	0.227	0.260	550	63

V_{TOT} , total pore volume; V_{micro} , micropore volume; V_{meso} , mesopore volume; $C_{\text{B}}/C_{\text{L}}$, concentration of Brønsted/Lewis acid sites estimated by pyridine adsorption-desorption at 423 K followed by IR spectroscopy.

Anisole (Acros Organics; 99 %), toluene (Aldrich; 99.5 %), fluorobenzene (Aldrich; 99 %), 2-methoxynaphthalene (Lancaster; 98 %), and 2-methylnaphthalene (Aldrich; 98 %) were used as substrates. The catalytic tests were carried out in liquid phase, at 373 K, under dry nitrogen atmosphere, in a three-neck round-bottom flask connected to a reflux condenser and equipped with magnetic stirring (750 rpm). Before each catalytic test, the zeolite was pretreated for 8 h under dry air flow (100 ml min^{-1}) at 773 K. The standard conditions were the following: 500 mg of activated zeolite was added to a mixture containing 35 mmol of substrate, 7 mmol of acetic anhydride (Fluka; 99 %) and 15 ml of nitrobenzene (Lancaster; 99 %), as solvent. Solvent and reagents were previously dried on 3A molecular sieves. Small samples (0.1 ml) were periodically taken and analyzed by GC-FID on a capillary Varian CP-Sil-8 CB column. Products were identified by reference samples or by mass spectrometry.

Since the acetic anhydride was in substoichiometric amount, the conversion of substrate (C) has been referred to the maximum possible conversion into monoacetylated products (here 20 %).

$$C_{\text{SUB}} = C (\text{converted substrate})/C (\text{maximum substrate conversion})$$

where:

$$C (\text{converted substrate}) = 1 - [\% (\text{SUB at time} = t)/\% (\text{SUB at time} = 0)].$$

Turnover frequency (TOF) was computed assuming, in agreement with the relevant literature, that the acetylation reaction takes place on the protonic Brønsted sites without the direct participation of the Lewis acid sites [9–12].

RESULTS AND DISCUSSION

In all cases, the selectivity to acetylated compounds was higher than 98 %. In particular, the main products of the reaction were the monoacetylated derivatives, the other major component observed in the reaction mixture being the acetic acid due to the acetic anhydride consumption. Figures 1–3 show the conversion curves of the five substrates with respect to time over H-BEA, H-FAU, and H-MWW, respectively.

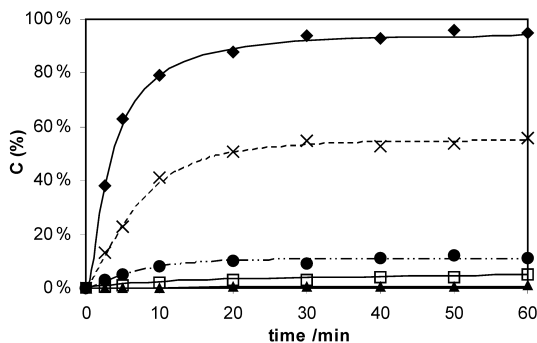


Fig. 1 Conversion (C) of anisole (◆), 2-methoxynaphthalene (×), toluene (●), 2-methylnaphthalene (□), and fluorobenzene (▲) vs. time over H-BEA.

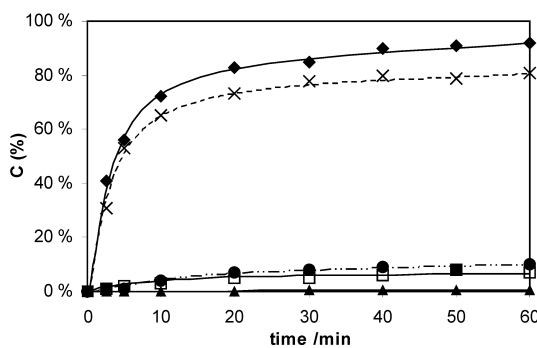


Fig. 2 Conversion (C) of anisole (◆), 2-methoxynaphthalene (×), toluene (●), 2-methylnaphthalene (□), and fluorobenzene (▲) vs. time over H-FAU.

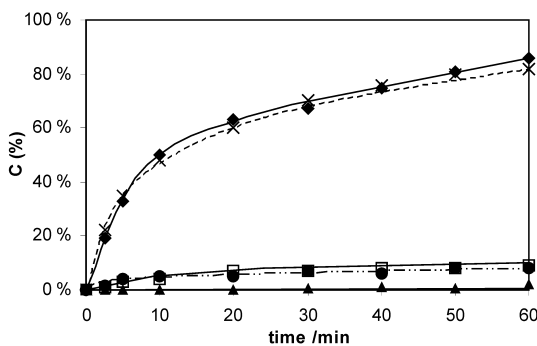


Fig. 3 Conversion (C) of anisole (◆), 2-methoxynaphthalene (×), toluene (●), 2-methylnaphthalene (□), and fluorobenzene (▲) vs. time over H-MWW.

After a reaction time of 60 min, over the three catalysts, the order of substrate reactivity was anisole \geq 2-methoxynaphthalene $>$ toluene \geq 2-methylnaphthalene $>$ fluorobenzene. The acetylation rate is therefore primarily controlled by electronic factors, activating or deactivating substituents on the aromatic ring having a strong influence on the reactivity of the substrates. Indeed, optimal results were recorded with methoxy-bearing arenes, and conversions as high as 95 % were obtained after 1 h in the anisole acetylation. Conversely, in all cases, the reactivity of poorly activated or nonactivated arenes (as fluorobenzene) was very low and of scarce practical relevance, at least under the conditions here tested.

By considering the initial rates of acetylation (the TOFs after 2.5 min of reaction), H-FAU displayed on average better performances than H-BEA and H-MWW, and these differences are even more marked in the case of anisole or 2-methoxynaphthalene. Even if H-FAU possesses the lowest amount of Brønsted sites (Table 1), it showed excellent results in terms of both conversion and specific activity. It is also worth highlighting that the gap between the TOFs of monocyclic and bicyclic substrates decreases in the order: H-BEA $>$ H-FAU $>$ H-MWW and that, over the last material, such difference is almost negligible. This trend is even more evident looking at the conversion profiles in Figs. 1–3, and it suggests that the diverse morphology of the solid catalyst plays a role in influencing the reactivity of the aromatic substrate (though secondary with respect to the activating/deactivating electronic effect of the substituents on the aromatic ring).

Actually, over conventional Friedel–Crafts catalysts, the acetylation of naphthalenic derivatives is easier than that of benzenic derivatives with the same substituting groups [13]. Over H-BEA and H-FAU the opposite trend is observed, and this behavior indicates that some limitations are present in the desorption of the acetylated naphthalenic products from the micropores of both zeolites (more markedly for H-BEA and less markedly for H-FAU). Nevertheless, when H-MWW is used as catalyst, 2-methoxynaphthalene reacted slightly faster than anisole (TOF after 2.5 min: 3.7×10^{-2} vs. $3.2 \times 10^{-2} \text{ s}^{-1}$) and it is a clue that the catalytic sites within the micropore network cannot play a relevant role in the conversion of the substrates. Indeed, over H-MWW the two couples of benzenic and naphthalenic substrates (i.e., anisole/2-methoxynaphthalene and toluene/2-methylnaphthalene) show practically identical conversion profiles (Fig. 3), as if they were not affected by diffusion limitations.

These results indicate that with H-BEA and H-FAU the acetylation reaction takes place mainly within the internal porous system of the molecular sieve. So, the narrower the porous network, the larger was the difference in reactivity between monocyclic and bicyclic aromatics. On the other hand, with H-MWW a remarkable deactivation of the inner micropores and supercages can occur rapidly after the first minutes of reaction (as previously shown for the alkylation reaction [7]), and therefore the acetylation is solely carried out by the accessible acid sites in the external hemicages of the zeolite.

Such hypotheses are also supported by the isomer distribution values obtained in the acetylation of the two bicyclic arenes here considered, that is to say, 2-methoxynaphthalene and 2-methylnaphthalene (Table 2).

Indeed, typically, the acetylation of 2-methoxynaphthalene leads first to the kinetically favored isomer 2-methoxy-1-acetonaphthone, but longer reaction times or steric constraints enhance the formation of the thermodynamically favored 6-methoxy-2-acetonaphthone isomer [14–17]. In this case, after 1 h of reaction, the amount of 2,6-isomer production decreased according to the order: H-BEA $>$ H-FAU $>$ H-MWW (Table 2). Likewise, considering the selectivity to 2,6-isomer at isoconversion of ca. 50 %, the same trend was observed: H-BEA $>$ H-FAU $>$ H-MWW (i.e., 20, 7, and 5 %, respectively). These data clearly show that steric constraints are effective with H-BEA, whereas they are negligible with H-MWW. For the acetylation of 2-methylnaphthalene a different scenario occurs, as in all cases the 2,6-isomer is the major component, as already observed over conventional AlCl_3 catalysts [18]. However, with H-BEA the formation of the bulkier 1,2-isomer is somehow inhibited, whereas it is non-negligible with the other two zeolites (Table 2). In the acetylation of monocyclic substrates, in all cases, the *para*-isomers were the main products and no peculiar trends were recorded.

Table 2 TOF and selectivity in the acetylation of substituted aromatics over acidic zeolites.^a

Substrate	TOF ^b × 10 ³ (s ⁻¹)			Product ^c	Isomer	Distribution ^d (%)		
	H-BEA	H-FAU	H-MWW			H-BEA	H-FAU	H-MWW
Anisole	103	145	32	methoxy	<i>para</i>	99	98	99
				acetophenone	<i>ortho</i>	1	2	1
2-Methoxy naphthalene	41	107	37	methoxy acetophenone	1,2-	74	89	94
					2,6-	22	8	5
					2,8-	2	2	1
					others	2	1	–
Toluene	8.1	6.9	3.4	methyl	<i>para</i>	99	99	99
				acetophenone	<i>ortho</i>	1	1	1
2-Methyl naphthalene	1.4	3.5	1.7	methyl acetophenone	2,6-	71	46	51
					2,8-	16	26	25
					1,2-	2	16	15
					others	11	12	9
Fluorobenzene	0.3	0.3	0.2	fluoro acetophenone	<i>para</i>	>99	>99	>99

^aReaction conditions: 500 mg zeolite; substrate : AA ratio = 5; 15 mL PhNO₂; 373 K; 1 bar; 60 min.

^bTOF ([mol_{SUB}] [mol_{H+} s]⁻¹) after 2.5 min. The amount of H⁺ was computed according to the amount of Brønsted acid sites.

^cIn all cases, selectivity to acetylated products was >98 % after 60 min.

^dObtained from GC analysis of the reaction mixture after 60 min.

Moreover, by comparing the conversion profiles of anisole and 2-methoxynaphthalene (Figs. 1–3), it is possible to note that over H-BEA and H-FAU the reaction does not proceed further after the first 30–40 min of reaction (the conversion curves reach a plateau after that time), while over H-MWW the conversion values increase continuously, as if the catalyst did not suffer from deactivation. Such behavior is a further confirmation that the acetylation process takes place essentially on the protonic sites of external cups of the H-MWW zeolite, where the deactivation by irreversible adsorption of carbonaceous compounds is less likely, the inner sites being strongly deactivated. On the contrary, the active sites of H-BEA and H-FAU are mainly located within the micropore channel systems and hence they are subject to drastic deactivation, causing a loss of catalytic activity.

The presence of remarkable amounts of carbonaceous deposits in H-MWW is also confirmed by the weight loss observed during the calcination at 773 K in air of the spent catalyst (the used catalyst underwent a previous Soxhlet extraction with dichloromethane to remove the physisorbed fraction of deposits): the percent weight loss was 3.0 wt % for H-MWW, whereas it was 2.1 and 2.6 wt % for H-BEA and H-FAU, respectively.

Finally it is worth underlining that, if the external sites of H-MWW are the sole responsible for the acetylation reaction, it means that they are very active, as they are approximately only one-sixth of the total amount of Brønsted acid sites (i.e., 90 μmol g⁻¹ of external sites vs. 550 μmol g⁻¹ overall [7]) and that they are quite resistant to the deactivation caused by strongly adsorbed carbonaceous deposits.

CONCLUSIONS

The acid zeolites can be chosen as viable and sustainable alternatives to Friedel-Crafts catalysts, whenever aromatics activated toward the electrophilic substitution are used as substrates. In particular, anisole and 2-methoxynaphthalene are converted into their acetylated derivatives with good yields. Conversely, when poorly activated substrates are considered, the rapid deactivation of the catalyst could represent a major drawback in the development of zeolite-based acetylation processes.

Even though the reactivity of the arene is principally governed by the nature of the substituents on the aromatic ring, not only the reactivity, but also the selectivity to various isomers is influenced by the diverse morphology of the solid catalyst as well. In fact, over H-BEA, zeolite bicyclic aromatics reacted less easily and the formation of less bulky acetylated isomers was favored because of its network of narrow micropores. Over H-FAU, which possesses a wider porous system, the highest specific activities were observed and the differences between bicyclic and monocyclic arenes were less marked. Lastly, over H-MWW, the effective active sites for the acetylation reaction are mainly located on the external surface of the solid and minimal effects due to steric constraints were evidenced. This catalyst displayed promising features in terms of activity, and resistance to deactivation and further detailed studies should be carried out over MWW zeolites with higher external surface area or over delaminated MWW-type materials.

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