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Zeolite Catalysts as Solid Solvents in Fine Chemicals Synthesis

2. Competitive Adsorption of the Reactants and Products in the Friedel–Crafts Acetylations of Anisole and Toluene

E. G. Derouane,[1] G. Crehan, C. J. Dillon, D. Bethell, H. He, and S. B. Derouane-Abd Hamid

Leverhulme Centre for Innovative Catalysis, The University of Liverpool, Department of Chemistry, P.O. Box 147,
Liverpool L69 3BX, United Kingdom

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The liquid-phase acetylations of anisole by acetic anhydride and isopropenyl acetate and that of toluene by acetic anhydride, using zeolites HBEA, HMFI, and HFAU as catalysts, were carried out under batch conditions using various molar ratios of the reactants without added solvent. Evidence has been obtained for competitive adsorption effects of the reactants resulting from differences in their adsorption equilibrium constants (AEC). Estimated values of the AEC show that preferential adsorption is in the order toluene < acetic anhydride (AA) < anisole < isopropenyl acetate (IPA). In all cases, the acetylation products are adsorbed more strongly than the reactants, but the competitive adsorption of acetic acid and acetone appear to be negligible when AA and IPA are used as acetylating agents, respectively. The effect of dealumination was investigated for the acetylation of toluene by acetic anhydride, using HBEA as catalyst. Both the initial and the quasi-stationary-state reaction rates are proportional to Al content, i.e., the number of Brønsted sites at low Al content. The rates decrease at high aluminium content, indicating that competitive adsorption effects are enhanced due to the increased zeolite polarity and polarisability. Initial rate constants for the acetylation of anisole, derived by assuming a Langmuir–Hinshelwood model, show that the rate-determining step is most likely to be the reaction of anisole with an acyl cation equivalent formed by reaction of either acetic anhydride or isopropenyl acetate with the zeolite (HBEA). A possible mechanism is proposed in which the formation of an acyl cation–zeolite complex is the initial step. This proposal is based in part on the colour change of the zeolite when it is contacted with the reactant mixture and during reaction, the colour being attributed to the formation of the zeolite–acyl cation complex. The present work confirms that competitive adsorption effects, involving both reactants and products, need to be controlled in order to achieve maximum catalytic performance when zeolites are used as catalysts in the liquid phase. © 2000 Academic Press

Key Words: **heterogeneous catalysis; zeolite; zeolite dealumination; competitive adsorption; Friedel–Crafts reaction; solvent effect; fine chemicals.**

INTRODUCTION

This publication is the second one in a series devoted to the identification, understanding, and quantification of "solid solvent" effects when zeolites and other microporous solids are applied as catalysts to organic synthesis in the liquid phase.

Concentration effects in zeolites were identified by Rabo and Poutsma in the late 1970s (1), and the potential behavior of zeolites as solid solvents was further pointed out by Rabo and Gajda in the late 1980s (2). We enounced and quantified in the late 1980s the principles of molecular confinement in the intracrystalline volume of zeolites and showed that zeolites can indeed behave like solid solvents, as described and discussed in several recent papers (3–5). They were summarised in the first publication of this series (6). They provide a new framework for the understanding and use of zeolitic heterogeneous catalysts in organic synthesis, i.e., under conditions where reactions are usually operated at rather low temperature and/or in the liquid phase.

Friedel–Crafts reactions, in particular acetylation and benzoylation, are important routes for the synthesis of aromatic ketones that are intermediates in the manufacture of many fine and specialty chemicals as well as pharmaceutical compounds. For these reasons, we chose Friedel–Crafts acylation as a vehicle for developing our ideas.

Several recent publications have discussed the use of zeolites for such catalysis, principally using the acidic form of large-pore zeolites such as BEA and FAU applied to the acetylation of anisole and veratrole (7–11). These reports indicate that the reaction rate, when the reaction is performed under batch conditions, decreases rapidly as conversion proceeds (7–12). Rohan *et al.* (10) suggested that deactivation of zeolite HBEA (H-form of zeolite Beta) used as a catalyst for the acetylation of anisole by acetic anhydride was probably due to the retention of the *p*-methoxyacetophenone (*p*-MOAP) product inside the

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[1] To whom correspondence should be addressed. E-mail: derouane@liverpool.ac.uk.

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zeolite pores. For the same reaction, Freese *et al.* (11) concluded that two types of heavy organic residues (extractable and nonextractable) were probably responsible for catalyst deactivation. Smith *et al.* (12) suggested that acetic acid formed as a by-product could also lead to (reversible) catalyst deactivation.

We demonstrated in the first publication of this series (6) that reaction inhibition by preferential retention of the acetylated product by the zeolite, somewhat resembling product inhibition of enzyme catalysts, was responsible for the reversible deactivation of the catalysts. We also showed that dealumination by the coproduced acetic acid led to progressive and irreversible deactivation of the zeolite due to the dealumination of its framework.

An acyl cation produced by reaction of the acetylating agent with the zeolite was proposed to be the critical species reacting with the adsorbed aromatic substrate (13, 14), implying that reaction of the acyl cation–zeolite complex with the aromatic substrate was the rate-determining step. However, no evidence was provided for the formation of an acyl cation–zeolite complex, nor was it demonstrated that the rate constant for acylation was more dependent on the nature of the aromatic substrate than on the nature of the acylating agent. Two aromatic substrates, anisole and toluene, and two acetylating agents, acetic anhydride and isopropenyl acetate, were used in the present study to evaluate the validity of the above proposal.

Also, little attention has been devoted so far in the published literature to the analysis and quantification of the competitive adsorption effects arising from the different affinities of the reactants for the zeolite catalyst, although these effects should play a major role. Indeed, for a given stoichiometry of the reactants in the liquid phase, the maximum reaction rate will be observed when a 1 : 1 stoichiometry of the reactants (for Friedel–Crafts acylation) is achieved inside the zeolite channels, and this will depend on differences between the reactants' adsorption equilibrium constants (AEC). These in turn are expected to depend on zeolite pore size, polarity, and polarisability, the latter two factors being influenced by the zeolite Si/Al ratio.

These issues are addressed in the present contribution.

EXPERIMENTAL

Acetylation of Anisole by Acetic Anhydride: General Procedures

A 50-ml glass batch reactor equipped with a condenser and a mechanical stirrer was charged with a mixture of anisole (AN) and acetic anhydride (AA) whose molar ratio, AN/AA, was varied between 0.16 and 6. Anisole (Avocado Research Chemicals) was purified by distillation over CaH_2. Acetic anhydride (from Aldrich, purity greater than 99%) was used as received.

TABLE 1

Experimental Conditions for the Acetylation of Anisole (AN) by Acetic Anhydride (AA)

Parameter/experiment	A1	B1	C1	D1	E1
AN/AA molar ratio	0.16	0.51	1.0	2.0	6.0
Anisole (mmol)	15.0	30.0	59.0	118.0	180.0
Anisole (g)	1.62	3.24	6.38	12.76	19.46
Acetic anhydride (mmol)	90.0	59.0	59.0	59.0	30.0
Acetic anhydride (g)	9.19	6.02	6.02	6.02	3.06
Catalyst (HBEA) (g)	0.9	0.6	0.6	0.6	0.3

The system was purged with nitrogen to expel air and moisture and was heated to 90°C. The catalyst (HBEA, acidic form of zeolite H-Beta, Si/Al = ca. 12, from PQ Zeolites) was preactivated in air for 5 h at 550°C and added in an appropriate amount (10 wt% relative to acetic anhydride) to the reactor after introduction of the organic reactants. Upon addition of the reactants, the catalyst became pale orange in the colourless solution, and the colour deepened to brown-red with reaction time.

Table 1 details the composition of the mixtures, reactants, and catalysts used in the various experiments.

Acetylation of Anisole by Isopropenyl Acetate: General Procedures

The method used is similar to the one described above except that reactions were carried at 80°C and that slightly less catalyst was used (8 wt% relative to isopropenyl acetate). Isopropenyl acetate (Aldrich, purity greater than 99%) was used as received. The reactant mixture immediately turned bright red upon addition of the catalyst and darkened in colour with time.

The molar ratio of anisole (AN) to isopropenyl acetate (IPA) was varied from 1 to 20. Table 2 lists the composition of the mixtures, reactants, and catalysts used in these experiments.

TABLE 2

Experimental Conditions for the Acetylation of Anisole (AN) by Isopropenyl Acetate (IPA)

Parameter/experiment	A2	B2	C2	D2
AN/IPA molar ratio	1.0	5.0	10.0	20.0
Anisole (mmol)	58.0	290.0	320.0	340.0
Anisole (g)	6.27	31.36	34.60	36.76
Isopropenyl acetate (mmol)	58.0	58.0	32.0	17.0
Isopropenyl acetate (g)	5.81	5.81	3.16	1.66
Catalyst (HBEA) (g)	0.46	0.46	0.25	0.13

TABLE 3

Characteristics of the Catalysts Used in the Acetylation of Toluene by Acetic Anhydride

Catalyst type:	HMFI	HMOR	HFAU	HBEA				
Catalyst code:	MFI	MOR	FAU	BEA	BEA1	BEA5	BEA10	BEA10L
Dealumination	No	No	No	No	Yes	Yes	Yes	Yes
Dealumination treatment	—	—	—	—	HNO_3, 1 M, 4 h	HNO_3, 5 M, 4 h	HNO_3, 10 M, 4 h	HNO_3, 10 M, 12 h
Si/Al ratio (nominal)[b]	*27.5*	*18.0*	*27.5*	*12.5*[a]	**43.6**	**66.56**	**69.4**	**93.3**
Percentage of Al in the framework[b]	*100*	*100*	*100*	*100*	**80.3**	**69.1**	**57.8**	**36.4**
Al molar fraction in the framework[b]	*0.0351*	*0.0526*	*0.0351*	*0.0741*	**0.0224**	**0.0102**	**0.0082**	**0.0039**

[a] Used as reference to calibrate the MAS NMR spectra.

[b] Si/Al ratios (nominal = framework and extraframework Al included) and framework Al molar fraction values in italic characters are those provided by the manufacturer. Values in bold characters were determined by ^{27}Al MAS NMR using BEA as reference.

Acetylation of Toluene by Acetic Anhydride: General Procedures

Catalysts. Four different zeolite catalysts were used to investigate the effect of zeolite pore size, HBEA (as above), HMOR (acidic form of mordenite, Si/Al = ca. 18), HFAU (acidic form of dealuminated faujasite, Si/Al = ca. 27.5), and HMFI (acidic form of zeolite ZSM-5, Si/Al = ca. 27.5). All catalysts were obtained from PQ Zeolites.

In order to investigate the effect of the catalyst polarity (dependent on the zeolite Si/Al ratio), HBEA was dealuminated to several extents using a procedure adapted from Lami *et al.* (15): 1, 5, and 10 M solutions of nitric acid prepared from fresh concentrated nitric acid (Aldrich, 69%) were used to dealuminate HBEA by stirring 1 g of the parent zeolite in 100 ml of solution for 4 h at 50°C. Extreme dealumination of HBEA was achieved under similar conditions, the contact time with nitric acid 10 M being 12 h. The dealuminated zeolites were recovered by filtration, washed on the filter with a 0.1 M nitric acid solution (50°C), and subsequently washed repeatedly with deionized water. The samples were then dried and stored for further use.

Powder X-ray diffraction (Siemens D5005 diffractometer, Cu $K\alpha$ radiation) confirmed that the structural integrity of the BEA framework was preserved in all cases. ^{27}Al MAS NMR spectroscopy was used to determine the amount of extraframework Al species in the dealuminated HBEA zeolites (resonance at a chemical shift of ca. 0 ppm) and to quantify the Al content (Si/Al ratio) of their framework (tetrahedral ^{27}Al resonance at ca. 53 ppm). ^{27}Al chemical shifts are relative to aqueous aluminium nitrate (1 M) at 0 ppm, the usual reference. ^{27}Al MAS NMR Bloch decay spectra were acquired on a Bruker Avance DSX-400 multinuclear NMR spectrometer operating at 104.27 MHz using 0.35-μs (<10°) pulse lengths and 0.3-s recycle delays, with a spinning rate of ca. 4 kHz.

Table 3 summarises the characteristics of the above catalysts.

Reaction conditions. The HBEA zeolite catalyst was preactivated by progressive heating under nitrogen to 400°C, followed by exposure to air for 2 h at the same temperature and further increase of the temperature to 500°C for 2 h.

A 50-ml glass reactor designed according to Choudhary *et al.* (16) was used. The preactivated catalysts (0.5 g) contained in a side arm connected to the reaction vessel were pretreated under vacuum at 300°C for 4 h, the reactor system was filled with argon, and the catalyst was transferred to the reaction vessel after cooling. The toluene (T) and acetic anhydride (AA) reactant mixture, with molar ratio in the range T/AA = 1–20 and a total reactant volume of 30 ml, was preheated at 90°C in a water-jacketed burette and then emptied into the reaction vessel. The reaction was conducted at reflux, i.e., 115°C, with vigorous stirring.

Table 4 details the experimental conditions used.

Effect of zeolite pore size and polarity (Si/Al ratio). All pretreatments and reactions were conducted as described above, under reflux conditions, i.e., 115°C, using HMFI, HMOR, HBEA, and HFAU as catalysts, as mentioned above, and a ca. 9.7 : 1 molar ratio of toluene to acetic anhydride.

Experimental details are shown in Tables 5 and 6.

TABLE 4

Experimental Conditions for the Acetylation of Toluene by Acetic Anhydride: Effect of the Reactant Ratio

Parameter/experiment	A3	B3	C3	D3	E3
TOL/AA molar ratio	1.17	5.0	9.71	15.0	20.0
Toluene (mmol)	173.6	233.7	259.2	267.2	270.0
Toluene (g)	15.97	21.50	23.85	24.58	24.84
Acetic anhydride (mmol)	147.9	46.7	26.7	17.8	13.5
Acetic anhydride (g)	15.08	4.76	2.72	1.82	1.38
Catalyst (HBEA) (g)	0.5	0.5	0.5	0.5	0.5

TABLE 5

Experimental Conditions for the Acetylation of Toluene by Acetic Anhydride: Effect of the Zeolite Pore Size

Parameter/experiment	H-FAU	H-BEA	H-MOR	H-MFI
TOL/AA molar ratio	9.88	9.71	9.92	9.96
Toluene (mmol)	259	259.2	259	259
Toluene (g)	23.84	23.85	23.84	23.84
Acetic anhydride (mmol)	26.2	26.7	26.1	26.0
Acetic anhydride (g)	2.67	2.72	2.66	2.65
Catalyst (g) (a)	0.969	0.500	0.500	1.059
Catalyst Si/Al ratio	27.5	12.5	18	27.5
Al/(Al + Si) molar fraction (b)	0.0351	0.0741	0.0526	0.0351
Relative number of acidic sites engaged (a × b)	0.034	0.037	0.026	0.037

Analysis and Data Interpretation

Acetylation of anisole by acetic anhydride or isopropenyl acetate. As the reaction proceeded, 0.15-ml samples were taken periodically from the reaction mixture and added to aliquots, 0.15 ml, of an internal standard solution (1 g, i.e., 6 mmol of biphenyl in 25 ml of 1,2-dichloroethane). Analysis was achieved by gas chromatography (Varian 3800 gas chromatograph) using a 30-m VA-WAX capillary column.

p-Methoxyacetophenone (*p*-MOAP) was the main reaction product. Very little *o*-methoxyacetophenone was produced (less than 2%). Conversions are expressed with respect to the reactant in default, i.e., with respect to acetic anhydride or isopropenyl acetate in the experiments performed with $AN/AA > 1$ and $AN > IPA > 1$, respectively, and with respect to anisole for the experiments performed with $AN/AA < 1$. Conversions are thus simply defined as

$$X(\%, t) = (\text{moles of } p\text{-MOAP produced at time } t)/ (\text{moles of acetic anhydride, isopropenyl acetate, or anisole at } t = 0)$$

Reaction rates are calculated as the number of moles of *p*-MOAP produced per minute and per gram of catalyst.

Acetylation of toluene by acetic anhydride. At regular intervals, 0.3-ml samples of the reaction mixture were taken and centrifuged, to eliminate any zeolite particles, and exactly 0.1 ml was collected for analysis using an Eppendorf microliter pipette. GC analyses were performed using a Varian Star 3400 CX chromatograph equipped with an EC1 column. Aliquots of a solution of *n*-decane and cyclohexanone were used as internal standards.

p-Methylacetophenone (*p*-MAP) was the main reaction product. Selectivity to *o*-MAP in the products never exceeded 0.5%, even after 24 h, and the formation of *m*-MAP was never observed.

Conversions are expressed with respect to the reactant in default, i.e., acetic anhydride. Conversions are thus simply defined as

$$X(\%, t) = (\text{moles of } p\text{-MAP produced at time } t)/ (\text{moles of acetic anhydride at } t = 0).$$

Reaction rates are calculated as the number of moles of *p*-MAP produced per minute and per gram of catalyst.

RESULTS AND DISCUSSION

Kinetic Model for the Evaluation of the Adsorption Equilibrium Constants and Reaction Rates

As proposed recently, a Langmuir–Hinshelwood model describes best the kinetics of reaction catalysed by zeolites in the liquid phase (4, 5), e.g., Friedel–Crafts reactions (6), as it accounts for the competition of the reactants and products for the occupancy of the intracrystalline volume of the zeolite, where reaction occurs. This model is preferred to an Eley–Rideal model. Indeed, although only one reactant may be activated at the catalytic sites, the other reactant(s) and product(s) will block its access to the catalytic sites considering the molecular size of the zeolite (micro)pores, channels, and cavities.

For a Friedel–Crafts type reaction, with A being the acetylating agent, B being the aromatic substrate, P being the desired product, and neglecting products such as acetic acid, which are adsorbed to a lesser extent, the reaction rate

TABLE 6

Experimental Conditions for the Acetylation of Toluene by Acetic Anhydride: Effect of Dealumination on the Performance of Zeolite HBEA

Parameter/experiment	A4	B4	C4	D4	E4
TOL/AA molar ratio	9.71	9.63	9.70	9.99	9.74
Toluene (mmol)	259.2	259.2	259.1	258.7	259.2
Toluene (g)	23.85	23.85	23.84	23.80	23.85
Acetic anhydride (mmol)	26.7	26.9	26.7	25.9	26.6
Acetic anhydride (g)	2.72	2.75	2.64	2.64	2.71
Catalyst (HBEA)[a] and weight (g)	BEA, 0.5	BEA1, 0.5	BEA5, 0.5	BEA10, 0.5	BEA10L, 0.5

[a] See Table 3 for the description of the catalysts.

is

$$R = kK_AK_B[A][B]/(1 + K_A[A]K_B[B] + K_P[P])^2, \quad [1]$$

where [A], [B], and [P] are the concentrations of the acetylating agent, the aromatic substrate, and the acetylated aromatic product, respectively, k being the kinetic rate constant (inclusive of the number of catalytic sites), and K_A, K_B, and K_P representing the adsorption constants of the reactants (A and B) and product (P). As the intracrystalline volume of the zeolite is most likely to be saturated by the reactants and products for a reaction operated in liquid phase at low temperature, the factor "1" in the denominator can be neglected relative to the other terms, and Eq. [1] becomes

$$R = kK_AK_B[A][B]/(K_A[A] + K_B[B] + K_P[P])^2. \quad [2]$$

It is worth noting from Eq. [2] that R depends only on the molar amounts of reactants and product(s) present and not on their concentrations, as volume effects are cancelled.

Kinetics under quasi-initial conditions. In the very early stages of the reaction, $K_P[P]$ can be neglected at the denominator of Eq. [2] as little product is present. Equation [2] then becomes

$$R = kK_AK_B[A][B]\big/\big(K_A^2[A]^2 + 2K_AK_B[A][B] + K_B^2[B]^2\big), \quad [3]$$

whose reciprocal is

$$1/R = K_A[A]/kK_B[B] + 2/k + K_B[B]/kK_A[A], \quad [4]$$

which can be converted into a quadratic equation

$$\begin{aligned}&(1/R)([A]/[B]\\ &\quad = K_A/kK_B([A]/[B])^2 + 2/k[A]/[B]) + K_B/kK_A \quad [5]\end{aligned}$$

or, in a simplified form,

$$y = ax^2 + bx + c \quad [6]$$

with

$$\begin{aligned}y = (1/R)([A]/[B]),\ K_A/K_B = 2a/b, \quad \text{and}\\ k = 2/b \quad \text{or} \quad (a.c)^{-1/2}.\end{aligned} \quad [7]$$

It is worth noting that the values of a, b, and c in Eq. [6] are related to each other. For a perfect fit of the data, $2(a.c)^{1/2}/b$ should be equal to 1.

Fitting the experimental data using Eq. [5–7] enables the evaluation of K_A/K_B and k. The quality of the fit is determined mostly by the values of the coefficients a and b. The coefficient c corresponds to the ordinate at the origin. Data points extrapolating to this value are obtained under conditions where [A]/[B] is very small and R is also small, as a 1 : 1 stoichiometry of the reactants is far from being achieved in the intracrystalline volume of the zeolite. The relationships $K_A/K_B = 2a/b$ and $k = 2/b$ should thus be preferred to evaluate the ratio of the equilibrium constants and the rate constant.

Differentiation of Eq. [3] shows that the initial reaction rate goes through maximum when

$$([B]/[A])_{max} = K_A/K_B, \quad [8]$$

where $([B]/[A])_{max}$ is the B/A molar ratio at the maximum easily determined from an R vs ([B]/[A]) plot. Equation [8] thus provides an alternative way to determine the K_A/K_B ratio. It should be noted that, in order to optimise the determination of K_A/K_B, reaction rates corresponding to [B]/[A] ratios remote from the maximum should not be included; other effects may come into play when [B]/[A] is very high or very low, i.e., secondary effects due to the reactant in excess acting as solvent for the product(s) or a lower accuracy on the value of the ratio itself. Equation [8] translates in mathematical terms the fact that the reaction rate is maximal when the [A]/[B] ratio leads to equal occupancies of the intracrystalline volume of the zeolite by A and B; i.e., $\theta_A = \theta_B$, corresponding to a 1 : 1 stoichiometry of the reactants inside the zeolite. This will be shown with the discussion of our results for the acetylation of anisole by acetic anhydride.

Kinetics at quasi-stationary state. As demonstrated previously (6), competitive adsorption experiments where the reactants mixture is spiked with the product enable the evaluation of the value of K_P relative to one specified reactant. For this purpose, the adsorption equilibrium constant of acetic anhydride, K_{AA}, was used as reference and set equal to 1 (90°C).

Reaction rates measured at the quasi-stationary state can also be used to obtain an approximate value of K_P. In this case, neglecting the factor "1" as explained above, Eq. [1] becomes

$$R = kK_AK_B[A][B]/(K_A[A] + K_B[B] + K_P[P])^2. \quad [9]$$

Assuming that product inhibition dominates at the quasi-stationary state, the intracrystalline volume being mostly occupied by the product, P, one can neglect $K_A[A]$ and $K_B[B]$ in the denominator of Eq. [9], leading to

$$R = kK_AK_B[A][B]\big/K_P^2[P]^2 \quad [10]$$

or

$$R = kK_AK_B(a - x)(b - x)\big/K_P^2x^2, \quad [11]$$

where a and b are the concentrations (or moles) of reactants engaged and x is the concentration (or moles) of product

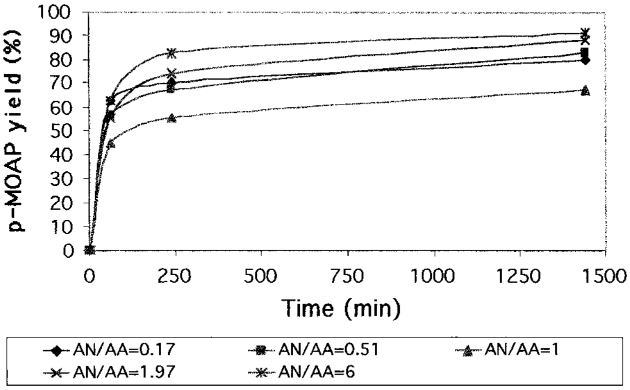

FIG. 1. *p*-MOAP yield (%) vs time as a function of the anisole to acetic anhydride (AN/AA) molar ratio. Reaction conditions are given in Table 1; $T = 90°\text{C}$. *p*-MOAP yields are normalised to the amount of reactant in deficit.

formed. Equation [11] enables the evaluation of the ratio kK_AK_B/K_P. As K_A/K_B and k can be evaluated using Eqs. [5–8], K_A^2/K_P and K_B^2/K_P can be determined. If K_A is used as reference, an approximate value of K_P is obtained.

Rates at the quasi-stationary state can be evaluated using either a logarithmic fit of conversion vs time for the whole test or a linear fit of conversion vs time near to the stationary state.

Effect of the Reactant Ratio on the Reaction Rate and Product Yield—Evidence for the Competitive Adsorption of Reactants and Products

Acetylation of anisole by acetic anhydride. Figure 1 shows the variation with time of the yield (%, with respect to the amount of reactant in deficit) in *p*-MOAP as a function of the anisole (AN) to acetic anhydride ratio (AA). The reaction conditions are given in Table 1.

As reported and discussed previously (6), the rate of production of *p*-MOAP is initially very high and rapidly decreases, due to product inhibition, after about 1 h on stream when conversion (of the limiting reactant) has reached about 50–60%. We estimated previously that the adsorption equilibrium constants ratio for *p*-MOAP relative to anisole was 6.3.

Both the product yield at the beginning of the quasi-stationary state ($t =$ ca. 250 min) and the initial reaction rate depend on the AN/AA molar ratio.

The product yield after 250 min goes through a minimum when the AN/AA molar ratio is increased, the minimum occuring for an AN/AA molar ratio in the range 0.5–1.0. This observation can be rationalised by considering (i) that anisole in excess acts as a solvent for *p*-MOAP at high AN/AA molar ratio, thus favouring the extraction of *p*-MOAP from the intracrystalline zeolite volume, (ii) that *p*-MOAP, whose production is faster when optimal stoichiometry of the reactants is achieved, inside the zeolite inhibits the reaction more effectively, and (iii) that acetic anhydride in excess can also act as a solvent for the *p*-MOAP product, thus reducing product inhibition by *p*-MOAP.

Initial reaction rates (R, mmol min^{-1}) can be derived by fitting time (min) yields (mmol) at low conversion to a quadratic equation whose first derivative expresses rate vs time as shown previously (6).

Figure 2 shows the dependence of the initial reaction rate (mmol of *p*-MOAP (min · g catalyst)$^{-1}$) as a function of the AN/AA molar ratio. The total amount of reactants was normalised to 118 mmol to account for dilution effects. The initial reaction rate goes through a maximum for an AN/AA molar ratio around 0.6–0.7 which, according to Eq. [8], corresponds to an AN/AA adsorption equilibrium constant ratio, K_{AN}/K_{AA}, in the range 1.4–1.7.

A quadratic plot according to Eqs. [5–7] of (1/R)([AN]/[AA]) vs [AN]/[AA], where R is the reaction rate (mmol of *p*-MOAP (min g catalyst)$^{-1}$), normalised to 118 mmol of reactants to account for dilution effects) leads to the equation

$$y = 0.3975x^2 + 0.4566x + 0.2423 \qquad [12]$$

and $2(a.c)^{1/2}/b = 1.36$ in fair agreement with the theoretical value of 1.

From Eqs. [7] and [12], $K_{AN}/K_{AA} = (2a/b) = 1.74$ at 90°C, K_{AN} and K_{AA} being the adsorption equilibrium constants for anisole and acetic anhydride, respectively. The latter value is in good agreement with the value expected from the qualitative examination of Fig. 2 and the use of Eq. [8] The value of the rate constant (at 90°C), $k_{AN/AA} = 2/b$ (Eq. 7) is 4.38 (mmol min g catalyst)$^{-1}$. Using $k_{AN/AA} = (a.c)^{-1/2}$, the calculated value of k is 3.22 (mmol min g catalyst)$^{-1}$. The two values are in reasonable agreement, the former one being preferred, as explained earlier.

These results demonstrate that there is indeed competition between the reactants for the intracrystalline volume of the zeolite. Anisole being more strongly adsorbed in the

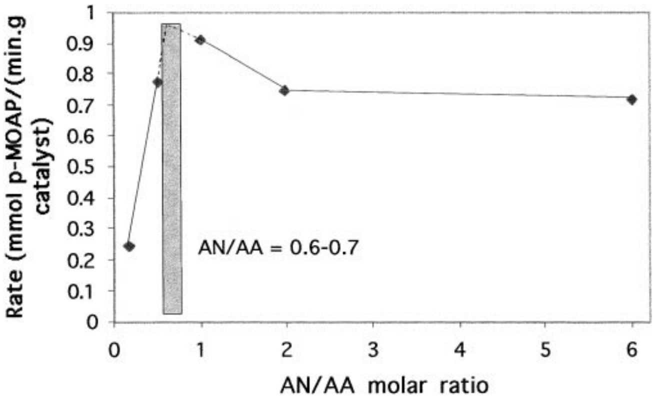

FIG. 2. Initial reaction rate (mmol of *p*-MOAP (min g catalyst)$^{-1}$, total amount of reactants normalised to 118 mmol) vs anisole/acetic anhydride molar ratio.

zeolite than acetic anhydride, the 1 : 1 AN/AA stoichiometric ratio inside the zeolite is achieved when the AN/AA is ca. 0.6 in the liquid phase (0.6–0.7 as determined from the position of the rate maximum and 0.57 as calculated from $K_{\mathrm{AN}}/K_{\mathrm{AA}} = 1.74$, evaluated using Eqs. [5–7]).

Equation [11] was used to evaluate the value of $K_{p\text{-MOAP}}$ from the quasi-stationary reaction rate at long reaction time, assuming a linear dependence of the time yield of *p*-MOAP in the time range, $t = 500$–1400 min). For run D1 (Table 1), we estimate that the quasi-stationary reaction rate is about 1.81×10^{-2} mmol (min g catalyst)$^{-1}$ when conversion is ca. 81%, i.e., when ca. 48 mmol of *p*-MOAP is produced. Using the above values of $k_{\mathrm{AN/AA}}$, K_{AA}, and K_{AN}, one obtains $K_{p\text{-MOAP}} = 11.80$. The latter value is in fair agreement with $K_{p\text{-MOAP}} = 9.65$, determined previously by adding small amounts of *p*-MOAP to the reaction mixture (6), and proves further the consistency of our model.

Acetylation of anisole by isopropenyl acetate. Figure 3 shows the variation with time of the yield (%, with respect to the amount of reactant in deficit) in *p*-MOAP as a function of the anisole (AN) to isopropenyl acetate (IPA) ratio. The reaction conditions are given in Table 2.

Both the initial reaction rate and the *p*-MOAP yield at quasi-stationary state increase, in this case, for higher values of the AN/IPA molar ratio. These observations can be rationalised qualitatively by assuming that isopropenyl acetate is more strongly adsorbed than anisole and that *p*-MOAP is more strongly adsorbed than isopropenyl acetate. A more favourable ratio of the reactants, closer to the ideal 1 : 1 stoichiometry is achieved when the AN/IPA molar ratio is increased, and thus also a higher initial reaction rate. Excess anisole acts as a solvent for *p*-MOAP, which is more strongly adsorbed than isopropenyl acetate, product inhibition is reduced, and the product yield is therefore higher. The competitive adsorption of acetone, as product, can be neglected, as also assumed previously for acetic acid and discussed later.

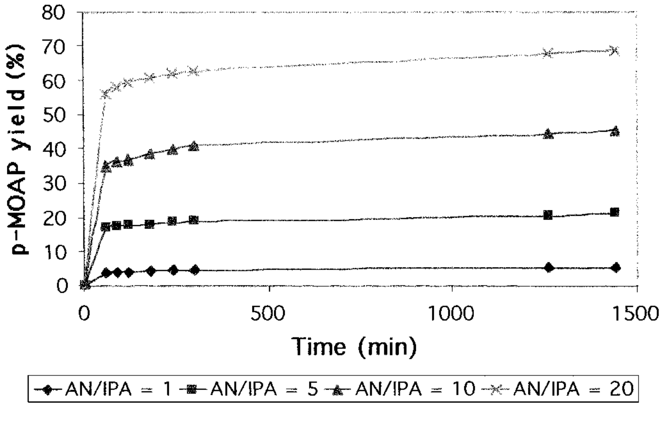

FIG. 3. *p*-MOAP yield (%) vs time as a function of the anisole to ispropenyl acetate (AN/IPA) molar ratio. Reaction conditions are given in Table 2; $T = 80°$C. *p*-MOAP yields are normalised to the amount of reactant in deficit.

Initial reaction rates (R, mmol min^{-1}) were derived as described above, a quadratic fit describing well conversion vs time in the initial stage of the reaction as substantiated by several other experiments. A quadratic plot according to Eqs. [5–7] of $(1/R)([\mathrm{AN}]/[\mathrm{IPA}]$ vs $[\mathrm{AN}]/[\mathrm{IPA}]$, where R is the reaction rate (mmol of *p*-MOAP (min g catalyst)$^{-1}$), normalised to 118 mmol of reactants to account for dilution effects) leads to the equation

$$y = 0.0246x^2 + 0.293x + 0.823 \qquad [13]$$

and $2(a.c)^{1/2}/b = 0.97$, in good agreement with the theoretical value of 1.

From Eqs. [7] and [13], $K_{\mathrm{AN}}/K_{\mathrm{IPA}} = (2a/b) = 0.17$ at 80°C, K_{AN} and K_{IPA} being the adsorption equilibrium constants for anisole and isopropenyl acetate, respectively. The value of the rate constant (at 80°C), $k_{\mathrm{AN/IPA}} = 2/b$, is 6.82 (mmol min g catalyst)$^{-1}$. Using $k_{\mathrm{AN/IPA}} = (a.c)^{-1/2}$, the calculated value of k is 7.03 (mmol min g catalyst)$^{-1}$, in good agreement with the former.

Two major conclusions can be derived by combining the latter results with those obtained for the acetylation of anisole by either acetic anhydride.

Assuming that the values of the adsorption equilibrium constants do not vary much in the temperature range 80–90°C, and remembering that $K_{\mathrm{AA}} = 1$ (4) and $K_{\mathrm{AN}} = 1.74$ as determined from the acetylation of anisole by acetic anhydride, the approximate value of K_{IPA} is estimated to be about 10.36 at 80°C. The latter is comparable to $K_{p\text{-MOAP}} = 9.65$–11.80, and this observation therefore confirms that product inhibition should indeed take place but should have a less dominant influence than in the AN/AA reactions. However, competition between the IPA and AN reactants, in favour of IPA, is now larger than in the latter case where the adsorption of AN over AA was slightly preferred.

In addition, the rate constants, $k_{\mathrm{AN/AA}}$ (90°C) = 3.22–4.38 and $k_{\mathrm{AN/IPA}}$ (80°C) = 6.82–7.03 ((mmol min g catalyst)$^{-1}$, are rather similar although two very different acetylating agents are used. Even after correction for the effect of temperature, assuming that the activation energy is about 11 kcal/mol (6), $k_{\mathrm{AN/IPA}}$ (90°C) is only ca. 10.5 (mmol min g catalyst)$^{-1}$. It suggests that a common rate-determining step, i.e., the attack of the acyl cation (zeolite complex) on the substrate, i.e., anisole in the former two cases, may control the reaction kinetics. If this is the case, a smaller rate constant should be observed when a less activated substrate, e.g., toluene, is acetylated.

It is interesting to note in this respect that the HBEA catalyst changes colour from white to brownish when it is contacted with the acetylating agents in the absence of aromatic substrate; moreover, this coloration disappears when water is added. We believe that these observations are

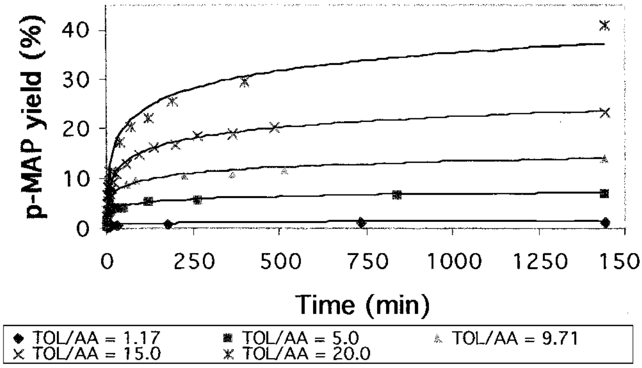

FIG. 4. p-MAP yield (%) vs time as a function of the toluene to acetic anhydride (TOL/AA) molar ratio. Reaction conditions are given in Table 4; $T = 115°\mathrm{C}$. p-MAP yields are normalised to the amount of reactant in deficit (AA).

evidence for the formation of an acyl cation–zeolite complex, and further attention will be devoted to proving this proposal.

Acetylation of toluene by acetic anhydride. Figure 4 shows the variation with time of the yield (%, with respect to the amount of reactant in deficit) in p-methylacetophenone (p-MAP) as a function of the toluene (TOL) to acetic anhydride (AA) molar ratio. The reaction conditions are given in Table 4.

Both the initial reaction rate and the p-MAP yield at quasi-stationary state increase with higher TOL/AA molar ratios. The increase of the initial rate can be understood if acetic anhydride is more strongly adsorbed than toluene, a higher TOL/AA thus favouring a better stoichiometry of the reactants inside the zeolite. In addition, toluene acts as a solvent for the p-MAP produced, product inhibition is reduced, and the p-MAP yield is therefore higher.

Initial reaction rates (R, mmol min^{-1}) at 115°C were again derived as described above, and a quadratic plot according to Eqs. [5–7] of $(1/R)([\mathrm{TOL}]/[\mathrm{AA}]$ vs $[\mathrm{TOL}]/[\mathrm{AA}]$, where R is the reaction rate (mmol of p-MAP (min g catalyst)$^{-1}$), normalised to 285 mmol of reactants to account for dilution effects), leads to the equation

$$y = 0.0867x^2 + 0.9194x + 3.129 \qquad [14]$$

and $2(a.c)^{1/2}/b = 1.13$, in reasonable agreement with the theoretical value of 1.

From Eqs. [7] and [14], $K_{\mathrm{TOL}}/K_{\mathrm{AA}} = (2a/b) = 0.19$ at 115°C, K_{TOL} and K_{AA} being the adsorption equilibrium constants for toluene and acetic anhydride, respectively. The value of the rate constant, $k_{\mathrm{TOL/AA}}(115°C) = 2/b$, is 2.17 (mmol min g catalyst)$^{-1}$. Using $k_{\mathrm{AN/AA}} = (a.c)^{-1/2}$, the calculated value of k is 1.92 (mmol min g catalyst)$^{-1}$. The two values are in good agreement. Correcting for the temperature effect, as done above for the acetylation of anisole with isopropenyl acetate, $k_{\mathrm{TOL/AA}}$ (90°C) is estimated to be about 0.77 (mmol min g catalyst)$^{-1}$.

Equation [11] was used to determine the value of $K_{p\text{-MAP}}$ from the quasi-stationary reaction rate at long reaction time. The procedure described above for the acetylation of anisole by acetic anhydride was followed using the data for runs A3–E3 (Table 4), leading to $K_{p\text{-MAP}} = 4.3 \pm 1.0$.

As expected from qualitative considerations, K_{TOL} is smaller than K_{AA} and K_{AN} as toluene is less polar than anisole and acetic anhydride, and $K_{p\text{-MAP}}$ lies between K_{AN} and $K_{p\text{-MOAP}}$. After correction for the temperature effect, the values of $k_{\mathrm{AN/AA}}$ and $k_{\mathrm{AN/IPA}}$ are comparable within a factor of about 2, whereas $k_{\mathrm{TOL/AA}}$ is smaller by about an order of magnitude. The latter observation is a confirmation that toluene is a substrate which is less activated than anisole, which is well known and also demonstrated by homogeneous acetylation results.

Adsorption Equilibrium Constants and Kinetic Rate Constants: Discussion

Table 7 summarises the above results. It also includes the dielectric constants, the total number of electrons, and an indication of the molecule to zeolite pore size ratio for the various substrates and products which are dealt with in this work. The combination of these parameters can be used to have a qualitative estimate of the interaction of the various molecules with the zeolite (3–5). Dispersion forces (van der Waals interactions) increase with molecular size and the total number of electrons in the molecules. The electrostatic contribution to the interaction of the substrate with the zeolite increases with its polarity, which is reflected in the value of its dielectric constant.

As mentioned earlier, the values of the rate constants, k, for the three reactions we studied indicate that

- a common intermediate, the acyl cation–zeolite complex, appears to determine the rate at which the acetylation of anisole by either acetic anhydride or isopropenylacetate occurs, and
- the acetylation of toluene is more difficult than that of anisole, as expected.

The adsorption equilibrium constants of the various substrates and products vary in a logical order when the effects of dispersion forces and polarity are considered together. In addition, it is also concluded that the competitive adsorption of acetic acid can indeed be neglected, as assumed earlier, but perhaps not for the acetylation of toluene by acetic anhydride, where some competition may occur between toluene as a reactant and acetic acid as a product. If so, the values of $k_{\mathrm{TOL/AA}}$ and K_{TOL} in Table 7 will only be slightly modified as the main competing product is p-MAP, which has the highest adsorption equilibrium constant. Similarly, the competitive adsorption of acetone when using isopropenyl acetate as acetylating agent should also

TABLE 7

Kinetic Rate Constants and Adsorption Equilibrium Constants Describing the Acetylation of Anisole and Toluene by Acetic Anhydride or Isopropenyl Acetate Using HBEA Catalysts with Si/Al = ca. 12

Reaction	k ((mmol min g catalyst)$^{-1}$)
Anisole + isopropenyl acetate	6.82–7.03 (80°C)
Anisole + acetic anhydride	3.22–4.38 (90°C)
Toluene + acetic anhydride	1.92–2.17 (115°C)

Substrates and products	K (relative to $K_{\mathrm{AA}} = 1$, for HBEA with Si/Al = ca. 12)	Dielectric constant	Number of electrons in the substrate or product	Molecular vs pore size ratio
p-Methoxyacetophenone (*p*-MOAP)		$\ggg 17$	80	large
-Quasi-stationary state	11.80 (90°C)			
-Initial rate (4)	9.65 (90°C)			
Isopropenyl acetate (IPA, initial rate)	10.36 (80°C)	ca. 25	54	large
p-Methylacetophenone (*p*-MAP, quasistationary state)	4.3 (115°C)	$\gg 17$	72	large
Anisole (AN)		>17	58	intermediate
-Initial rate	1.74 (90°C)			
-Quasi-stationary state	1.40–1.70 (90°C)			
Acetic anhydride (AA, initial rate)[a]	1.0 (90°C)	22	54	intermediate
Toluene (TOL, initial rate)	0.19 (115°C)	2.4	50	intermediate
Acetic acid[b]	—	6.1	32	small
Acetone[b]	—	20.7	32	small

[a] $K_{\mathrm{AA}} = 1$ used as reference.

[b] For discussion purposes.

be negligible, considering the high values of $K_{p\text{-MOAP}}$ and K_{IPA}.

Our analysis proves that a reasonable and almost quantitative understanding of the behaviour of zeolites as acylation catalysts can indeed be reached by considering the role of confinement effects and the action of zeolites as "solid solvents." The Langmuir–Hinshelwood model can be used to quantify reaction kinetics as both reactants and products compete for the intracrystalline volume of the zeolite where the active sites are located. We suggest that this kinetic approach could also be used to describe other zeolite-catalysed organic reactions occuring in liquid phase. We have also shown that the analysis of the kinetic data, initial rates, and rates at quasi-stationary state enables the determination of the relative adsorption constants of the reactants and products under dynamic conditions. Such values are likely to differ from the single-component adsorption values as the nature and magnitude of the intermolecular interactions between the molecules adsorbed in the zeolite channels will be different for single components and reaction mixtures.

Effect of the Zeolite Type on the Reaction Rate and Product Yield: Acetylation of Toluene with Acetic Anhydride on Zeolites H-FAU (Y), H-BEA, H-MOR, and H-MFI

Table 3 gives the general characteristics of the zeolite catalysts used. Table 5 summarises the experimental conditions. Although the amount of catalyst was varied, approximately the same number of acidic Brønsted sites were engaged in each case when the Si/Al ratio of the various zeolites used is considered. In all cases, the toluene/acetic anhydride ratio was also close to 10, in order to account for the difference between the adsorption equilibrium constants of toluene and acetic anhydride. Thus, a qualitative and direct comparison of the results is possible without need for a further detailed quantification.

Figure 5 shows the dependence of the *p*-MAP yield as a function of the zeolite type. HMOR is obviously the poorest catalyst. This is not unexpected as MOR has a unidimensional pore structure and the smallest pore size, except for MFI. In the case of MFI, mass transport limitations and

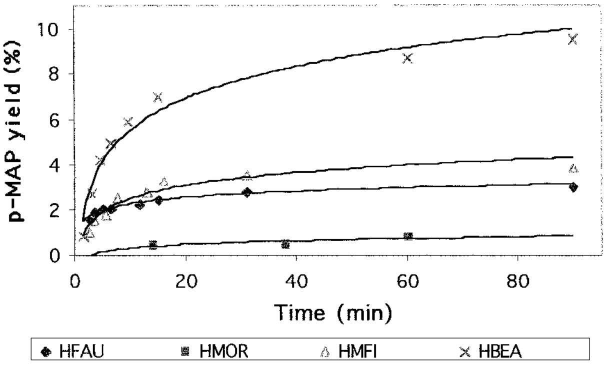

FIG. 5. Effect of the zeolite type on the acetylation of toluene by acetic anhydride. Reaction conditions are given in Table 5.

enhanced confinement effects are expected to take place. HFAU has a high initial activity, but it deactivates very rapidly, probably because poly-acetylated products which can be formed in its supercages (ca. 1.2 nm) cannot desorb (due to the smaller size of the supercage windows, ca. 0.73 nm) (8). For this reason, they are obviously not observed in our GC analyses. Their accumulation of in the supercages of FAU most probably prevents the access of the reactants to the HFAU active sites. HMFI has an initial activity lower than that of HFAU and HBEA, and also a lower p-MAP yield than HBEA at the quasi-stationary state, both resulting from its smaller pore size, leading to enhanced competitive adsorption effects and probably also mass transport limitations. HBEA is definitely the preferred catalyst: it has large and interconnected channels.

Effect of Dealumination on the Performance of Zeolite HBEA for the Acetylation of Toluene by Acetic Anhydride

The above-mentioned results demonstrate that competitive adsorption of the reactants and products, governed to a large extent by confinement effects, plays a major role in determining the reaction kinetics. However, the polarity of the zeolite, determined by its Si/Al ratio, should also affect the competitive adsorption of the reactants and products as the polarity of those varies within a rather broad range. We have therefore investigated the effect of zeolite polarity by studying the acetylation of toluene by acetic anhydride using HBEA catalysts dealuminated to various extents.

The experimental conditions, nearly similar for all runs, are given in Table 6. The characteristics of the fresh and dealuminated HBEA catalysts are summarised in Table 3, i.e., their nominal Si/Al ratio including both framework and extra-framework Al, the percentage of Al in framework position characterised by the ^{27}Al NMR resonance at ca. 53 ppm, and the molar fraction of Al in T-site (framework) positions. It should be noted that the ^{27}Al resonance at 53 ppm (characteristic of framework aluminium) for the unmodified and fresh HBEA zeolite was used as reference. Even if some undetected extra-framework aluminium was present, our analysis below would only be affected on a relative basis and our conclusions regarding turnover frequencies remain valid.

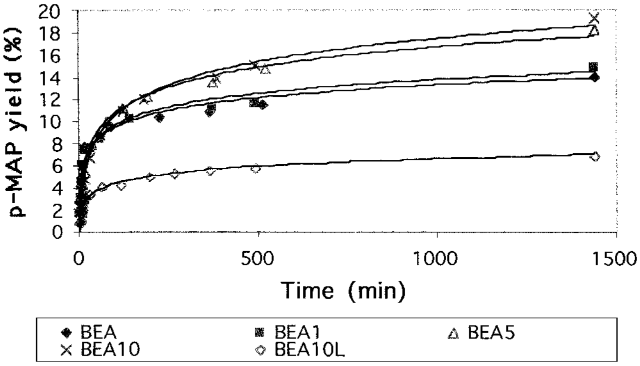

FIG. 6. Effect of dealumination on the activity of zeolite HBEA for the acetylation of toluene by acetic anhydride. Reaction conditions are given in Table 6.

Figure 6 shows the effect of dealumination on the performance of zeolite HBEA, measured by the yield of p-MAP (%) vs time, as a function of reaction time. Product inhibition by p-MAP is observed in all cases as time increases.

Figure 7 shows that the yield of p-MAP at the quasi-stationary state is highly dependent on the molar fraction of Al in the framework (T-sites) of the zeolite. A maximum is observed for Al/(Al + Si) = 0.005–0.010 (catalysts BEA5 and BEA10). The low yield observed for BEA10L probably results from a kinetic factor as BEA10L has a very low concentration of acidic sites. We attribute the lower yields for BEA and BEA1 to their higher aluminium content, i.e., their higher polarity which enhances the competitive adsorption of polar molecules, in particular that of the p-MAP product.

As shown in Fig. 8, the yield of p-MAP in the very early stages of the reaction is also affected strongly by the Al content of the HBEA catalyst. A linear dependence of the

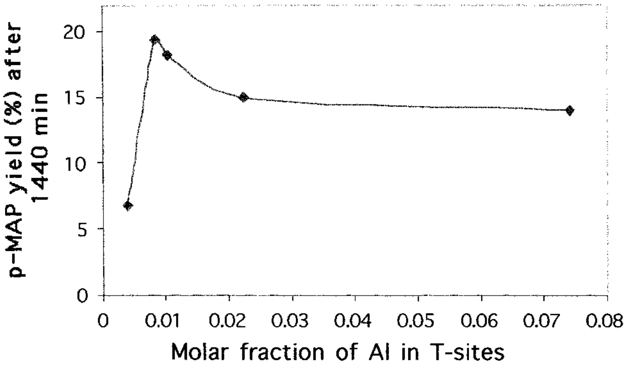

FIG. 7. Effect of dealumination on the p-MAP yield (%) after 1440 min (near quasi-stationary state).

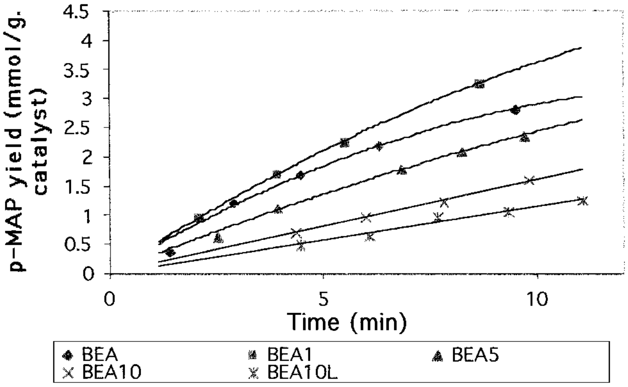

FIG. 8. Effect of dealumination on the *p*-MAP yield (mmol (g catalyst)$^{-1}$) vs time for the initial acetylation of toluene by acetic anhydride using HBEA. Reaction conditions are summarised in Table 6.

p-MAP yield (mmol g catalyst^{-1}) with time is observed for BEA5, BEA 10, and BEA 10L, as expected if product inhibition is small. By contrast, the initial *p*-MAP yield variations for catalysts BEA1 and BEA can only be fitted by a quadratic function, which indicates the presence of product inhibition. As expected, the latter effect is more pronounced for catalyst BEA1 and BEA, in order.

Reaction rates (RR) and turnover frequencies (TOF) as a function of the framework content of HBEA have been calculated for initial (I) and quasi-stationary (QSS, ca. 1000 min) conditions. The initial reaction rates (I-RR, mmol (min g catalyst)$^{-1}$) were derived by fitting time (min) yields (mmol g catalyst^{-1}) at low conversion to a quadratic equation whose first derivative expresses rate vs time as shown previously (6). Quasi-stationary-state rates (QSS-RR) were determined by assuming that the time yield of *p*-MAP varies almost linearly in the time range $t = 500$–1400 min. As one mole of framework T-sites corresponds to 60 g of catalyst (the molecular weight of SiO_2 is 60), turnover frequencies, TOF, are readily determined using Eq. [15]:

$$\mathrm{TOF}\,(\mathrm{min}^{-1}) = [\mathrm{RR}\ (\mathrm{mmol}\ (\mathrm{min\ g\ catalyst})^{-1} \times 60]/[1000 \times \mathrm{Al}/(\mathrm{Al}+\mathrm{Si})]. \qquad [15]$$

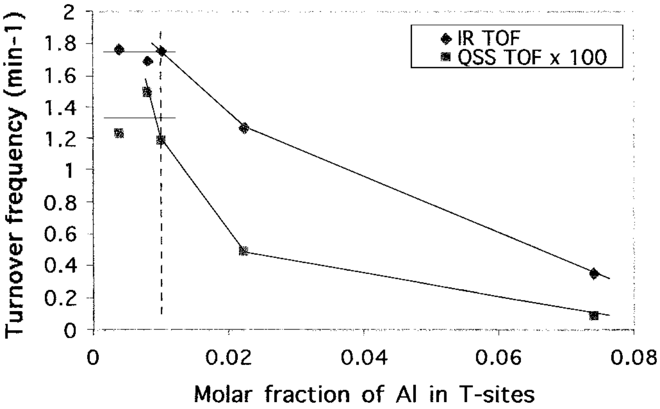

FIG. 9. Dependence of the initial (IR TOF) and quasi-stationary-state (QSS TOF) turnover frequencies for the acetylation of toluene by acetic anhydride as a function of the molar fraction of Al in HBEA.

The values of I-RR, QSS-RR, I-TOF, and QSS-TOF are listed in Table 8. Figure 9 shows the variation of I-TOF and QSS-TOF as a function of the molar fraction of Al in T-site positions.

It is first observed that the ratio QSS-TOF/I-TOF is in the range 0.3–0.8 × 10^{-2}. The low value of this ratio reflects the fact that the number of accessible acidic sites is strongly reduced at quasi-stationary state due to the high occupancy of the intracrystalline volume of the zeolite by the *p*-MAP product.

Most strikingly, the values of I-TOF and QSS-TOF are constant, within experimental error, in the range $\mathrm{Al}/(\mathrm{Al}+\mathrm{Si}) = 0$–0.01, i.e., for HBEA catalyst which have a Si/Al ratio higher than 100. Both values then decrease as the Al content increases, the effect being more pronounced for QSS-TOF than for I-TOF.

These observations can be interpreted in terms of variation of the zeolite polarity as a function of its Al content. At high Si/Al ratio, the zeolite polarity is almost unaffected by its Al content and so are also the adsorption equilibrium constants of the reactants and products, these equilibrium constants being in effect partition coefficients which describe the distribution of the various components

TABLE 8

Initial (I-RR) and Quasi-stationary (QSS-RR) Rates and Initial (I-TOF) and Quasi-stationary-State (QSS-TOF) Turnover Frequencies as Functions of the Framework Molar Fraction of Aluminium in HBEA Zeolites Used as Catalysts for the Acetylation of Toluene

Catalyst[a]	Al/(Al + Si)[a]	I-RR (mmol (min g cat)$^{-1}$)	QSS-RR (mmol (min g cat)$^{-1}$)	I-TOF (min^{-1})	QSS TOF × 100 (min^{-1})
BEA 10L	0.0039	0.1147	0.00080	1.765	1.231
BEA 10	0.0082	0.2312	0.00204	1.692	1.493
BEA 5	0.0102	0.2976	0.00202	1.751	1.188
BEA 1	0.0224	0.4741	0.00183	1.270	0.490
BEA	0.0741	0.4412	0.00118	0.357	0.096

[a] See Table 3.

between the bulk liquid phase and the zeolite "solution" phase (5, 6). It is thus not surprising that I-TOF and QSS-TOF are constant when the Si/Al ratio of HBEA is higher than about 100, provided, as it is the case in our conditions, that identical amounts of catalyst and reactants are used.

It is interesting to note in this respect that when the polarity of HBEA is sufficiently reduced, i.e., for Si/Al ratios greater than 100, the ideal reactant stoichiometry will be more easily achieved and that product inhibition will become less important, as a result of the decreased competition of all species, reactants and products, for the intracrystalline volume of the zeolite. Increasing temperature should have a similar effect as it should reduce the occupancy of the zeolite channels.

We have seen earlier that the adsorption equilibrium constant of toluene was much smaller than that of acetic anhydride (Table 7). As toluene is nearly nonpolar compared to acetic anhydride, it is expected that the competitive adsorption of acetic anhydride will be enhanced when the zeolite polarity increases. Consequently, a less favourable stoichiometry of the reactants will be achieved in the zeolite intracrystalline volume, and the value of I-TOF should decrease as the Al content of HBEA increases.

Similarly, the reaction product, *p*-MAP, is more polar than any of the reactant, and its adsorption is thus favoured when the zeolite polarity increases. It leads to increased product inhibition and consequently to a decrease of the measured QSS-TOF value at higher Al content.

In conclusion, the performance of zeolite catalysts for acid-catalysed reactions conducted in liquid phase, such as Friedel–Crafts acetylation, does not depend only on the reactants ratio and zeolite pore size but also on the polarity of the zeolite. As increasing the zeolite Al content increases the number of active sites (kinetic effect) and simultaneously enhances undesired competitive adsorption effects (thermodynamic effect), the optimisation of the overall catalytic process will necessarily require the optimisation of the catalyst itself, namely, that of its Si/Al ratio in addition to other variables such as crystallite size and external surface relative hydrophobicity. The importance and effect of the latter factors will be discussed in a subsequent publication.

Reaction Mechanism

The kinetic data shown in Table 7 led us to conclude that a common intermediate, i.e., an acyl cation–zeolite complex, was involved in the rate-determining step for the acetylation of anisole by either acetic anhydride or isopropenyl acetate, as the rate constant coefficients were comparable for both reactions.

We and others (6, 10, 11) also observed that the catalyst colour was turning to brown, with various degrees of intensity, during reaction. This change in colour has been attributed to the accumulation of "coke" in the catalyst (10). We observed, fortuitously, that the colour of zeolite HBEA becomes yellow-brown when the catalyst is contacted with

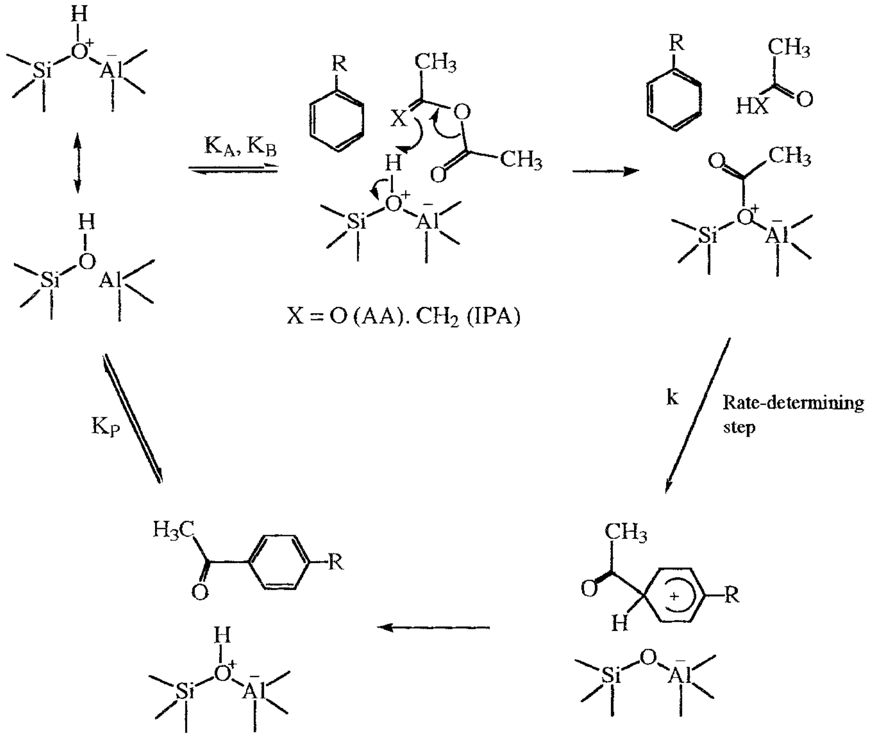

FIG. 10. Proposed mechanism for the acetylation of aromatic substrates using acidic zeolite catalysts.

acetic anhydride or isopropenyl acetate, even in the absence of any aromatic substrate, and that this colouration disappears upon addition of water. This observation clearly indicates that some reaction occurs between zeolite HBEA and the acetylating agent, and that the species formed is destroyed by water. Work is in progress to identify the nature of this species and its evolution when water is added. Combining the above two facts, we propose that the change in zeolite coloration is associated to the formation of the acyl cation–zeolite complex mentioned above. This proposal will be substantiated and discussed in a forthcoming publication.

Consequently, a likely mechanism for the acetylation of aromatic substrates using zeolite catalysts can be described by the scheme shown in Fig. 10. The acetylating agent reacts firstly with the zeolite to form an acyl cation–zeolite complex. The subsequent reaction of the aromatic substrate with this complex is the rate-determining step. Provided that there are no mass transfer limitations, the adsorption of the reactants and the desorption of the products are at equilibrium when the actives sites for acetylation, i.e., the acyl cation–zeolite complexes, have been generated by reaction of the zeolite with the acetylating agent present in the reaction mixture.

Our conclusion does not differ too much, in its principle, from earlier literature reports, and our results support earlier suggestions. They suggest that Friedel–Crafts acetylation reactions could be achieved more efficiently if the acetylating agent and the aromatic substrate feeds to the catalyst were alternated rather than being simultaneous. The undesired effect of competitive adsorption equilibria would be minimised. Higher yields and continuous operation should be achievable.

CONCLUSIONS

We have demonstrated that the competitive adsorption of reactants, which is affected by the reactant molar ratio and nature, and the nature of the zeolite itself (structure type and aluminium content), determines the efficiency of the Friedel–Crafts acetylation of various aromatic substrates by acetic anhydride or isopropenyl acetate. The occurrence of product inhibition effects, previously reported (4), has also been confirmed.

Kinetic parameters (rate constants and turnover frequencies) and thermodynamic parameters (adsorption equilibrium constants) have been determined.

The values of the adsorption equilibrium constants for the reactants and products can be rationalised considering their nature, i.e., their size (confinement effect) and polarity and the type of zeolite (pore size and aluminium content) used as catalyst.

The analysis of the kinetic parameters (rate constants) shows that an acyl cation–zeolite complex, formed when the zeolite is contacted with the acetylating agent, is probably the active species involved in the rate-determining step leading to the acetylation of the aromatic substrate. Turnover frequencies, both in the initial stages of reaction conditions and at the quasi-stationary state, are affected by the aluminium content of the zeolite which determines the zeolite polarity. Competitive adsorption effects are enhanced at low zeolite Si/Al ratio as the reaction products are polar, in addition to having a larger molecular size than each of the reactant.

This work confirms further that zeolites should be best considered as solid solvents when they are used as catalysts for liquid-phase organic conversions, Adsorption equilibrium constants are effectively partition coefficients determining the distribution of the reactants and products between the bulk liquid phase and the zeolite “solid solvent” phase, the partitioning of the reactants and products being determined by their nature and relative amount, the type of zeolite used, and of course other conventional factors such as temperature.

This work also implies that nonstationary reactor systems should be preferred to batch reactors in order to minimise the detrimental effects of competitive adsorption on both reaction rate and quasi-stationary yield. We proposed earlier (6) that higher throughput for batch operations could be reached by operating at moderate conversion with recycling of the unconverted reactants. We will demonstrate, discuss, and model quantitatively in a susbequent publication the advantageous use of a fixed-bed tabular reactor for the continuous Friedel–Crafts acetylation of aromatic substrates.

The present work indicates that a higher productivity could also be achieved by alternating the exposure of the catalyst to the acetylating agent and the aromatic substrate. The latter could be achieved by switching the nature of the feed to a fixed catalyst bed.

As a final conclusion, we wish to emphasise the obvious. The optimisation of liquid-phase heterogeneously catalysed processes for the synthesis of fine chemicals will only result from a close interaction and synergy between organic chemists understanding the molecular aspects of the reaction, physical and solid-state chemists enabling the optimisation of the catalyst composition, and chemical engineers designing new catalytic reactors circumventing the constraints imposed by kinetic and thermodynamic limitations.

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