Zeolite Catalysts as Solid Solvents in Fine Chemicals Synthesis

1. Catalyst Deactivation in the Friedel–Crafts Acetylation of Anisole

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

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

The liquid phase acetylation of anisole by acetic anhydride (anisole : acetic anhydride in a molar ratio of 2 : 1) using zeolite HBEA (Si/Al = 11) as catalyst was carried out in a batch reactor at 90°C, without and with addition of the product, *p*-methoxyacetophenone (*p*-MOAP) (molar ratio anisole/*p*-MOAP = 3 and 6). As expected, acetic acid and *p*-MOAP are produced in equal amounts during the initial stages of the reaction but acetic acid is consumed at long reaction time and high conversion. Partial zeolite dealumination of the used catalyst was evidenced by ^{27}Al MAS NMR spectroscopy and the regenerated catalyst showed a lower activity agreeing with its reduced Al content, i.e., acidity. Without added *p*-MOAP, acetylation occurs rapidly at low conversion but deactivation becomes important as conversion increases. The reaction rate is largely decreased when *p*-MOAP is added to the reaction mixture, indicating inhibition of the reaction by *p*-MOAP. A detailed kinetic analysis using a Langmuir–Hinshelwood model was performed to quantify the nature and extent of the reaction inhibition by *p*-MOAP. It shows that the adsorption equilibrium constant for *p*-MOAP exceeds by a factor of at least 6 the adsorption equilibrium constant for any of the reactants and that the occupancy of the intracrystalline volume of the zeolite by *p*-MOAP increases rapidly with conversion, thereby reducing the access of the reactants to the catalytic sites. Comparison of our results with literature data enabled us to derive an approximate activation energy for this reaction, i.e., ca. 11 kcal mol^{-1}. A good agreement is observed between the calculated and experimental reaction rates as a function of conversion. It is concluded that the deactivation of the catalyst as conversion increases is mainly due to product inhibition, i.e., the competitive adsorption of the reactants and products in the zeolite intracrystalline volume which can be rationalized in terms of the zeolite acting as a solid solvent. Our work suggests that the application of zeolites and other microporous solids as catalysts to fine chemicals synthesis would be better performed using catalytic reactor configurations minimizing the role played by competitive adsorption effects. © 1999 Academic Press

INTRODUCTION

This publication is the first of a series which will be devoted to the identification and quantification of "solid solvent" effects when zeolites and other microporous solids are applied as catalysts to organic synthesis in the liquid phase, with the objective of producing fine or specialty chemicals and pharmaceuticals.

The principles of molecular confinement in the intracrystalline volume of zeolites and the consideration that zeolites behave as solid solvents (1–3) set a new scene for their use as heterogeneous catalysts in organic synthesis, because such reactions are usually operated at rather low temperature and/or in the liquid phase.

Zeolite catalysis in liquid phase distinguishes itself from zeolite catalysis in vapor phase by:

• the high concentrations of reactants, intermediates, and products which lead to a high utilization of the intracrystalline volume of the zeolite,

• the competition of the reactants for the zeolite intracrystalline volume which is governed by molecular shape selectivity, confinement, and polarity effects,

• the increasing concentration of product(s) in the liquid phase when operating in batch conditions, resulting as reaction proceeds in a less favorable desorption of the products and a decrease of the catalyst productivity because of the possible accumulation of some products in the zeolite pores, and

• the possible adsorption of the solvent which may compete for the intracrystalline volume where most reaction occurs.

These effects, which arise from the ability of zeolites or other microporous solids to act as solid solvents (2, 3), are probably responsible to a large extent for the generally poor practical performance of zeolite catalysts for the synthesis of fine chemicals in batch conditions. Partition equilibria determine the distribution of the reactants and products between the bulk liquid phase and the zeolite "solution" phase, and adsorption equilibrium constants influence the

[1] To whom correspondence should be addressed. Fax: +44-151-794-3589. E-mail: derouane@liverpool.ac.uk.

partition coefficients. Thus, the optimal productivity of microporous catalysts, under such conditions, can indeed be achieved only when the reactants occupy fully the zeolite intracrystalline volume (no competition from the solvent, if present) and achieve the proper stoichiometric ratio inside the zeolite pores (which will in general be a different reactant ratio from that in the liquid phase if their adsorption equilibrium constants differ) and when the product(s) is (are) easily desorbed, i.e., when the access of the reactants to the intracrystalline volume is not inhibited.

Friedel–Crafts reactions are of major importance in organic synthesis. In particular, acetylation and benzoylation are useful routes for the synthesis of aromatic ketones that are intermediates in the manufacture of many fine and specialty chemicals as well as pharmaceutical compounds. So far, only limited success has been reported when using zeolites for such catalysis, except when using large pore zeolites (BEA, FAU) (4) in the synthesis of p-methoxyacetophenone by acetylation of anisole (5) and that of 3,4-dimethoxyacetophenone by acetylation of veratole (6).

Several very recent publications have discussed possible reasons for the apparent deactivation of zeolite catalysts applied to Friedel–Crafts catalysis. We proposed that, when operating in batch conditions, low conversions and reaction inhibition could be attributed to the action of zeolites as solid solvents, resulting in the competitive adsorption of reactants and product(s) inhibition (3). Rohan *et al.* (7) demonstrated 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 in part to the retention of the p-methoxyacetophenone (p-MOAP) product inside the zeolite pores. For the same reaction, Freese *et al.* (8) concluded that two types of heavy organic residues (extractable and nonextractable) were probably responsible for catalyst deactivation. Smith *et al.* (9) suggested that acetic acid formed as a by-product could lead to (reversible) catalyst deactivation.

We now report on the acetylation of anisole with acetic anhydride in the absence of additional solvent, in batch conditions, demonstrating quantitatively that the p-methoxyacetophenone product inhibits the reaction. A detailed analysis of the reaction kinetics enables the derivation of relative adsorption equilibrium constants for the reactants and products and confirms that microporous solids act indeed as solid solvents as defined in a previous publication (3). We also show that formation of acetic acid may lead to partial zeolite dealumination and hence may affect the integrity of the catalyst.

EXPERIMENTAL

Procedure

Reactions were performed under inert atmosphere (N_2) for up to 10 h and at $90°C$ in a glass batch reactor equipped with a condenser and a mechanical stirrer. All precautions were taken to operate under moisture-free conditions. The catalyst (HBEA, acidic form of zeolite H-Beta, Si/Al = 11, from PQ Zeolites) was preactivated in air for 5 h at $550°C$ and added (0.6 g) to the reactor after introduction of the organic reactants (Table 1). A 2:1 molar ratio mixture of anisole (12.76 g, 118 mmol) and acetic anhydride (6.02 g, 59 mmol) was used. Upon addition of the reactants the catalyst became pale orange in the colorless solution and deepened to brown-red with reaction time.

To investigate possible inhibition by the products, p-MOAP was also added to the reaction mixture to achieve anisole/p-MOAP initial molar ratios equal to 3 and 6, all other variables and conditions being the same.

Anisole (Avocado Research Chemicals) was purified by distillation over CaH_2. Acetic anhydride and p-MOAP (both from Aldrich, purity greater than 99%) were used as received.

Table 1 details the composition of the reactant mixture.

Analysis and Data Interpretation

As reaction proceeded, 150-μl samples were taken periodically from the reaction mixture and added to aliquots (150 μl) 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 VA-WAX 30-m capillary column.

TABLE 1

Experimental Conditions

Experiments and conditions	Run A, no p-MOAP added	Run B, p-MOAP added, molar ratio (anisole/p-MOAP = 6)	Run C, p-MOAP added, molar ratio (anisole/p-MOAP = 3)
HBEA (catalyst) (g)	0.6	0.6	0.6
Anisole (g)	12.76 (118 mmol)	12.76 (118 mmol)	12.76 (118 mmol)
Acetic anhydride (g)	6.02 (59 mmol)	6.02 (59 mmol)	6.02 (59 mmol)
p-MOAP (g)	—	3.0 (20 mmol)	6.0 (40 mmol)

p-Methoxyacetophenone (*p*-MOAP) was the main reaction product, 1 mole of *p*-MOAP and 1 mole of acetic acid being produced by the acetylation of 1 mole of anisole with 1 mole of acetic anhydride. Very little *o*-methoxyacetophenone was produced (less than 2%). Contrary to the observation of Rohan *et al.* (7), we did not observe the hydrolysis of acetic anhydride at short contact time (see Results and Discussion). As acetic anhydride was the reactant in default, 100% conversion corresponds to the formation of 59 mmol of *p*-MOAP and conversions were thus simply defined as follows:

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

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

After about 24 h, the brown reaction mixture was filtered and the catalyst (pale yellow to brown, depending on the experimental run) subsequently washed with toluene (25 ml), acetone (25 ml), and diethyl ether (25 ml) before recalcination at 550°C overnight. The recovered (white) zeolite catalyst was then submitted to ^{27}Al MAS NMR to examine possible dealumination.

RESULTS AND DISCUSSION

1. Time Dependence of the Yields of p-MOAP and Acetic Acid

The reaction was performed using an anisole to acetic anhydride molar ratio of 2:1 as indicated in Table 1 (run A). Figures 1 and 2 show the variation with time of the yields (%), referred to the initial amount of acetic anhydride, of

p-MOAP and acetic acid, for a period of about 9 h and at very short reaction time, respectively.

As seen from Fig. 1, the rate of production of *p*-MOAP is initially very high and rapidly decreases after about 50 min on stream when conversion has reached about 60%. The conversion of acetic anhydride (the limiting reagent) to *p*-MOAP reaches about 95% after about 9 h. The production of acetic acid follows closely that of *p*-MOAP up to a conversion of about 80%, after which the amount of acetic acid in the product mixture decreases slowly. After 500 min on stream, the deficit in acetic acid yield is about 18%, indicating that about 10.6 mmol of acetic acid has been consumed.

Figure 2 shows that equal amounts of acetic acid and *p*-MOAP are produced initially. The anomaly observed for the first data point (5 min) corresponding to acetic acid could be due to experimental error as a 1:1 acetic acid/*p*-MOAP molar ratio is observed subsequently. Otherwise, one would expect that the amount of acetic acid produced would remain larger than that of *p*-MOAP as the reaction proceeds. This is not the case and it confirms that acetic anhydride is not noticeably hydrolyzed, under our conditions, when initially contacted with the zeolite.

Initial reaction rate. The initial rate of production of *p*-MOAP (run A) is, as we will show later, 5.6 mmol (min · g cat)$^{-1}$. Approximate initial rates at 60 and 120°C can also be estimated from the results of Rohan *et al.* (Fig. 1, Ref. 7) and Smith *et al.* (Table 4, Ref. 9) and can be compared to ours after appropriate correction for differences in the reactant ratio and HBEA catalyst Al content (i.e., number of Brønsted acid sites). From the Arrhenius plot, we have estimated an approximate apparent activation
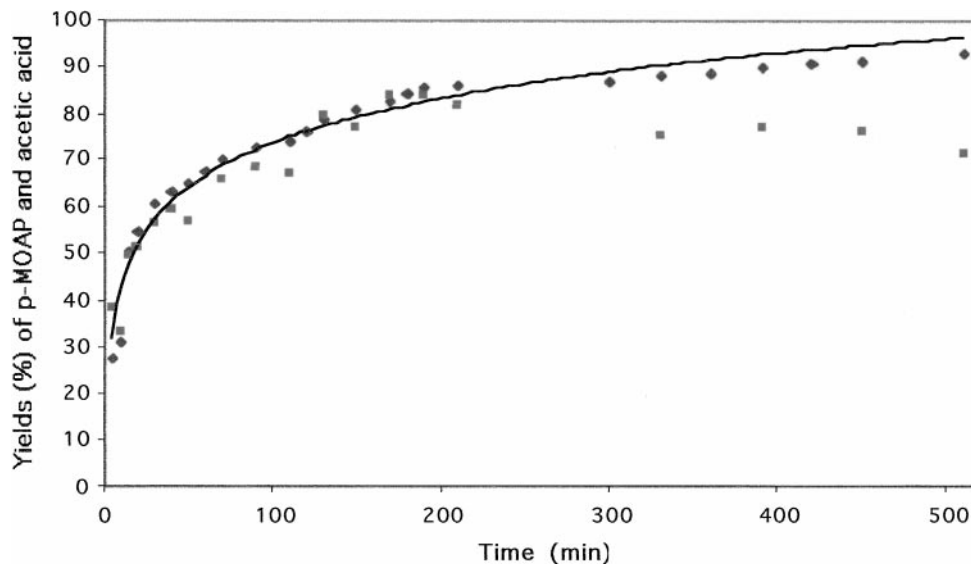

FIG. 1. Yield (%) of *p*-MOAP and acetic acid as a function of reaction time (0 to 600 min). The data are fitted by a logarithmic equation. Acetic acid consumption at high conversion/long reaction times is observed. ◆, *p*-MOAP; ■, acetic acid.
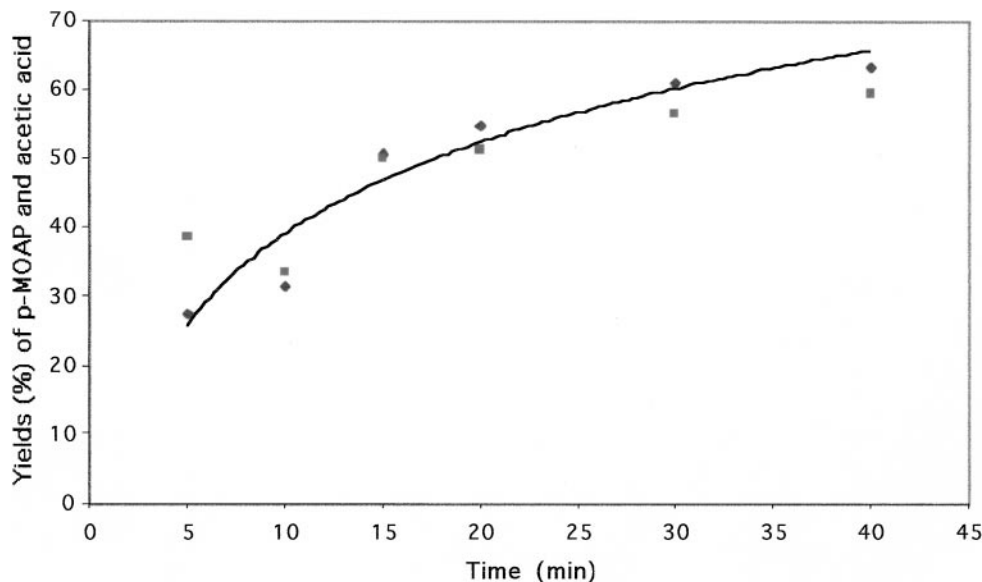
FIG. 2. Yield (%) of *p*-MOAP and acetic acid as a function of reaction time (0 to 20 min). The data are fitted by a logarithmic equation. *p*-MOAP and acetic acid are produced in equimolar amounts. ◆, *p*-MOAP; ■, acetic acid.

energy, 11 kcal mol^{-1}, for the acetylation of anisole. This value should be compared to activation energies (13–15 kcal mol^{-1}) characterizing classical aromatic acylation in homogeneous phase (10).

Consumption of acetic acid at long reaction times. Two reasons may explain the deficit in acetic acid observed at long reaction times. One is the partial dealumination of the zeolite framework; the other is the reaction of acetic acid with silanol defects of the zeolite. The former reaction is of particular importance as partial dealumination would result in the irreversible loss of acidic sites and thus also irreversible catalyst deactivation.

Reaction of acetic acid with zeolite defects is a likely process as the deficit of acetic acid (ca. 12 mmol) exceeds by a nonnegligible amount the number of aluminum sites present in the catalyst (8.3×10^{-1} mmol Al), even if we assume that a maximum of 7 mmol of acetic acid (three yielding Al acetate and four neutralising the SiOH defects appearing upon dealumination) could be required to extract 1 mmol of Al from the zeolite framework. This could also contribute to catalyst deactivation at long reaction times because the species formed could lead to partial pore plugging and increased diffusional constraints for the heavier products (e.g., *p*-MOAP). However, such deactivation should be reversible to a large extent if the occluded products are quantitatively removed by regeneration of the zeolite in oxidative conditions between successive runs.

Reuse of the catalyst after regeneration in air at 550°C overnight showed a substantial decrease in activity as illustrated in Fig. 3, the conversion after long reaction times being about 14% lower than that observed for the fresh catalyst and the initial reaction rate being reduced by about 20%, i.e., down to 4.38 mmol (min · g cat)$^{-1}$. ^{27}Al MAS NMR was thus used to test the occurrence of dealumination. Spectra obtained in the same conditions before and after the first reaction run are shown in Fig. 4. Dealumination indeed occurred as shown by the increase (ca. 20%) of the resonance at 0 ppm characterizing nonframework Al species and a small decrease of the total ^{27}Al NMR resonance. In addition, chemical analysis (atomic absorption) of the liquid phase after reaction showed the presence of ca. 0.3×10^{-2} mmol Al, confirming that aluminum is indeed extracted from the zeolite framework under the reaction conditions.

In contrast to us, Smith *et al.* (9) concluded that the regenerated zeolite retained its activity even in its fourth use (a small decline is, however, observable). Their conclusions are, however, based on product yields obtained after 2 h at 120°C and not on initial rate measurements. In addition, the amount of catalyst used in their experiments (relative to the reactants) is five times larger than we used. Freese *et al.* (8) did not observe dealumination either. However, reaction times in their case did not exceed 240 min and they also used a relatively large amount of catalyst. We believe that these factors explain the discrepancy between their observations and ours.

2. Deactivation of the Catalyst By Product Inhibition

We proposed and showed recently that inhibition by the product(s) could be a major reason for the apparent deactivation of zeolite and microporous catalysts when they are used for the synthesis of fine chemicals under conditions where competitive adsorption processes are important, i.e., at low temperature and/or in liquid phase (3).
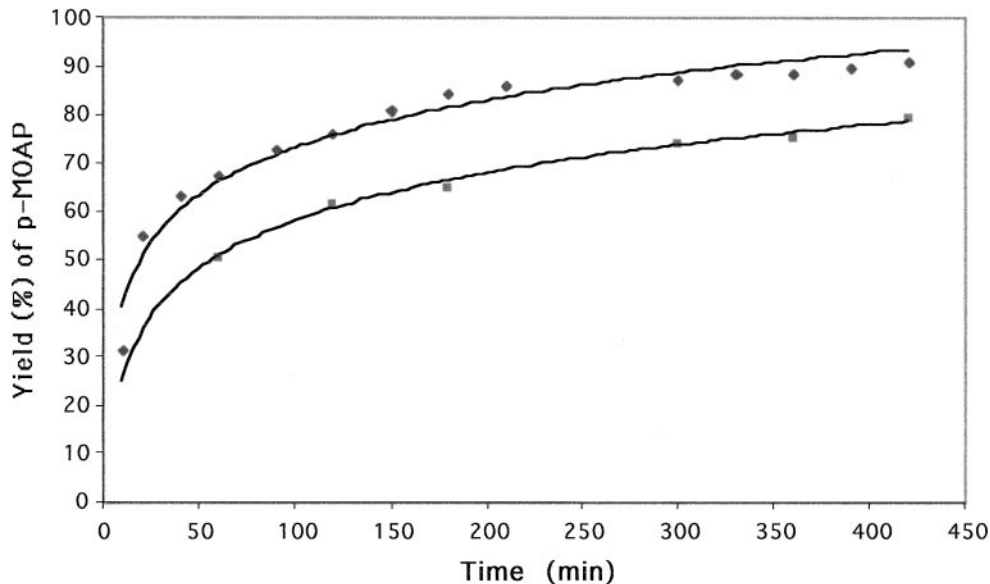
FIG. 3. Comparison of the yields (%) of *p*-MOAP as a function of reaction time (0 to 600 min) for a fresh catalyst and a catalyst regenerated in air overnight at 550°C. ◆, Fresh catalyst; ■, regenerated catalyst. The data are fitted by a logarithmic equation.
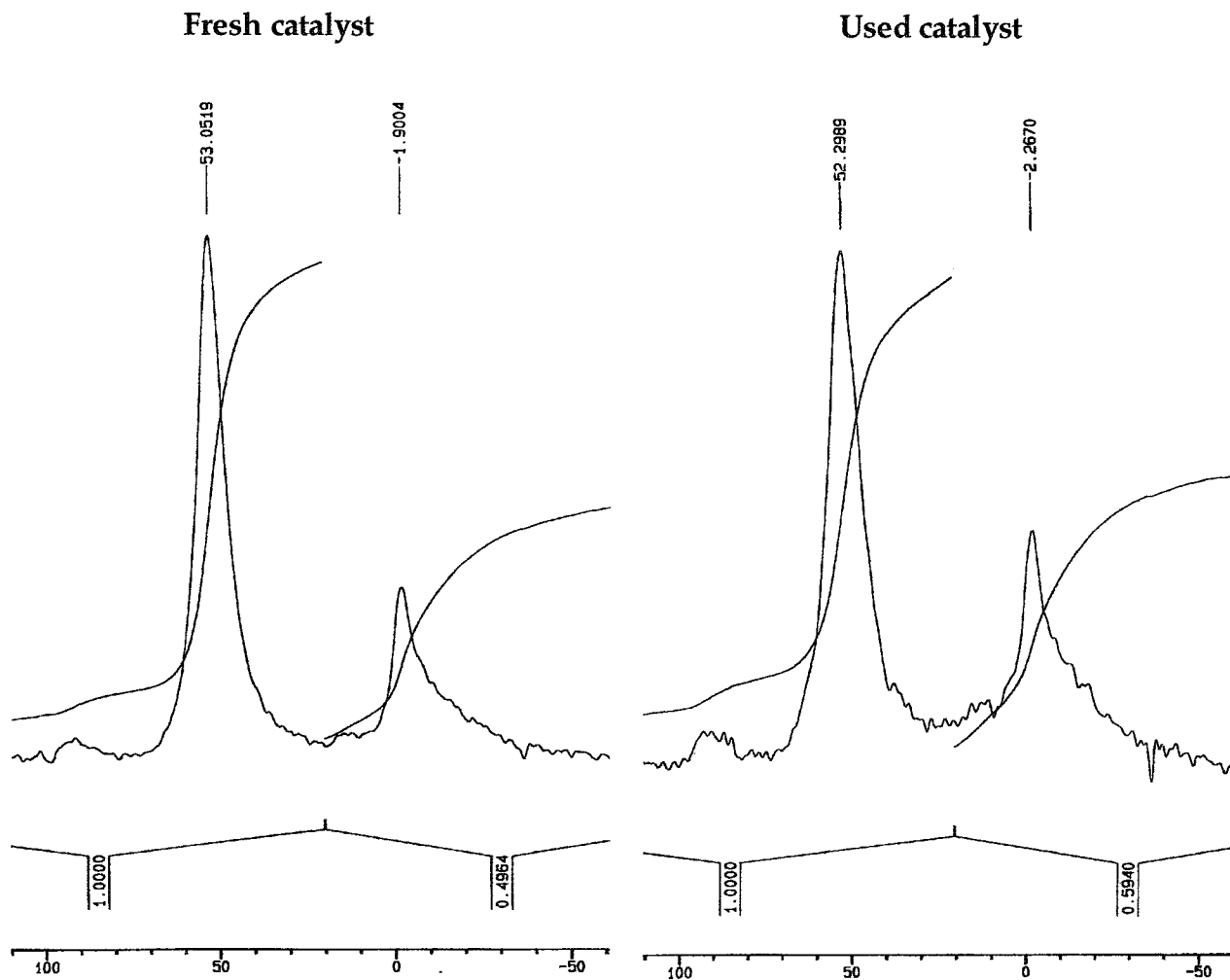

FIG. 4. ^{27}Al MAS NMR spectra showing the partial dealumination of the catalyst by the acetic acid produced.

Recent work by Rohan *et al.* (7) showed that this was indeed the case for the acetylation of anisole with acetic anhydride, the formation or addition of *p*-MOAP inhibiting its production. They concluded that *p*-MOAP was retained in the zeolite catalyst mesopores and that large molecules formed by the polyacetylation of anisole were responsible for pore blockage and progressive catalyst deactivation. They also indicated that this effect was less pronounced when the anisole/acetic anhydride ratio was increased. Freese *et al.* (8) observed that a used catalyst could be partially regenerated by extraction with dichloromethane and that activity was completely restored after calcination in air at 500°C. We will show in the following discussion that zeolite solid solvent effects can account quantitatively for deactivation by primary product inhibition only.

Figure 5 shows the *p*-MOAP yield (mmol) vs time (min) plots for the acetylation of anisole without (run A in Table 1) and with (runs B and C in Table 1) *p*-MOAP added. Note that "*p*-MOAP yield" in this figure refers only to the *p*-MOAP produced by acetylation and not to the total amount of *p*-MOAP present in the reaction mixture. Deactivation by product inhibition, i.e., *p*-MOAP addition, is obvious from both the progressive decrease in the initial rates and the lower overall conversions observed at long reaction times. It should, however, be recognized that conversions are limited only by the amount of reactant in deficit and thus that all reactions will eventually lead to 100% conversion of acetic anhydride although the reaction rate in the late stages of the reaction will progressively become very small, leading to a quasi-stationary conversion of less than 100%.

Initial reaction rates (R, mmol min^{-1}) were derived by fitting time (min) yields (mmol) (Y) at low conversion (up to 20 min, conversion less than 35%) to a quadratic equation whose first derivative expresses rate vs time. The amounts of *p*-MOAP present at nearly stationary conversion were also estimated. The results are shown in Table 2.

Although the amount of *p*-MOAP produced by acetylation decreases when *p*-MOAP is added to the reaction mixture, which demonstrates product inhibition, the total amount of *p*-MOAP present in the reaction mixture after about 9 h, i.e., at quasi-stationary state, remains about the same. This constant amount of *p*-MOAP indicates that inhibition by *p*-MOAP controls the quasi-stationary conversion. It suggests that the catalyst is deactivated when its intracrystalline volume becomes inaccessible because of occupation or "critical" pore blockage by *p*-MOAP. Zeolite HBEA can adsorb ca. 20 wt% of organics in its intracrystalline volume, i.e., 0.12 g in our case corresponding to ca. 0.8 mmol of *p*-MOAP. Considering that ca. 55 mmol *p*-MOAP are present in the liquid phase at quasi-stationary conversion, the partitioning of *p*-MOAP between the liquid phase and the zeolite should be in a ratio close to 65.

The kinetic observations can be rationalized by assuming that all zeolite active (acidic) sites are equivalent and by considering that reactants and product(s) compete for the occupancy of the intracrystalline volume of the zeolite. A Langmuir–Hinshelwood model can describe this situation, as discussed earlier (3). Although only one reactant may be activated at the catalytic sites, it is obvious that the other reactant(s) and product(s) will block its access to the
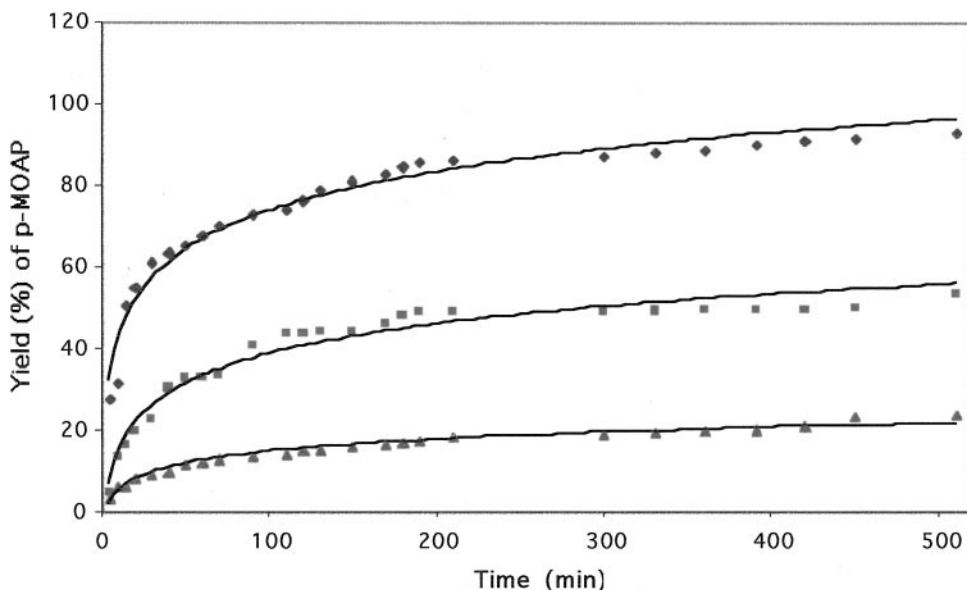

FIG. 5. Yields (%) of *p*-MOAP vs time observed without and with addition of *p*-MOAP to the reaction mixture at $t = 0$. ◆, no *p*-MOAP; ■, anisole/*p*-MOAP = 6; ▲, anisole/*p*-MOAP = 3. The data are fitted by a logarithmic equation.

<div align="center">

TABLE 2

Reaction Parameters for the Acetylation of Anisole with Acetic Anhydride with and without p-MOAP Added

</div>

Parameter	Run A	Run B	Run C
p-MOAP introduced (mmol)		20	40
p-MOAP produced (mmol)	55.63	33.16	13.63
Total p-MOAP at stationary state (mmol)	55.63	53.16	53.63
p-MOAP yield, Y(mmol), vs time (t, min)[a]	$Y = -0.088t^2 + 3.358t$	$Y = -0.030t^2 + 1.050t$	$Y = -0.0145t^2 + 0.511t$
Reaction rate, R (mmol min^{-1}), vs time (t (min), $t < 20$) for 0.6 g catalyst	$R = 3.358 - 0.176t$	$R = 1.050 - 0.060t$	$R = 0.511 - 0.029t$

Note. $T = 90°$; batch operation, other parameters as in Table 1.
[a] All regression coefficients are greater than 0.990.

catalytic sites considering the atomic size of the zeolite pores, channels, and cavities.

Within this approximation, a general reaction rate for a simple reaction such as

$$A + B \rightarrow P \qquad [1]$$

is given by Eq. [2] which assumes that only one major product, P, is competitively adsorbed, with A and B being the reactants and P the product (3),

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

k being the kinetic rate constant (inclusive in this case of the number of catalytic sites) and K_A, K_B, and K_p representing the equilibrium 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 when the reaction is operated in liquid phase at low temperature, the factor "1" in the denominator can be neglected relative to the other terms and the above equation becomes

$$R = kK_A K_B[A][B]/(K_A[A] + K_B[B] + K_P[P])^2. \qquad [3]$$

In the present situation, A may represent acetic anhydride, B anisole, and P p-MOAP. The competitive adsorption of acetic acid is neglected as it is most unlikely to occur at low conversion and as its adsorption equilibrium constant is most probably smaller than that of the reactants and p-MOAP, considering its smaller size.

Equation [3] is independent of reaction volume and concentrations can be replaced to evaluate initial rate constants by the relative amounts of reactants (and products, if it applies) engaged in the reaction mixture, i.e., a for acetic anhydride, b for anisole, and p for p-MOAP. It then

becomes

$$R = kK_A K_B ab/(K_A a + K_B b + K_P p)^2. \qquad [4]$$

For a and b constant (our conditions) Eq. (4) can be rewritten as

$$R = N/(D + K_P p)^2, \qquad [5]$$

with $N = kK_A K_B ab$ and $D = K_A a + K_B b$, leading to

$$R = N/(K_P^2 p^2 + 2K_P Dp + D^2), \qquad [6]$$

whose reciprocal is a quadratic equation,

$$1/R = K_P^2 p^2/N + 2K_P Dp/N + D^2/N, \qquad [7]$$

or

$$1/R = lp^2 + mp + n, \qquad [8]$$

with $l = K_P^2/N$, $m = 2K_P D/N$, and $n = D^2/N$. It should be noticed that l, m, and n are not independent coefficients as $m = 2(l \cdot n)^{1/2}$ and K_P/D equals $2l/m$, $(l/n)^{1/2}$, or $m/2n$.

The fit of the reciprocal of the initial rate data for runs A, B, and C (Table 2) to a quadratic equation (Fig. 6) leads to

$$1/R = 0.0004p^2 + 0.0240p + 0.2978, \qquad [9]$$

for which the value of $2(l \cdot n)^{1/2} = 0.0218$ is in reasonable agreement with the value of m in Eq. [9], $m = 0.0240$. No attempt was made to improve further the kinetic modeling data. The observance of a relationship such as Eq. [8] between l, m, and n, when using the initial reaction rate results of Table 2 should be acknowledged as supporting our model.
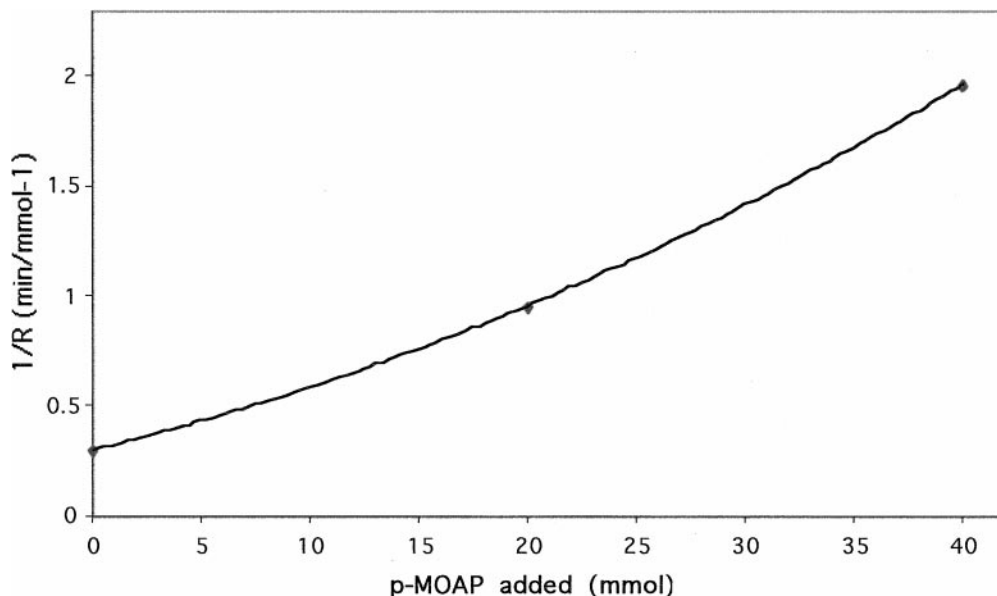
FIG. 6. Quadratic plot fitting the reciprocal of the initial rate constants for runs A, B, and C vs the amount of p-MOAP added.

Taking $m = 0.0240$, an approximate value of K_P/D $(m/2n)$ can be derived; i.e., $K_p/D = 0.0403$. If we further assume that K_B is equal to $1.53\ K_A$ (11) and set K_A arbitrarily to 1, recalling that $D = K_A a + K_B b$, we obtain $K_P = 9.65$. p-MOAP is thus indeed adsorbed more strongly than either reactant and it is therefore responsible for catalyst deactivation by product inhibition.

Deactivation is thus not likely to be the result of accumulation of p-MOAP in the mesopores of the zeolite catalyst, as proposed by Rohan *et al.* (7), but may well be due to the role of zeolites as solid solvents. Adsorption equilibria favor the adsorption of the larger (or more polar) molecules in the intracrystalline microporous volume, either reactants or products, and affect thereby the local stoichiometry of the reactants or prevent their access to the catalytic sites because of product(s) accumulation in the zeolite pores. Although congestion in the zeolite pores could indeed occur because of the formation of polyacetylated products (7), we have found no evidence for their formation and our results can be interpreted without invoking such effects. It may be worth adding that such polyacetylated products are too large to be formed in the zeolite micropores and that it seems unlikely that mesopores would be completely blocked by those.

Another test for the above model is the comparison of the initial rates for runs B and C with the rates observed for run A at similar contents of p-MOAP in the reactant mixture (Table 3). However, such a comparison is only qualitative as the amounts of reactants remaining in the reaction medium vary with conversion. The yield of p-MOAP vs time when p-MOAP is not added at $t = 0$ can be represented, for conversions higher than 25%, by

$$Y\,(\text{mmol } p\text{-MOAP}) = 9.6\,\ln(t) + 2.3, \qquad [10]$$

of which the first derivative or reaction rate, R, is

$$R\,(\text{mmol } p\text{-MOAP min}^{-1}) = 9.6/t. \qquad [11]$$

Table 3 shows a reasonable agreement between the reaction rates observed with and without addition of p-MOAP at $t = 0$ for similar total amounts of p-MOAP in the reaction mixture, suggesting again that product inhibition via preferential adsorption of p-MOAP in the micropores of the zeolite is most probably responsible for the progressive deactivation of the catalyst.

3. Modeling of the Reaction Kinetics

Assuming as mentioned before that the zeolite intracrystalline space is fully occupied by the reactants and products and that the competitive adsorption of acetic acid can be neglected, one can calculate the relative occupancy of the zeolite micropores by anisole, acetic anhydride, and p-MOAP from their previously determined relative adsorption

TABLE 3

Reaction Rates for the Production of p-MOAP with and without Addition of p-MOAP in the Initial Reaction Mixture

Amount of p-MOAP[a]	No p-MOAP added, rate (mmol min^{-1})	p-MOAP added, rate (mmol min^{-1})
0	3.3576	—
20	1.3709 ($t = 7$ min)	1.050
40	0.2400 ($t = 40$ min)	0.511

Note. The variation of the yield of p-MOAP with time fitted the equation: $Y(\text{mmol}) = 9.5963\,\ln(t) + 2.2945$.

[a] The amount of p-MOAP is either the amount added at $t = 0$ for runs B and C or the amounts produced at $t = 7$ min and $t = 40$ min for run A.

constants, as conversion increases. We have attempted this for the reaction conducted without addition of *p*-MOAP (run A).

Recalling that $K_{\text{acetic anhydride}} = K_A = 1$, $K_{\text{anisole}} = K_B = 1.53$, and $K_{p\text{-MOAP}} = K_P = 9.65$ (these are relative values), the occupancy (θ, %) of the intracrystalline zeolite volume by the various components is given by

$$\theta_A = 100 K_A(a - x)/[K_A(a - x) + K_B(b - x) + K_P x]$$

for acetic anhydride   [12]

$$\theta_B = 100 K_B(b - x)/[K_A(a - x) + K_B(b - x) + K_P x]$$

for anisole   [13]

$$\theta_P = 100 K_P x/[K_A(a - x) + K_B(b - x) + K_P x]$$

for *p*-MOAP,   [14]

with *a* and *b* being the respective amounts of acetic anhydride and anisole engaged at $t = 0$ and *x* the amount of *p*-MOAP formed at time *t*.

Figure 7 represents the variations of these occupancies with increasing conversion and shows that retention of *p*-MOAP in the zeolite micropores rapidly becomes important. For example, at about 50% conversion, ca. 70% of the zeolite intracrystalline volume is occupied by *p*-MOAP and thus catalytic activity is noticeably decreased. It is also obvious that competition between the reactants for the intracrystalline volume of the zeolite takes place. This issue will be discussed in a subsequent publication (11).

Assuming that Langmuir–Hinshelwood kinetics can describe the reaction, as discussed above (Eq. [3]), the theoretical variation of the reaction rate as a function of conversion is easily calculated by using Eqs. [12] and [13]; i.e.,

$$R = k \cdot \theta_A \cdot \theta_B. \qquad [15]$$

θ_A and θ_B in the above equation are given by

$$\theta_\iota(\%) = K_\iota(i - x)/[K_A(a - x) + K_B(b - x) + K_P x], \quad [16]$$

where *i* is the number of moles of either *A* or *B* initially present (*a* or *b*) and *x* is the number of moles of product (*p*-MOAP) formed. *R* can be normalized by setting its value to 100 at zero conversion.

The variation of the experimental rate as a function of conversion can be obtained from the results shown in Fig. 2 and Eq. [11]. (Note that the quadratic equation given in Table 2 should be used for conversions below 20%.) Experimental rates were also normalized to 100 for the observed rate at $t = 0$.

Figure 8 compares the calculated and experimental rates as a function of conversion. The experimental and calculated rates are in excellent agreement and this supports the validity of the approximations mentioned in the previous discussion.

Combining all of the above results and conclusions, it is thus clear that the role of the zeolite as a solid solvent and the existence of competitive adsorption phenomena involving the reactants and products are the major factors explaining the deactivation of the zeolite catalyst as a function of reaction time.
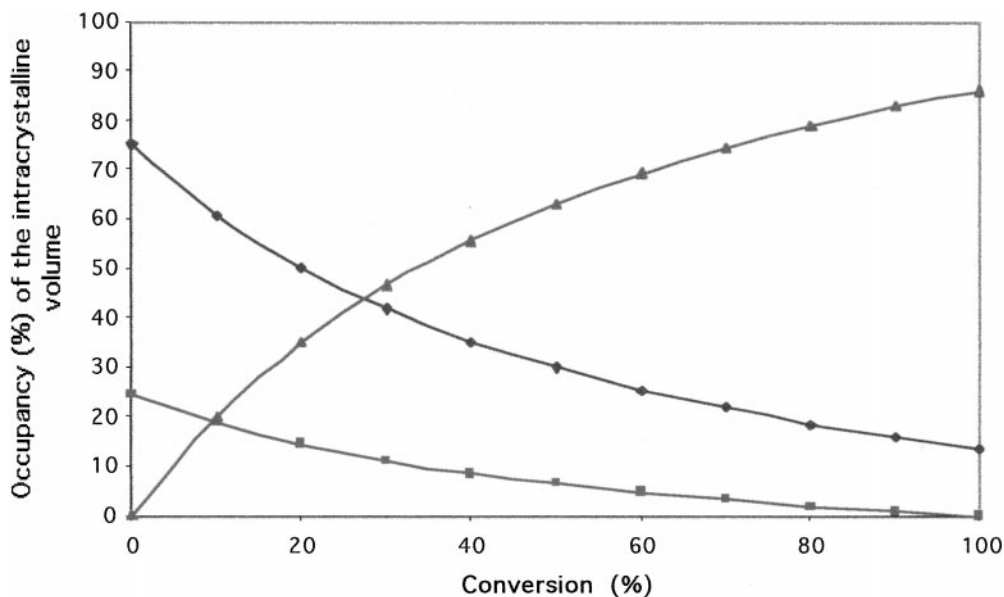

FIG. 7.   Relative occupancy (θ, %) of the intracrystalline volume of the zeolite by anisole (◆), acetic anhydride (■), and *p*-MOAP (▲), assuming no competition from acetic acid and full occupancy of the zeolite micropores.
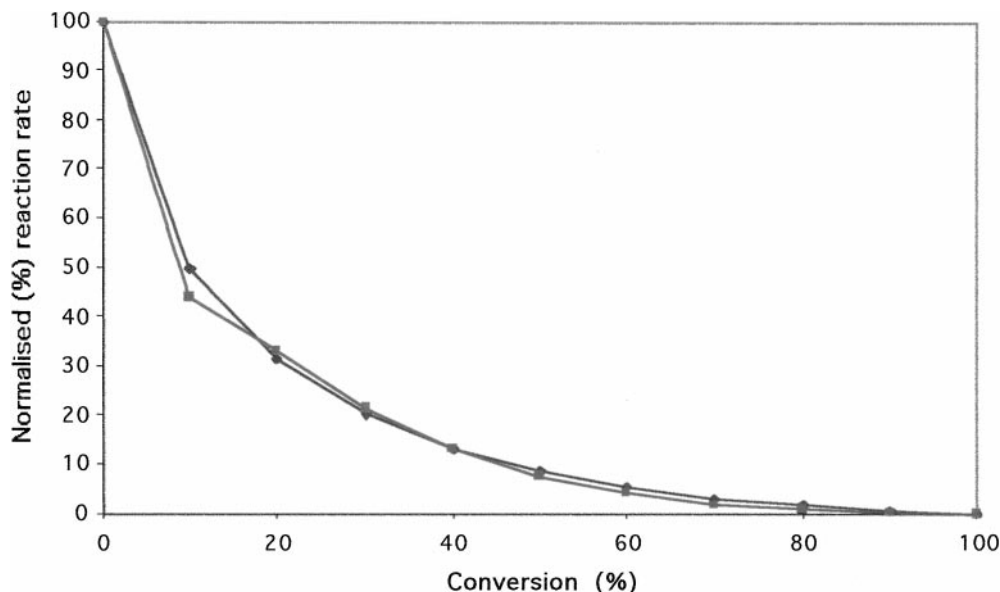
FIG. 8. Comparison of the normalized calculated (◆) and experimental reaction rates (■) for the acetylation of anisole with acetic anhydride assuming no competition from acetic acid and full occupancy of the zeolite micropores.

CONCLUSIONS

Deactivation of zeolite HBEA used as a catalyst for the acetylation of anisole with acetic anhydride is due to both dealumination and product inhibition by p-MOAP. The latter factor plays the major role and is reversible.

Acetic acid produced in the course of the reaction accumulates in the product mixture when the reaction is performed in batch conditions, resulting in partial dealumination at long reaction times. Such deactivation is irreversible.

Product inhibition by p-MOAP occurs because the equilibrium constant for the adsorption of p-MOAP in the micropores of the HBEA catalyst is much larger than that of the reactants, acetic anhydride and anisole. Contrary to the proposal of Rohan *et al.* (7), we thus conclude that p-MOAP is retained in the micropores and not the mesopores of the catalyst and that obstruction of the micropores by larger molecules resulting from multiple acetylation is unlikely. This is also consistent with the low yield of o-MOAP, whose formation in the micropores is probably hindered by transition-state, molecular shape selectivity. Larger molecules ("coke") may, however, be formed and adsorbed at the catalyst external surface.

The present work clearly shows that competitive adsorption effects can play a major role when applying zeolites to fine chemicals synthesis in the liquid phase and supports our view that zeolites should be considered not only as catalysts but also as solid solvents. The availability of the reactants in their intracrystalline volume where the active sites are located depends on adsorption equilibria, involving both reactants and products, which regulate their concentrations and thus reaction rate and catalyst performance.

This work also shows that one reason for the low success met so far when applying zeolite catalysts to the synthesis of fine chemicals is the importance of competitive adsorption effects, which is enhanced by operation at (usually) low temperature and in liquid phase. It indicates that nonstationary reactor systems should be preferred to batch reactors and that higher throughput for batch operations should be reached by operating at moderate conversion with recycling of the unconverted reactants.

ACKNOWLEDGMENTS

REFERENCES

1. Derouane, E. G., André, J. M., and Lucas, A. A., *J. Catal.* **110**, 58 (1988).
2. Derouane, E. G., *in* "A Molecular View of Heterogeneous Catalysis" (E. G. Derouane, Ed.), pp. 5–27. De Boeck Université, Bruxelles, 1998.
3. Derouane, E. G., *J. Mol. Catal. A* **134**, 29 (1998).
4. Spagnol, M., Gilbert, L., and Alby, D., *Ind. Chem. Lib.* **8**, 29 (1996).
5. Spagnol, M., Gilbert, L., Benazzi, E., and Marcilly, C., *PCT Int. Appl. WO 96* **35**, 655 (1996).
6. Spagnol, M., Gilbert, L., Benazzi, E., and Marcilly, C., *PCT Int. Appl. WO 96* **35**, 656 (1996).
7. Rohan, D., Canaff, C., Fromentin, E., and Guisnet, M., *J. Catal.* **177**, 296 (1998).
8. Freese, U., Heinrich, F., and Roessner, F., *Catal. Today* **49**, 237 (1999).
9. Smith, K., Zhenhua, Z., and Hodgson, P. K. G., *J. Mol. Catal. A* **134**, 121 (1998).
10. Brown, H. C., and Jensen, F. R., *J. Am. Chem. Soc.* **80**, 2296 (1958).
11. Derouane, E. G., Dillon, C. J., Bethell, D., and Derouane-Abd Hamid, S. B., in preparation.