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Acetylation of Anisole by Acetic Anhydride over a HBEA Zeolite—Origin of Deactivation of the Catalyst

D. Rohan, C. Canaff, E. Fromentin, and M. Guisnet[1]

UMR CNRS 6503, Laboratoire de Catalyse en Chimie Organique, Faculté des Sciences, 40 avenue du Recteur Pineau, 86022 Poitiers Cedex, France

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The liquid phase acetylation over a HBEA zeolite (Si/Al = 10) of anisole with acetic anhydride in equimolar amounts was carried out in a batch reactor at 60°C. *p*-Methoxyacetophenone is selectively and rapidly formed on the fresh catalyst. However, a rapid deactivation occurs which could be attributed to a large extent to the pronounced inhibiting effect that *p*-methoxyacetophenone has on the acetylation. In a flow reactor and at a higher temperature (90°C), the catalyst deactivation is much slower particularly when an anisole rich mixture (anisole/acetic anhydride molar ratio of 5) is used as a reactant. Catalyst samples were recovered after various times on stream and the organic material which was retained in significant amounts on the zeolite was analysed by GC and GC/MS. The major part of this material, which consists of *p*-methoxyacetophenone, can be recovered by soxhlet extraction in methylene chloride. Due to its high polarity, this reaction product is strongly retained in the large mesopore volume of the HBEA zeolite. The minor part can only be recovered after dissolution of the zeolite in a hydrofluoric acid solution. It consists mainly of di- and triacetylated anisole entrapped in the zeolite micropores. As shown by nitrogen adsorption, these compounds cause pore blockage. The latter is responsible for part of the catalyst deactivation, the other part being due to *p*-methoxyacetophenone located in the mesopores. The use of an excess of anisole enhances catalyst stability as it limits both the retention of *p*-methoxyacetophenone and the formation of the polyacetylated anisoles. © 1998 Academic Press

INTRODUCTION

Acylation is a key step in the manufacture of aromatic ketones used as intermediates in the fine chemical and pharmaceutical industry, e.g. in the synthesis of Ibuprofen and (S)-Naproxen (1–4). The conventional method of preparation of these ketones is the homogeneous Friedel–Crafts acylation of aromatics with carboxylic acid derivatives and particularly acid chlorides using generally Lewis acid anhydrous metal halides as catalysts (5). More than stoichiometric amounts of the catalyst are required, with production of a substantial amount of inorganic by-product, in particular corrosive hydrochloric acid, with considerable environmental problems (6). This is why the search for alternative acylation processes using other carboxylic acid derivatives such as anhydrides, and solid and reusable catalysts is particularly active (7–12).

Many studies were devoted to the use of zeolites as catalysts for aromatic acylation. Indeed these crystallized acid solids present the advantage over the conventional acid metal halides that selectivity is not only determined by the characteristics of the acid sites but can be orientated towards the desired product by their pore system (13, 14). The possibility of using zeolites as catalysts for acylation of various aromatics by acetic anhydride has furthermore been well demonstrated (15–17). In particular beta zeolites were found to be selective catalysts for the synthesis of *p*-methoxyacetophenone by acetylation of anisole (18) and FAU zeolites for the synthesis of 3,4-dimethoxyacetophenone by veratrol acetylation (19).

However, one of the general problems to be solved in the use of zeolite catalysts in the synthesis of organic compounds is their deactivation by deposition of heavy reaction products within the pores or on the outer surface of the crystallites. Unfortunately, most of the academic studies are carried out in batch reactors, which makes the investigation of deactivation difficult, the emphasis being generally placed on the activity and selectivity and not on the stability of the catalysts. The aim of this paper is to understand the origin of the deactivation of a HBEA zeolite (Si/Al = 10) during the acylation in the liquid phase of anisole by acetic anhydride in a fixed bed reactor, i.e., the reactor used industrially. The amount and composition of the compounds, strongly retained inside the micropores ("coke") or inside the mesopores and macropores of the HBEA zeolite, as well as their effect on the catalyst stability were established. We show that operating with an anisole-rich reactant mixture is preferable to limiting catalyst deactivation.

EXPERIMENTAL

Acetylation of Anisole

The reactions were carried out in the liquid phase both in a batch reactor at 60°C in an inert atmosphere and in a

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[1] Corresponding author. E-mail: michel.guisnet@cri.univ-poitiers.fr.

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fixed-bed reactor at 90°C and a nitrogen flow of 12 ml/min. A HBEA10 zeolite provided by PQ Zeolites was used (total and framework Si/Al ratios of 11 and 15.5, respectively). The conditions were as follows: 500 mg, 100 or 50 mg catalyst, previously activated overnight in air (60 ml/min) at 500°C, either an equimolar mixture of anisole and acetic anhydride or a mixture containing approximately a fivefold molar excess of anisole. Small samples of the reaction mixture were taken periodically and analysed by gas chromatography on a 25 *M* capillary column of CP Sil 8 CB.

p-Methoxyacetophenone (*p*-MAP) was the main reaction product. One molecule of anisole is acylated by one molecule of acetic anhydride (AA) with production of one molecule MAP and one molecule of acetic acid. At short time on stream, part of AA was also hydrolysed into acetic acid, 2 molecules being formed per molecule of transformed AA. Therefore, the conversions (X) of anisole and of AA were calculated as follows from the distribution of the product mixture:

$$X_{\text{anisole}} = \frac{\%\,\text{mol (MAP)}}{\%\,\text{mol (anisole + MAP)}}$$

$$X_{\text{AA}} = \frac{\%\,\text{mol (MAP + (Acetic acid} - \text{MAP)/2)}}{\%\,\text{mol (AA + MAP + (Acetic acid} - \text{MAP)/2)}}.$$

When necessary (i.e., at high conversion), we have also considered the amounts of di- and triacylated anisole and of dimethoxydypnone, for the determination of the conversions.

Recovery and Analysis of the Organic Material Retained on the Zeolite

A simple method was developed which consists of two extractions on the deactivated zeolite:

(i) Extraction by soxhlet. The deactivated catalyst was left for 4 h under a nitrogen flow (12 ml/min) before removal from the reactor and weighed. In order to recuperate the organic material on the external surface of the zeolite, the deactivated catalyst was then treated in a soxhlet for 8 h with methylene chloride. The solvent was evaporated and the remaining organic material was weighed and analysed by GC-MS.

(ii) Extraction of inner carbonaceous compounds (20). 300 mg of the deactivated zeolite (which has previously undergone extraction by soxhlet) was dissolved in a 40% solution of hydrofluoric acid. Threefold extraction with methylene chloride was carried out. All the carbonaceous compounds were found to be soluble in methylene chloride. After evaporation of the solvent, the carbonaceous components were weighed and analysed by GC-MS.

In order to specify the amount of retained products, elemental analysis of the deactivated catalyst was carried out in the CNRS laboratory of Solaize, Vernaison, before and after soxhlet treatment by methylene chloride.

The pore volume of the catalysts (after reaction and soxhlet treatment) was measured by N_2 adsorption on a Micromeritics ASAP 2000. Before measurement the catalysts were pretreated under a 10^{-3} mbar vacuum at 40°C.

RESULTS AND DISCUSSION

1. Deactivation of the Catalyst in a Batch Reactor

The reaction of an equimolar mixture of anisole and acetic anhydride was carried out at 60°C in a batch reactor. Anisole is mainly transformed into *p*-methoxyacetophenone (*p*-MAP). Very little *o*-methoxyacetophenone is produced (selectivity to *p*-MAP >98%). Furthermore, as the reaction progresses, traces of di- and triacetylated methoxyacetophenone are formed. Figure 1 shows that the initial rate of production of *p*-MAP is very high but that the catalyst deactivates very quickly.

This deactivation was thought to be due to *p*-methoxyacetophenone which remained strongly adsorbed on the acid sites of the zeolite, hence limiting the adsorption of anisole. To confirm this proposal the reaction rate obtained with the equimolar mixture of anisole and acetic anhydride (35 mmol of each) was compared to that obtained for a similar mixture of anisole (33.5 mmol), acetic anhydride (35 mmol) and *p*-MAP (1.5 mmol). A decrease of 80% in the reaction rate is observed, demonstrating a large inhibiting effect of the main reaction product, *p*-MAP, on the acylation of anisole. To limit this inhibiting effect of *p*-MAP, other operating conditions were chosen: flow reactor instead of the batch reactor and higher temperature (90°C instead of 60°C).

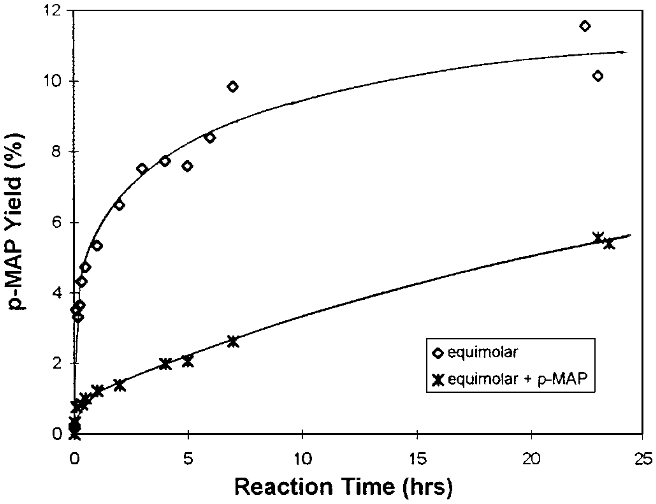


FIG. 1. Reaction at 60°C of an equimolar mixture of anisole and acetic anhydride (35 mmol of each) in a batch reactor on 100 mg HBEA10. Influence of the addition of *p*-methoxyacetophenone (*p*-MAP) on the rate of anisole acetylation.

2. *Influence of Time on Stream on the Rate of Anisole Transformation*

The acetylation of anisole was carried out in liquid phase at 90°C in a fixed bed reactor over various amounts of catalyst (50 to 500 mg), the flow rate of reactants being always equal to 5 ml/h. Two reactant mixtures were used: an equimolar mixture of anisole and acetic anhydride and an anisole rich mixture (molar ratio close to 5 : 1).

Whatever the reactant mixture, the amount of catalyst and the time-on-stream (TOS), the selectivity to *p*-methoxyacetophenone (*p*-MAP) is very high (>98%). *o*-MAP, traces of di- and triacetylated anisole and dimethoxydypnone are the only side products. It should be also remarked that at short TOS, with the equimolar reactant mixture, part of acetic anhydride undergoes hydrolysis to form acetic acid. Initially, there is generally an increase in the conversion of anisole (Fig. 2a) but not in the conversion of acetic

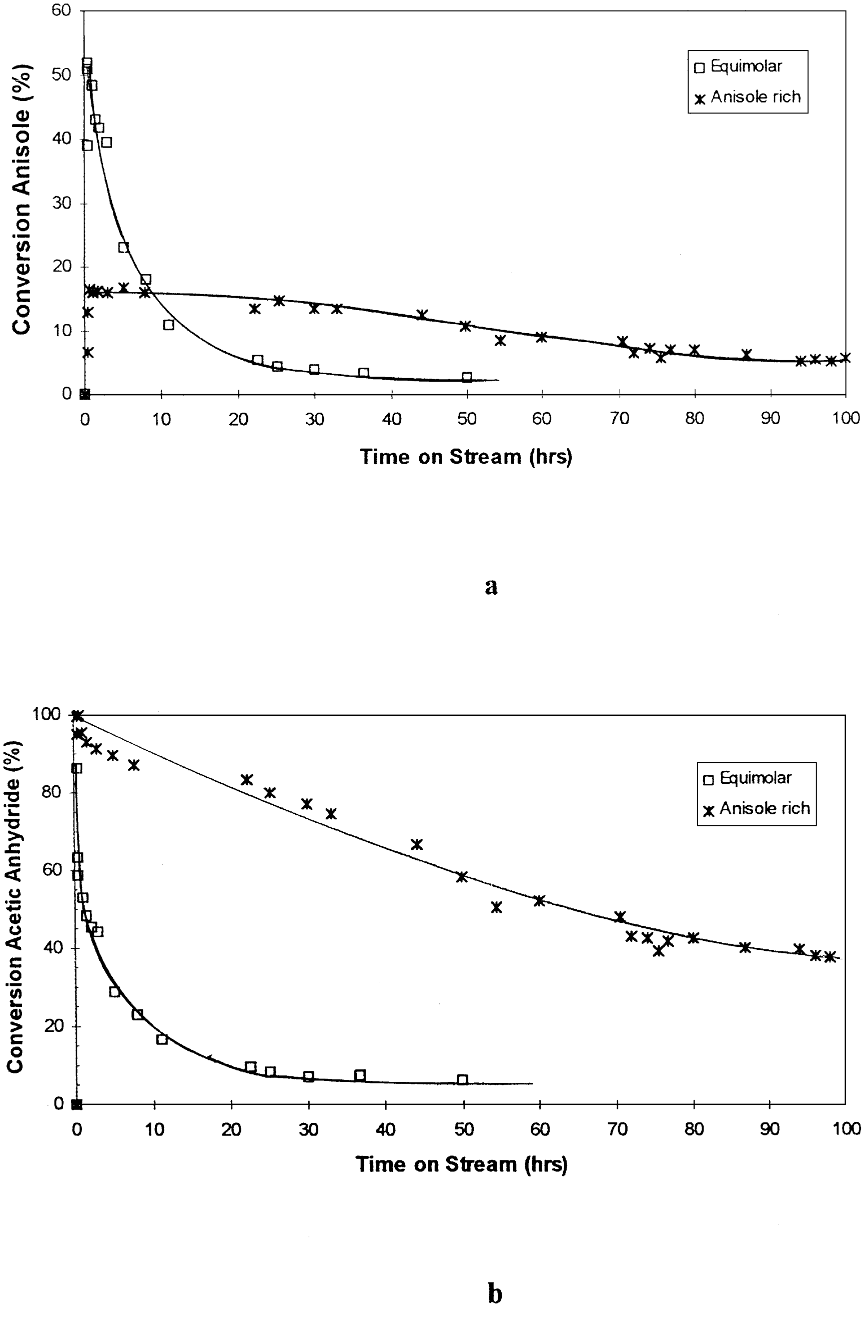


FIG. 2. Acylation of anisole at 90°C in a fixed bed reactor on 500 mg catalyst. Weight hour space velocity (WHSH) for anisole is 5.3 h^{-1} with the equimolar reactant mixture and 8.5 h^{-1} with the anisole rich mixture (a) anisole conversion vs time on stream, (b) acetic anhydride conversion vs time on stream.

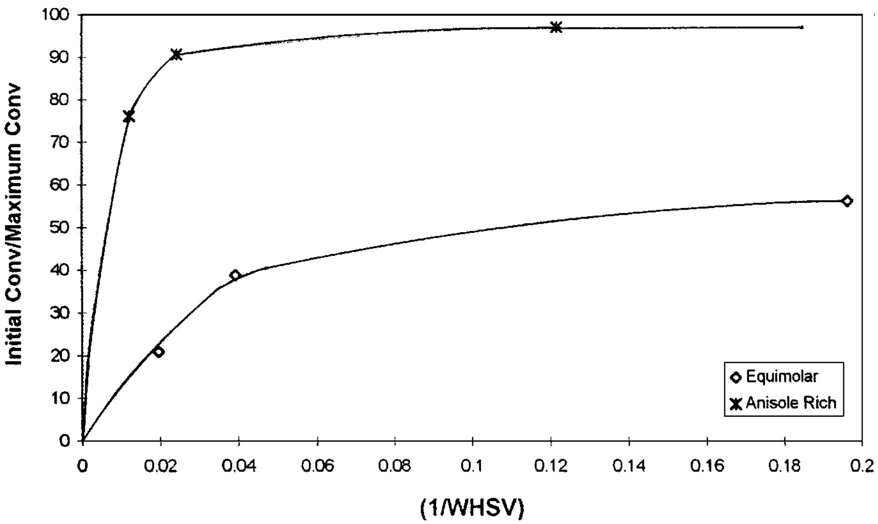


FIG. 3. Acylation of anisole at 90°C in a fixed bed reactor on 50 to 500 mg catalyst. Ratio between the initial conversion of anisole and the maximum conversion which can be obtained vs the inverse of the weight hour space velocity (WHSV) for anisole.

anhydride (Fig. 2b). This increase is most likely due to the strong retention of *p*-MAP in the zeolite pores as suggested by the large inhibiting effect of *p*-MAP shown in the batch reactor. However, for both reactant mixtures there is a decrease in the conversion of anisole and of acetic anhydride with increasing TOS (Fig. 2). This decrease is much more pronounced in the case of the equimolar reactant mixture. The same can be observed when acylation is carried out with 50 mg of zeolite, hence with a contact time 10 times shorter.

The ratio between the initial conversion of anisole (obtained by extrapolation of the conversion at zero time on stream) and the maximum conversion possible with the amount of acetic anhydride used is plotted in Fig. 3 as a function of the inverse of WHSV for anisole (weight of anisole introduced per weight of catalyst per hour). This figure shows that for the anisole rich mixture the maximum conversion is obtained at short contact time, while a plateau at approximately 50% of the maximum conversion is obtained with the equimolar mixture. This plateau is probably due to the inhibiting effect of *p*-MAP. This inhibiting effect would be less significant for anisole rich mixtures because the catalyst is continuously washed by the large excess of anisole.

3. *Carbonaceous Deposits: Amount and Composition*

The zeolite catalysts were recovered in the experiments carried out at larger contact time (i.e., with 500 mg zeolite) for various time-on-stream (TOS) values. Before recovery the zeolite samples were treated under nitrogen flow at the reaction temperature for 4 h. Figure 4 shows that whatever the reactant mixture a large amount of carbonaceous compounds are retained on the zeolite sample: a maximum of 80% of the zeolite weight for the equimolar anisole–acetic anhydride mixture and of 50% for the anisole rich mixture.

A large part of the retained compounds are soluble and extracted in methylene chloride by simple soxhlet treatment of the zeolite sample. The other part, which is much less significant (<7%), can only be recovered in methylene chloride after dissolution of the zeolite in a hydrofluoric acid solution. From here on, the carbonaceous compounds recovered by simple soxhlet treatment will be called EXT, whereas that recovered after zeolite dissolution, coke.

The amount of EXT passes through a maximum at short TOS while the amount of coke increases with TOS (Fig. 4). The amounts of EXT and coke are more significant from the equimolar reactant mixture than from the anisole rich mixture. Whatever the reactant mixture and TOS, *p*-MAP is the main component of EXT (approximately 90%); dimethoxydypnone is also observed in a relatively large amount at short TOS. Di and triacetylated anisole are also found from the equimolar reactant mixture. Most likely they are not observed with the anisole-rich mixture as in this case di- and triacetylation are obviously limited. The large amount of *p*-MAP (and acetylated derivatives) which is retained over the zeolite samples confirms the strong retention of this polar compound. It should be emphasised that the micropores of the BEA zeolite cannot accommodate the very large amount of *p*-MAP formed at short TOS. The molecules of this compound are therefore located on the outer surface of the crystallites, presumably in the large volume of mesopores and macropores in the BEA zeolite. This volume, approximately 0.5 $cm^3\ g^{-1}$, is large enough to accommodate all of the EXT. The desorption of the components of EXT (MAP, in particular) is very slow at least under nitrogen flow. We can therefore conclude that this desorption can play a limiting role in the acetylation of anisole. The decrease in the amount of EXT when TOS increases can be related to the decrease in *p*-MAP in the desorbed

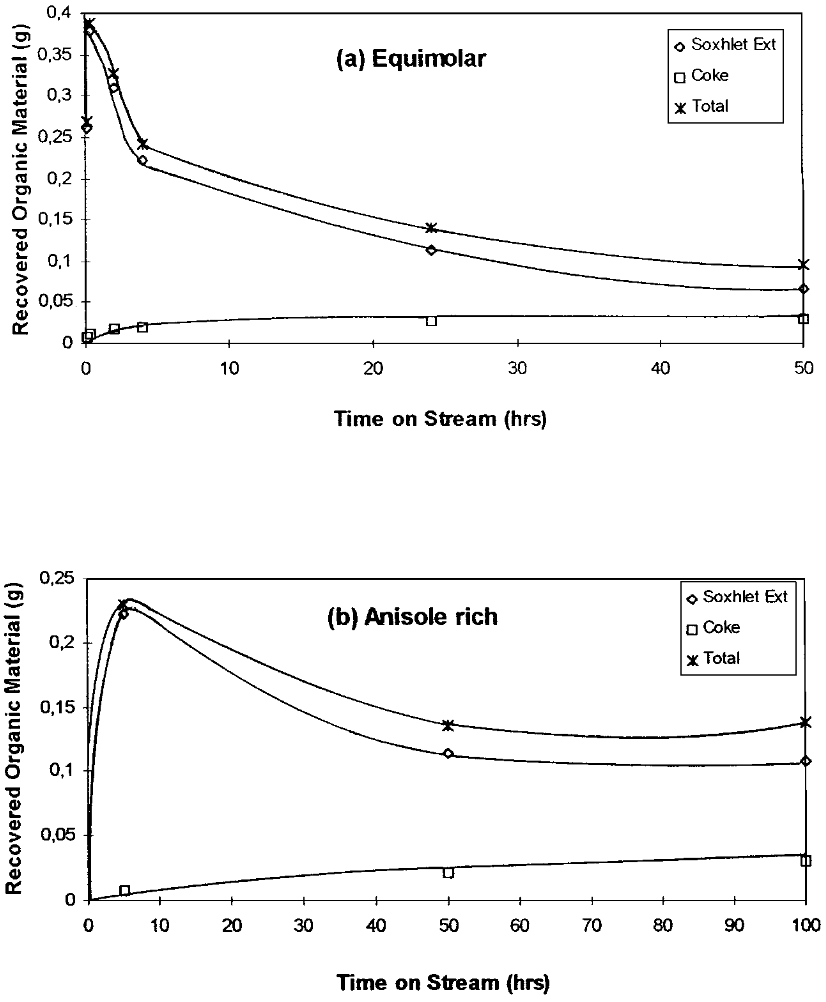
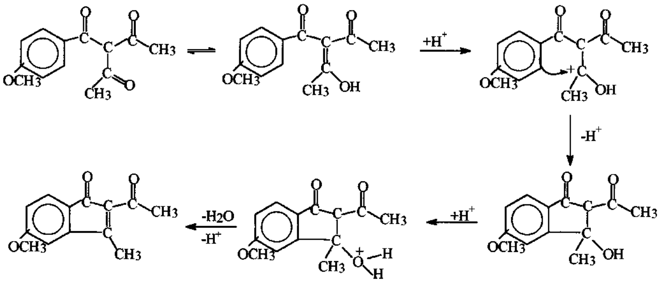


FIG. 4. Acylation of anisole at 90°C in a fixed bed reactor on 500 mg catalyst. Weight hour space velocity (WHSH) for anisole is 5.3 h^{-1} with the equimolar reactant mixture and 8.5 h^{-1} with the anisole rich mixture. Amount of retained organic material (g) over HBEA after reaction for (a) equimolar reaction mixture and (b) anisole rich reaction mixture vs time on stream.

product as suggested by the slower decrease observed with the anisole rich mixture (Fig. 4).

Whatever the reactant mixture, coke consists of *p*-MAP and heavier products. These products can be classified into 10 families (see Table 1). Six families (4–9) are only observed in trace amounts and we have assembled the heaviest products ($280 < M < 350$) which cannot be identified by GC/MS into family 10. An estimation of the amount of the components of each family was obtained by simple integration of the chromatographic peaks (no calibration was carried out). Figures 5a and b show that only the components of family 1 are directly formed, those of the main other families (2, 3, and 10) being formed only for coke contents greater than 1.5 wt% whatever the reactant mixture.

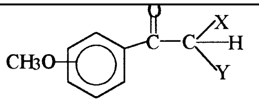
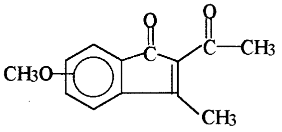
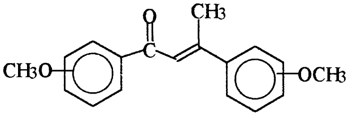
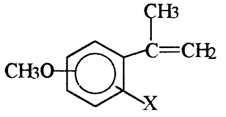
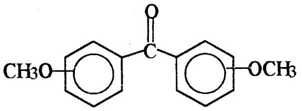
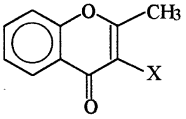
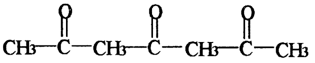
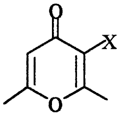
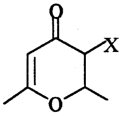
Family 1 corresponds to mono (MAP), di- and triacetylated anisoles. Diacetylated anisole is the major coke component (65–80%), *p*-MAP being also present in large amounts (25–35%), whereas only minute amounts of triacetylated anisole can be observed. Family 2 mainly consists of three isomers having a molecular weight equal to 216 and traces of their monoacetylated derivatives ($M = 258$). These compounds would result from secondary transformations (cyclisation and dehydration) of diacetylated *p*-MAP.



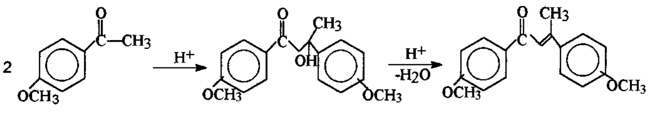
The mass spectrum of one isomer with explanation of the fragmentations is given in Fig. 6. Family 3 consists of

TABLE 1

Heavy Reaction Products—Main Families

Family	Chemical Structure and Molecular Weight	
1. Methoxyacetophenone and acetylated derivatives		M= 150 X=Y=H M=192 X=Ac Y=H M=234 X=Y=Ac
2. 2-acetyl, 3-methyl, methoxy-indene-1-one.		M=216
3. Dimethoxydypnone		M=282
4. Methoxy alpha-methyl styrene and acetylated derivative		M=148 X=H M=190 X=Ac
5. Dimethoxybenzophenone		M=242
6. 2-methylchromone and acetylated derivative		M=160 X=H M=202 X=Ac
7. 2,4,6-heptanone	 $CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$	M=142
8. 2,6-dimethylpyran-4-one and acetylated derivative		M=124 X=H M=166 X=Ac
9. 2,6-dimethylpyran-5,6dihydro 4-one and acetylated derivative		M=126 X=H M=168 X=Ac
10. Heavy products	$C_{18}H_{15}O_3X$ $C_{20}H_{16}O_3$ $C_{20}H_{17}O_3X$ $C_{22}H_{20}O_4$	M=280 X=H M=322 X=Ac M=304 M=306 X=H M=348 X=Ac M=324

dimethoxydypnone isomers. The mass spectrum of one isomer with explanation of the fragmentations is given in Fig. 7. These compounds result from the aldolisation of *p*-MAP followed by dehydration of the resulting alcohol.



It should be remarked that, as previously shown (21), dehydration is much faster than cyclisation and aldolisation, which explains the absence of alcohol intermediates in coke. Methoxy alpha methyl styrene (Family 4) which is observed in traces with monoacylated derivatives, can result from the scission by an acid mechanism of dimethoxydypnone (21). The acylium ion which is formed attacks an anisole molecule with production of dimethoxybenzophenone (Family 5).

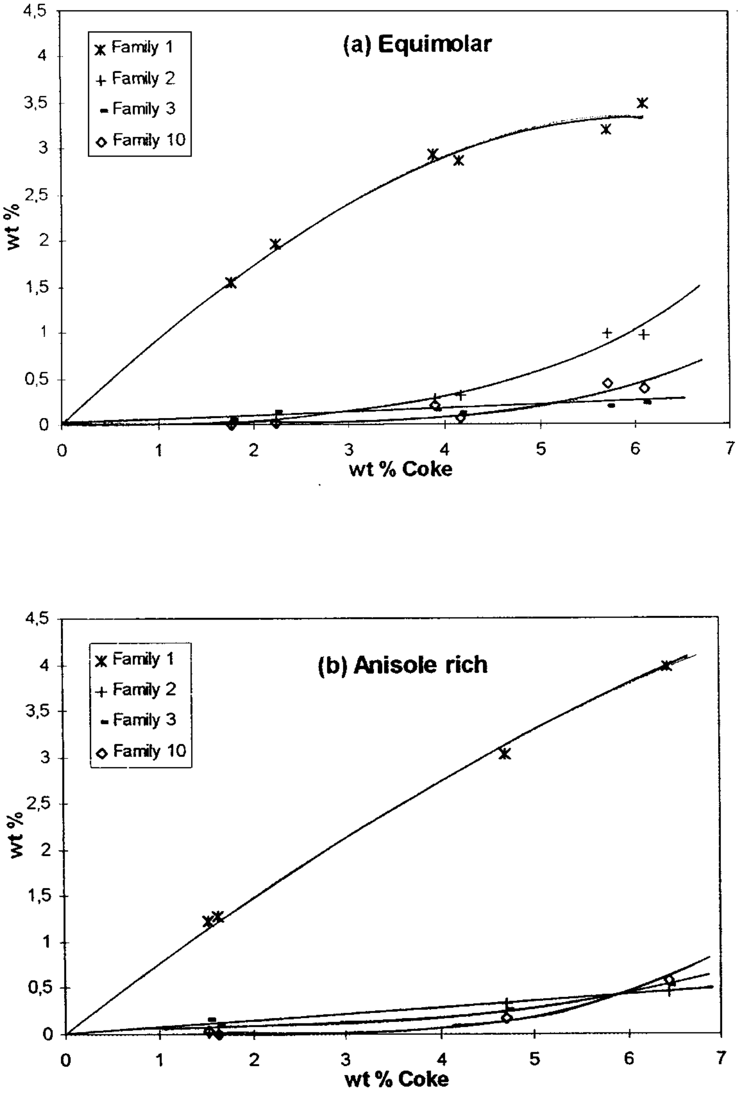
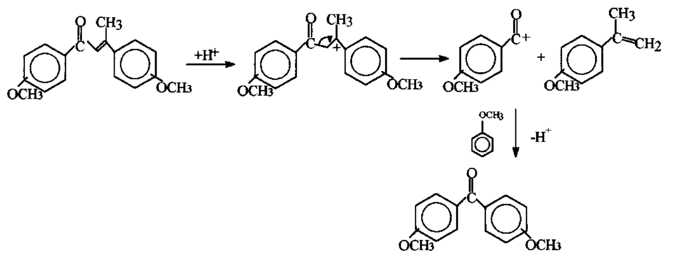


FIG. 5. Acylation of anisole at 90°C in a fixed bed reactor on 500 mg catalyst. Weight percent (wt%) of the four principal families of coke components vs the total percentage of coke. Reaction for (a) equimolar reaction mixture and (b) anisole rich reaction mixture.



2 Methylchromone which is observed in traces with its monoacetylated derivative (Family 6) would result from cyclisation dehydration of *o*-acetoxyacetophenone, as previously described (22). The other families (7–9) result from the transformation of ketene, formed from acetic anhydride through an acid mechanism. These are, furthermore, the only components of coke formed from pure acetic anhydride (experiments and subsequent coke analysis which were carried out on pure acetic anhydride illustrate this).

The dimensions of the main components of coke (Families 1–3) were estimated using the program Cerius 2, developed by Biosym/Molecular Simulations. *p*-MAP (6.6 × 4.2 × 11.8) and diacetylated anisole (6.6 × 6.8 × 13) of Family 1 which are smaller than the apertures of the channels of beta zeolite (5.5 × 5.5 ⇔ 7.6 × 6.4 (23)) could diffuse into the channels. Therefore, their retention in the zeolite pores is not due to their steric blockage but most likely to their strong adsorption (they are very polar) on the acid sites. This is probably also the case with 2-acetyl, 3-methyl, methoxyindene-1-one (8.2 × 4.4 × 13) (Family 2).

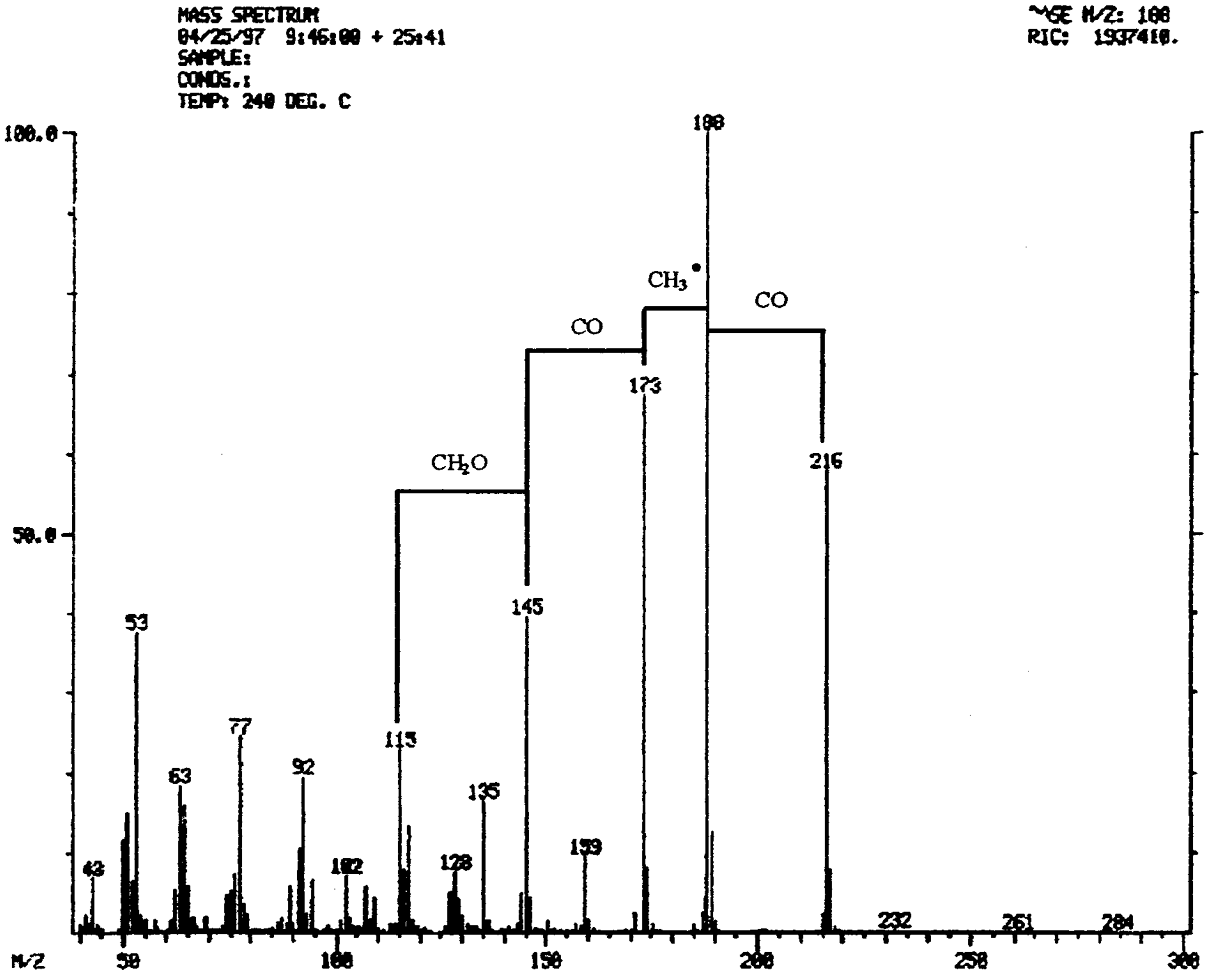


FIG. 6. Mass spectrum of a coke component of family 2 (2-acetyl, 3-methyl, methoxyindene-1-one, M = 216).

On the other hand, dimethoxydypnone molecules (9.8 × 7.2 × 17.2) (Family 3) are larger than the apertures of the channels; hence, they are certainly trapped at the channel intersections (12–13 Å (24)).

4. Influence of Coke on Nitrogen Adsorption Capacity

Figure 8 shows that coke blocks the access mainly to the micropore volume and has practically no effect on the mesopore volume. Another important observation is that the effect of coke does not depend on the reactant mixture used for its formation. From extrapolation of the curve in Fig. 8, corresponding to the micropore volume, it can be estimated that complete blockage of the pores would occur at a coke content of approximately 14 wt%. If we consider a density of 1.1 g/cm^3 for coke molecules (i.e., a density close to that of *p*-MAP) the real volume occupied by coke molecules would be equal to 0.125 cm^3 g^{-1} zeolite, i.e. close to the total micropore volume of the fresh zeolite sample, 0.165 cm^3 g^{-1}. This means that coke is nearly homogeneously distributed in the zeolite crystallite, whatever the reactant mixture.

Pore blockage has obviously a negative effect on the rate of anisole acylation. However, the comparison of the change in the micropore volume and in the anisole conversion versus TOS shows that pore blockage by coke is not the only cause of deactivation. Thus, after 50 h time-on-stream approximately 30% of the pore volume remains accessible to nitrogen, whereas the activity is less than 5% of the initial activity. This deactivating effect, larger than the blockage effect can be explained by limitations due to coke in the diffusion of reactant inside the zeolite pores not occupied by coke molecules. However, a most likely explanation could be that not only coke molecules but also EXT molecules retained in the mesopores would limit the access of the reactant to the zeolite acid sites. These EXT molecules (in particular, *p*-MAP) which are very polar could also limit the acetylation rate owing to their strong adsorption on the acid sites, thus inhibiting the adsorption of the reactant.

In order to confirm the effect of EXT, the activity of a deactivated sample (obtained by the reaction of an equimolar reactant mixture for 25 h) was compared to that of the same sample from which EXT was removed.

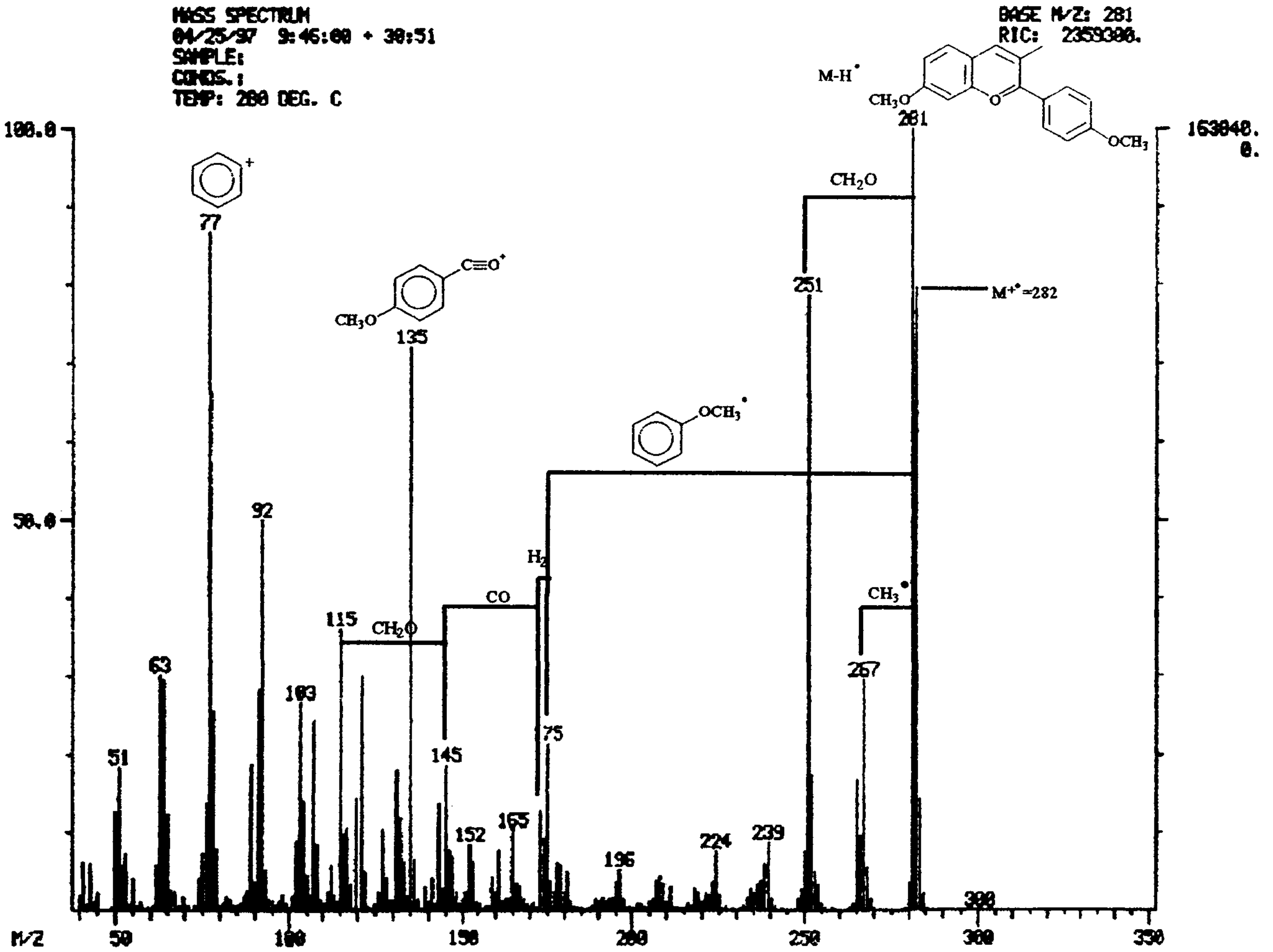


FIG. 7. Mass spectrum of a coke component of family 2 (dimethoxydypnone, M = 282).

This removal was carried out by sweeping the deactivated catalyst, directly in the fixed-bed reactor so as to avoid contact with air, with methylene chloride (5 ml/h) for 2 h at room temperature. The amount of EXT recovered by this treatment was close to the one recovered by soxhlet extraction. The anisole conversion passed from 5% before EXT removal to approximately 15% afterward (instead of 40–50% on the fresh catalyst). This result indicates that *p*-MAP, which is the main component of EXT, limits the acetylation of anisole. It also confirms that coke deposited inside the micropores plays a major role in deactivation.

Furthermore, it has been shown in part 2 that the catalyst stability is better for the anisole-rich mixture than for the equimolar mixture. This better stability can be explained by (i) the slower coke formation (Fig. 2) and (ii) the lower amount of EXT in the mesopores (Fig. 4).

CONCLUSION

Anisole acylation with acetic anhydride over a HBEA zeolite carried out in a batch reactor in the absence or in the presence of *p*-methoxyacetophenone (*p*-MAP) indicates that *p*-MAP inhibits its own production. During experiments performed in a fixed-bed reactor, deactivation of the zeolite is observed, this deactivation being more pronounced from the equimolar anisole–acetic anhydride mixture than from the anisole-rich mixture. The analysis of the zeolite samples after reaction at different times on stream shows that a very large amount of *p*-MAP (particularly from the equimolar anisole–acetic anhydride mixture), is retained inside the mesopores of the zeolite and that larger molecules are trapped in the zeolite micropores. These larger molecules which result from polyacetylation of anisole, followed by cyclisation and dehydration, or from aldolisation–dehydration of *p*-MAP, are formed more rapidly from the equimolar anisole–acetic anhydride mixture. These molecules cause a blockage of the access of nitrogen (hence, of the reactants) to the pores which is responsible for part of the deactivation. However, another significant part of deactivation is due to *p*-MAP strongly retained in the mesopores. To have good catalyst stability it is preferable to operate with an

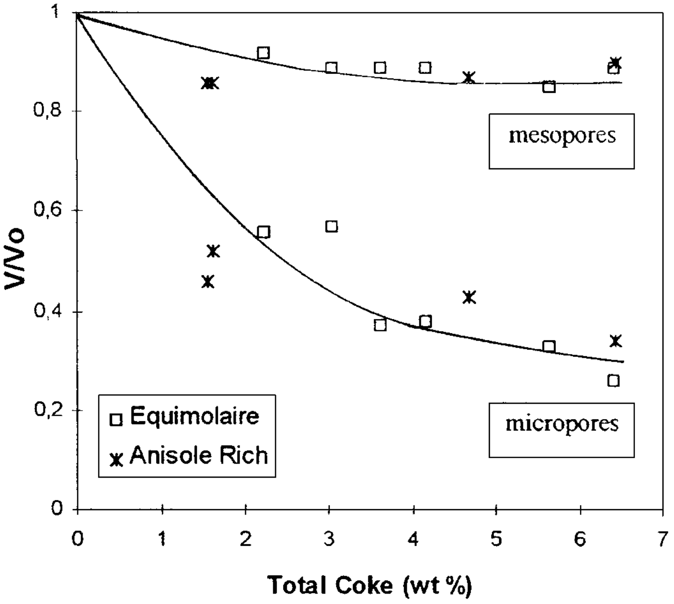


FIG. 8. Acylation of anisole at 90°C in a fixed bed reactor on 500 mg catalyst. Influence of coke on the relative adsorption capacity for nitrogen (V/Vo).

anisole-rich mixture with the excess anisole limiting the retention of *p*-MAP in the mesopores and the formation of polyacetylated anisole and of aldolisation products which block the access of the reactants to the micropores.

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