

Zeolite catalyzed acylation of heterocyclic compounds. Part II. Acylation of benzofuran over Y zeolites. Effect of reaction conditions on the activity and stability

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Abstract

The acylation of benzofuran by acetic anhydride was carried out in the liquid phase (333 K) in the presence of Y-zeolites (Si/Al = 4.8–86). The most active zeolites were those with a Si/Al ratio \approx 15. Adsorption experiments at room temperature were carried out and the product distribution in the material ('coke') deposited in the course of the reaction was determined in order to understand the deactivation of the catalyst. Various parameters were found to affect the composition of the deposit especially the reaction procedure which has a drastic influence on the ageing of the catalyst.

Keywords: Acylation; Zeolite; Benzofuran; Acetic anhydride; Deactivation

1. Introduction

Heterocyclic aromatic compounds and their derivatives obtained through substitution reactions, for instance, are of interest in the field of pharmaceutical chemistry [1,2].

However, in the context of environmental protection, new methods have to be investigated for reactions like electrophilic aromatic substitutions. Actually the use of soluble catalysts for reactions like Friedel–Crafts acylations creates corrosion problems, waste and troublesome workups [3,4].

More than ever, solid catalysts like zeolites [5–9], clays [10] or resins [11] are used instead of the traditional catalysts. One of the advantages of these catalysts is that the environment is protected since (i) they are easy to recover and regenerate

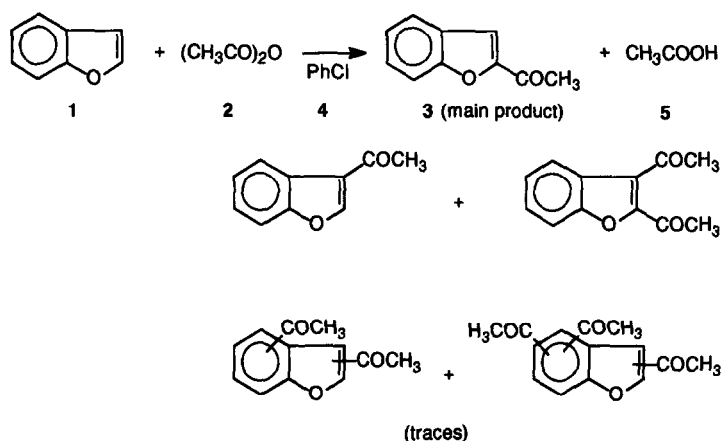
and (ii) they produce no salts. Zeolites are good catalysts for the acylation of aromatic compounds, both in the gas phase [5,7] and in the liquid phase [6,8,9]. Recently, Finiels et al. showed that Y zeolites could catalyze the acylation of thiophene by acyl chlorides in the liquid phase [8]. The Friedel–Crafts acylation by acetic anhydride (2) of benzofuran (1) into 2-acetylbenzofuran (3) (Scheme 1) over Y zeolites was also reported [9].

In the latter case, the main observations were the following:

The activity of the zeolites depended on their Si/Al atomic ratio.

Deactivation occurred in the course of the reaction which led to a steadying of the conversion after about 5 hours under the conditions chosen for the reaction.

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Scheme 1. Reaction products.

Although **3** (the main reaction product) was found to inhibit the reaction, this did not appear sufficient to justify the resulting deactivation.

Moreover, it was found that the reaction procedure affected significantly the activity of the zeolite: there was no reaction if the substrate (**1**) was introduced before **2**.

The aim of the present study is to understand the effect of the reaction procedure on the reaction rate and to obtain information on the deactivation of the catalyst. Consequently, we report here: Complementary studies on the effect of the operating conditions and of the Si/Al atomic ratio of the zeolites.

Adsorption experiments in the liquid phase.

An attempt to identify the irreversibly adsorbed materials ('coke').

2. Experimental section

2.1. Materials

Benzofuran (99.5%) and chlorobenzene (99%) were purchased from Aldrich. Acetic anhydride (99%) was purchased from Janssen. The composition of the various HY zeolites (Table 1) was determined by chemical analysis (CNRS, Service Central d'Analyse, 69390 Vernaison). The framework Si/Al atomic ratio was deduced from the unit cell parameter (determined by X-ray diffraction, ASTM method D 3942-80) using the equation given by Breck and Flanigen [12].

2.2. General procedure

The experiments were carried out in a 100 cm³ stirred glass reactor under N₂. The freshly calcined

Table 1
Characteristics of the Y zeolites

| Zeolite | Unit cell formula | Al _{EF} ^a | Si/Al _{framework} atomic ratio | Acid sites/g of zeolite ^b |
|---------------------|---|-------------------------------|---|--------------------------------------|
| LZY82 ^c | Na _{0.8} H _{32.2} Al ₃₃ Si ₁₅₉ O ₃₈₄ | 15.5 | 4.8 | 16.8 × 10 ²⁰ |
| CBV720 ^d | Na _{0.3} H ₁₁ Al _{11.3} Si _{180.7} O ₃₈₄ | 2.4 | 16 | 5.7 × 10 ²⁰ |
| ZF520 ^e | Na _{0.7} H _{9.3} Al ₁₀ Si ₁₈₂ O ₃₈₄ | 5.7 | 18 | 4.8 × 10 ²⁰ |
| CBV760 ^d | Na _{0.6} H _{1.6} Al _{2.2} Si _{189.9} O ₃₈₄ | 9.8 | 86 | 0.8 × 10 ²⁰ |

^a Extra-framework aluminum per unit cell.

^b Deduced from unit cell formula.

^c Union Carbide.

^d Conteka.

^e Zeocat.

zeolite (773 K under dry air, 1 g) was introduced in the reactor while hot without exposure to ambient atmosphere. Then the standard procedure was the following: the solvent (chlorobenzene, 30 cm³) was added, followed by the acylating agent **2** (58 mmol). The mixture was stirred at 333 K for 15 min before starting to add benzofuran (29 mmol). It was then heated at 333 K for the time required for the reaction.

In the procedure without added solvent, Ac₂O (371 mmol, 35 cm³) and benzofuran (29 mmol) were added together to the zeolite, the mixture being stirred and heated for the time required for the reaction. To make sure that the product could be readily isolated from the reaction mixture and to verify that the chromatographic analysis gave a correct value of the yield in **3**, the reaction mixture was treated as follows: the crude mixture was filtered, and quenched with an aqueous NaHCO₃ solution, the aqueous layer was separated and extracted twice with CH₂Cl₂, the combined organic layers were dried (Na₂SO₄) and evaporated to give 4.4 g of a residue containing the product. This residue was treated by flash-chromatography (cyclohexane/AcOEt, 80 : 20) to give 1.2 g of 2-acetylbenzofuran (27%) which corresponded exactly to the yield deduced from the gas chromatographic analysis of the reaction mixture. The isolated 2-acetylbenzofuran was identified by ¹H NMR, CD₂Cl₂, δ = 2.55 (s, 3H), 7.30 (t, 1H), 7.42 (d, 1H), 7.48 (s, 1H), 7.50 (t, 1H), 7.71 (d, 1H).

For the reaction in the presence of AcOH (**5**), 14 mmol of **5** and Ac₂O were added together following the standard procedure.

Analyses were performed with a gas chromatograph equipped with a flame ionization detector and using a DB1 capillary column (length: 30 m; diameter: 0.25 mm; film thickness: 0.25 μm). Quantitative analyses were obtained by calibration with mixtures made of commercial samples with 2-methylnaphthalene as external standard. The ¹H NMR spectra were taken with a Bruker 200 MHz spectrometer. GC–mass spectral analyses were performed with a Finigan INCOS 500.

2.3. Adsorption experiments

The experiments were carried out in a 100 cm³ stirred glass reactor under N₂. The freshly calcinated zeolite (773 K under dry air, 1 g) was introduced in the reactor while hot without exposure to ambient atmosphere. Then a mixture of chlorobenzene (78.6 mmol, 8 cm³) and benzofuran (**1**, 3.7 mmol, 0.4 cm³), or acetic anhydride (**2**, 4.2 mmol, 0.4 cm³), or both **1** and **2** (same quantities) was introduced. The experiment was carried out at room temperature with a stirring speed of 250 rpm during 24 h. The mixture was analysed by gas chromatography. The volume occupied by the reactants was estimated on the basis of their molecular weight and liquid density.

2.4. Coke extraction

The extraction of the carbonaceous compounds deposited in the zeolites was carried out according to the procedure described by Magnoux et al. [13]. At the end of the reaction, the zeolite was filtered hot on Büchner. The catalyst was then dissolved and stirred for 1 h in 10 cm³ of a 40% aqueous solution of HF. This procedure did not cause any transformation of the carbonaceous compounds. Insoluble coke (graphitic particles) if any was present was weighed. The aqueous layer was then extracted with 20 cm³ of CH₂Cl₂ and neutralized with NaHCO₃. The extraction was carried out three times. The residue obtained by evaporation of the solvent was weighed and analyzed by GC–MS. The coke percent was taken as the weight of residue × 100 / weight of zeolite.

3. Results and discussion

The characteristics and sources of the zeolites used as catalysts are given in Table 1.

3.1. Reaction products

The results obtained in various experiments of acylation of benzofuran by acetic anhydride over

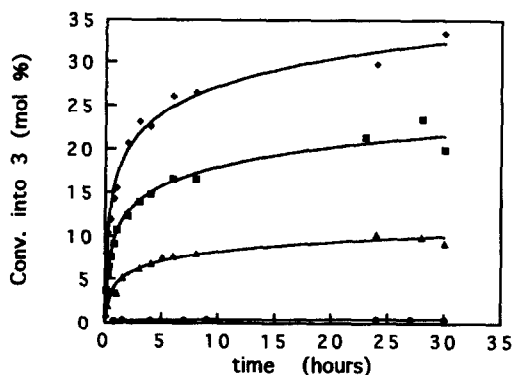


Fig. 1. Acylation of **1** by **2** at 333 K over Y zeolites. Effect of the Si/Al ratio. Solvent: **4** (chlorobenzene). (●): LZZY82 (Si/Al=4.8); (◆): CBV720 (Si/Al=16); (■): ZF520 (Si/Al=18); (▲): CBV760 (Si/Al=86).

Y zeolite (333 K) are summarized in Table 2. The main product was 2-acetylbenzofuran (**3**), only traces of the other products indicated in Scheme 1 were detected.

3.2. Effect of the Si/Al atomic ratio of Y-zeolites

As shown in Fig. 1, the highest conversion into **3** was obtained with CBV720 (Si/Al=16). If we consider the initial activity, this corresponds to a turn over number (molecules of **3** formed per acid site per hour) of about 7.

The zeolite with the highest number of acid sites (lowest Si/Al atomic ratio, see Table 2) was inactive for the reaction. The maximum activity (Fig. 2) could be due either (i) to the optimum acid strength for obtaining the activation of the acylating agent and/or (ii) to the minimum in deactivation i.e. in coke formation [13]. Actually, the maximum in activity per gram of zeolite could be the result of a compromise between the number and the strength of the sites involved. Usually, when the number of acid sites decreases (Si/Al increases), their strength increases [14]. Another factor which could increase the effect of the rise in acid strength of the sites would be the resistance to deactivation. It is known that dealuminated zeolites have a lesser tendency to accumulate irreversibly adsorbed materials than non-dealuminated zeolites [13]. For Y zeolites, the maximum activity is obtained generally when Si/Al=3.5–4.

Actually, as can be seen in Fig. 2, the amount of coke deposited follows more or less the same trend as the activity for the formation of **3** measured after 1 h reaction. The ratio coke/**3** (Table 2) does not differ very much from one zeolite to the other (0.2–0.4 under standard conditions) except for LZZY82 which is not active. We notice that it is lower for CBV760.

Table 2

Acylation of **1** (benzofuran) by **2** (acetic anhydride) at 333 K over Y zeolites (reaction time 30 hours). **3**: 2-acetylbenzofuran; **4**: chlorobenzene; **5**: acetic acid

| Experiment | Catalyst | Reactant (mmol) | | | | Reactant introduced first | Yield ^a mol% | Coke wt % | Coke/ 3 |
|----------------|----------|-----------------|------------------|----------|----------|---------------------------|----------------------------|--------------|----------------|
| | | 1 | 2 | 4 | 5 | | | | |
| 1 | ZF520 | 29 | 0 | 295 | 0 | 1 | – | 23 | – |
| 2 | ZF520 | 29 | 58 | 295 | 0 | 1 | 0.4 | 11.7 | 29.2 |
| 3 ^b | ZF520 | 29 | 58 | 295 | 0 | 2 | 22 | 9.8 | 0.4 |
| 4 | ZF520 | 29 | 5 | 295 | 0 | 2 | 7 | 15.2 | 2.2 |
| 5 | ZF520 | 29 | 58 | 295 | 14 | 2 | 21 | 18 | 0.86 |
| 6 | ZF520 | 29 | 371 ^c | 0 | 0 | – | 27 | 23.1 | 0.85 |
| 7 ^b | LZZY82 | 29 | 58 | 295 | 0 | 2 | 0.5 | 2.5 | 5 |
| 8 ^b | CBV720 | 29 | 58 | 295 | 0 | 2 | 32 | 12.8 | 0.4 |
| 9 ^b | CBV760 | 29 | 58 | 295 | 0 | 2 | 10 | 2.4 | 0.2 |

^a mol percent of **1** converted into **3**.

^b Standard procedure.

^c Used as the solvent.

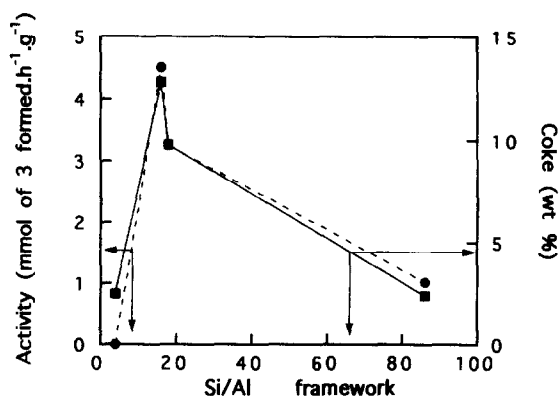


Fig. 2. Acylation of **1** (29 mmol) by **2** at 333 K over Y zeolites; activity ($\text{mol} \cdot \text{h}^{-1} \cdot \text{g}^{-1}$; reaction time = 1 h) (●) and coke content after reaction (■). LZY82 (Si/Al=4.8), CBV720 (Si/Al=16), ZF520 (Si/Al=18), CBV760 (Si/Al=86).

3.3. Effect of the operating conditions on the activity and stability of the catalysts

The effect of the reaction procedure (sequence of introduction of the reactants) and of the operating conditions on the activity was studied on one of the more active catalysts (ZF520). As reported in the previous paper [9], the procedure of introduction of the reactants could modify greatly the reactivity: if **1** was introduced before **2** on the zeolite, the activity was markedly reduced (0.4 mol% of **1** converted into **3** instead of 22% if it was introduced after **2**) (Table 2). However, as can be seen in Table 2, the amount of coke deposited was about the same in both cases so that it was concluded that there was competition towards adsorption between **1** and **2**.

In order to better understand this phenomenon, adsorption experiments were carried out in the

liquid phase (room temperature, **4** as the solvent).

In every case, the quantity (in mol) adsorbed was greater per gram of zeolite than that of acid sites (Table 3). It can thus be assumed that a large amount of each of the various compounds was physically adsorbed. Apparently, the access to the pores was not blocked. However, only about 1/3 of the pore volume determined by N_2 adsorption was accessible to the reactants.

When **1** and **2** were introduced simultaneously it was observed that **2** was adsorbed even in the presence of **1** (Table 3). However, when **1** was introduced before **2** a much smaller amount of **2** was adsorbed. Nevertheless the adsorption of **2** was not completely inhibited. Hence the fact that by first introducing **1** the reaction was completely inhibited cannot be explained by a preferential adsorption of **1**, except if it blocks the acid sites through a process (not yet identified) which inhibits the activation of **2**.

Other parameters concerning the reaction mixture were also examined: the amount of **2**, the addition of acetic acid and the absence of solvent (Fig. 3).

When the amount of **2** introduced was reduced to 5 mmol (experiment 4, Table 2), the conversion of **1** into **3** was reduced to 7 mol%, which corresponded to a conversion of **2** of about 40 mol%. However the amount of coke deposited on the catalyst increased up to 15.2 wt%.

The effect of acetic acid (**5**), a by-product of the reaction was studied. No reaction was observed between **1** and **5** (≈ 2 mol per mol of **1**) under the conditions of the reaction with **2**, which

Table 3

Adsorption of the various compounds on ZF520 (1 g) at room temperature, during 5 h, with chlorobenzene (8 cm^3) as the solvent

| Compounds (mmol) | Adsorption after 5 h (mmol) | Volume occupied by the reactants (cm^3) | mmol adsorbed/acid site | Volume occupied by the substrate/porous volume |
|--|-----------------------------|--|-------------------------|--|
| 2 (4.2) | 1.12 | 0.11 | 1.4 | 0.31 |
| 1 (3.7) | 1.2 | 0.13 | 1.5 | 0.37 |
| 2 (4.2) + 1 (3.7) ^a | 0.96 + 0.62 ^b | 0.16 | 2 | 0.46 |
| 2 (4.2) + 1 (3.7) ^c | 0.32 + 0.96 ^b | 0.13 | 1.6 | 0.37 |

^a **2** and **1** introduced at the same time.

^b Respectively.

^c **1** introduced before **2**.

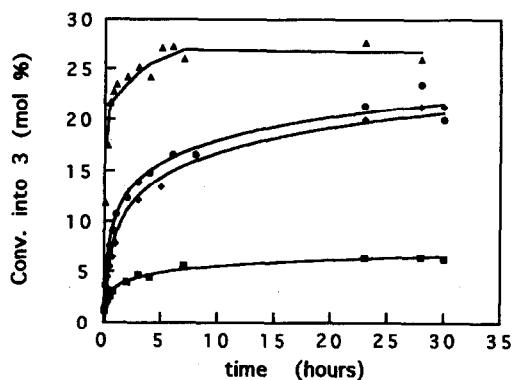
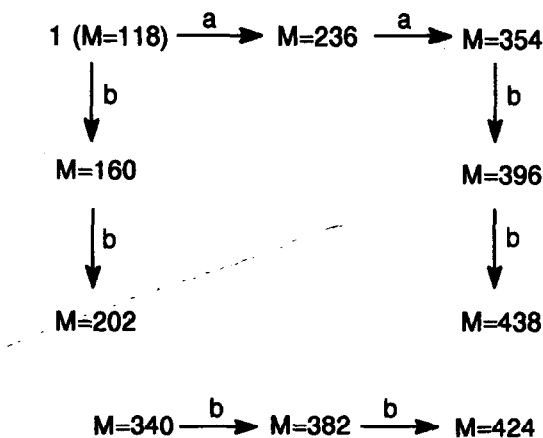


Fig. 3. Acylation of **1** (29 mmol) by **2** at 333 K over ZF520 zeolite. (●): standard reaction; (◆): effect of the presence of **5** (14 mmol); (■): effect of concentration of **2** (5 mmol); (▲): **2** as the solvent.



Scheme 2. Molecular weight of the compounds found in the coke (a) autocondensation; (b) acylation.

means that **5** was not readily activated by the zeolite to give the acylium ion. On the other hand, **5** (at a concentration corresponding to that obtained at about 50% conversion of the substrate) had practically no effect on the conversion of **1** into **3** (experiment 5, Table 2). However we noticed that the amount of coke deposited increased from 9.8 to 18 wt% which means that here the irrevers-

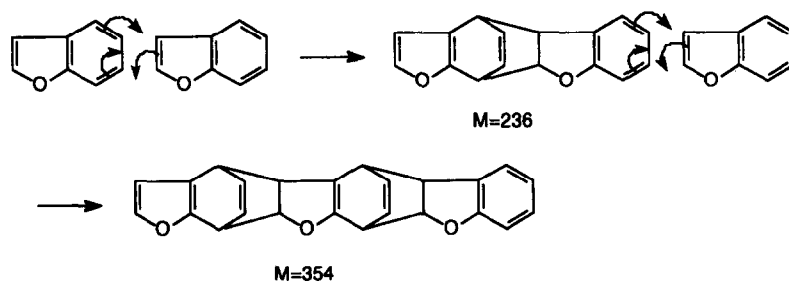
ibly adsorbed material was of a different nature and had a lower poisoning effect on the catalyst.

Experiment 6 was carried out without added solvent. In this case, **1** and **2** were introduced at the same time. It shows that the amount of irreversibly adsorbed material (coke) was more than twice as high as when **4** was the solvent (compare experiments 3 and 6, Table 2). However the conversion of **1** into **3** was also higher than with **4** as the solvent. Hence the same remark as above can be made concerning the nature and toxicity of the deposit.

3.4. Nature of the irreversibly adsorbed material

As indicated above depending on the procedure and conditions of the reaction the nature of the irreversibly adsorbed material was modified. Hence we attempted to obtain information on the composition of the 'coke' by gas chromatographic and gas chromatography–mass spectrometry analyses (GC–MS) of the material recovered after dissolution of the zeolite (see Experimental part). In none of the cases considered below was 'insoluble coke' detected.

By considering the molecular weights, the formation of most of the compounds detected in the material recovered after dissolution of the zeolite can be summarized as in Scheme 2. We assume that most of the heavy compounds were formed inside the pores of the zeolite since they were not detected in the liquid-phase although we have no definite proof for that at the moment. They probably result from the acylation of compounds obtained by condensation of benzofuran. Actu-



Scheme 3. Condensation of benzofuran.

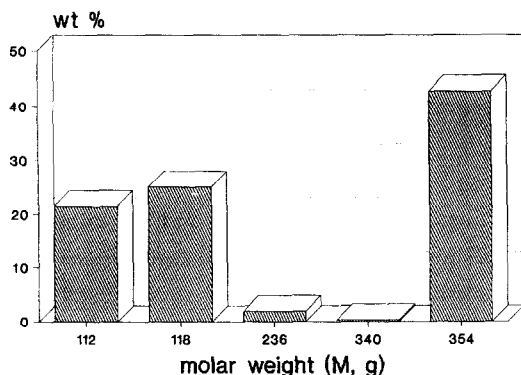


Fig. 4. Reaction of **1** over ZF520 at 333 K during 30 h. Solvent: **4**. Molecular weight distribution of the coke.

ally, we see that most of the major products contained in the coke can be regarded as resulting either from the acylation of a benzofuran trimer ($M=354$, Scheme 3) or from the acylation of a compound ($M=340$) obtained by a more complex and yet unknown condensation process: this compound which was only present as traces in the organic material recovered after dissolution of the zeolite could not be analysed by other means than GC-MS and apparently is not acylated. Traces of others compounds ($M=252, 294, 336, 378$) were also observed.

Transformation of the substrate in the absence of an acylating agent

When **1** alone was allowed to react over zeolite ZF520, 23% of coke was deposited (Table 2, experiment 1). The molecular weight distribution of the constituents of this material is given in Fig. 4. It can be noticed that even after filtration under vacuum, the coke contained about 46% by weight of **4** ($M=112$) and of **1** ($M=118$). An explanation could be that, especially when **1** was in excess, **4** and **1** could be trapped in the zeolite by some oligomers of **1** or by strongly adsorbed materials which would restore benzofuran when the zeolite dissolved. The coke contained only one main compound with a higher molecular weight than the reactant and the solvent ($M=354$). Scheme 3 shows a possible mechanism for the formation of this compound through a Diels-Alder condensation involving three molecules of **1**. However several possibilities exist for the con-

densation of the intermediate dimer with the third molecule of benzofuran. Therefore the structure of the trimer shown in Scheme 3 is speculative since it was not yet possible to isolate quantities of this compound which could be large enough to perform conventional NMR or IR analyses. The compound with $M=236$ (the dimer) represents only 1.9% of the total amount of coke, probably because the size of the trimer is such that it fits particularly well inside the void space of the zeolite. Its high concentration with respect to that of the dimer could be the consequence of a confinement effect [15].

Effect of the procedure of the reaction

As reported already [9], the experimental procedure has a great influence on the yield of the reaction. This yield was much higher in particular when acetic anhydride (**2**) was introduced on the zeolite before benzofuran (**1**). In both cases (Table 2, experiments 2 and 3) the amount of coke deposited was about the same, however its composition was noticeably different.

When **1** was introduced before, the acylation reaction was practically non-existent, consequently very little of the main reaction product was found in the catalyst (Fig. 5a). Surprisingly, the compound ($M=354$) found when **1** alone was allowed to react was found here in small quantity. However, heavy compounds were detected, two of which ($M=396, M=438$) could result from the acylation or diacylation of the above-mentioned compound ($M=354$). The other major product ($M=382$) could result from the acylation or diacylation of the compound with $M=340$ (Scheme 2). As was the case when **1** reacted in the absence of **2**, the solvent ($M=112$) and substrate ($M=118$) were entrapped in the zeolite. Each time this happened, the compounds with $M=396$ or 438 were also detected in the irreversibly adsorbed material.

When **2** was introduced first, the reaction took place and many of the products (**3**, $M=160$ and diacetylbenzofurans, $M=202$) were entrapped in the catalyst (Fig. 5b). However, the fragmentation of the diacylated products indicates that those

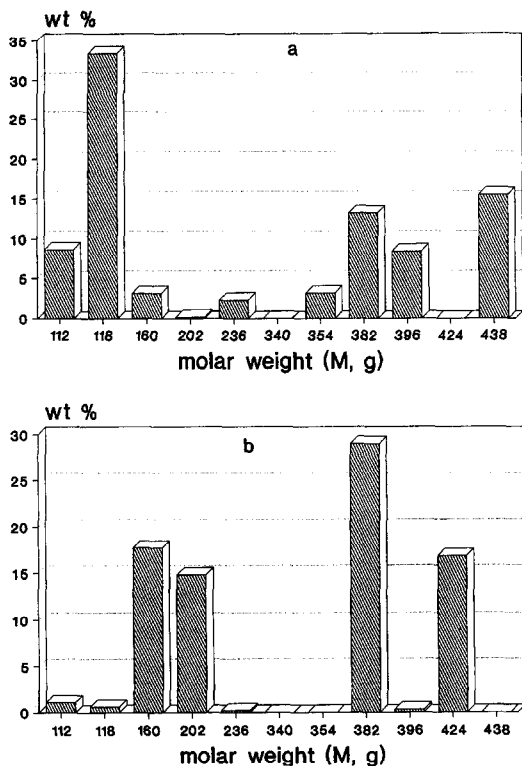


Fig. 5. Acylation of **1** (29 mmol) by **2** (58 mmol) over ZF520 at 333 K during 30 h. Solvent: **4**. Molecular weight distribution of the coke. (a) Introduction of **1** before **2**, (b) introduction of **2** before **1**.

found in the coke were acylated on the benzenic ring, while the only diacylated product detected in the liquid phase during the reaction was 2,3-diacetylbenzofuran. Among the heavier products, mainly compounds with $M=382$ and 424 were found. The compound with $M=354$ (the benzofuran trimer) was not detected in this case and the compounds resulting from the acylation of the benzofuran trimer ($M=396, 438$) were found in very small quantities.

It is clear that the nature of the coke depends on the procedure. If the substrate is introduced first, the coke is mainly composed of products resulting from the oligomerisation of **1**. They rapidly block the zeolite pores so that the acylation of the substrate can no longer occur. If it is the acylating agent which is introduced first, the condensation of benzofuran through a Diels–Alder process is apparently inhibited so that the deactivation is slower. In this case, deactivation is probably due mainly to a strong adsorption of the

compounds resulting from the acylation of a compound with $M=340$, which leads to a more progressive blockage of the zeolite pores.

Effect of acetic anhydride concentration

Two quantities of acetic anhydride were used: 5 mmol and 58 mmol (standard conditions) which correspond to concentrations of 0.15 and $1.58 \text{ mol} \cdot \text{dm}^{-3}$ respectively. As reported in a previous paper [9], the kinetic order with respect to **2** (on the basis of initial rates) was close to zero which means that **2** adsorbs strongly on the catalytic centers.

As shown in Table 2 (compare experiments 3 and 4), the amount of coke was smaller (about 1.5 times) when the concentration in **2** was higher (58 mmol). The compounds with $M=382$ and $M=424$ remained the major components of the heavy fraction of the coke. The quantities of these components followed the same trend as the total amount of coke (Fig. 5b and Fig. 6) since their proportions were about the same. However the total amount of coke in the catalyst depends to a certain extent on the quantity of substrate and of solvent entrapped. Indeed large quantities of these two compounds were found when the concentration of **2** was the lowest (compare Fig. 5b and Fig. 6). In both cases, the coke contained the main reaction product (**3**) but when the concentration of **2** was higher, it also contained the diacylated product ($M=202$), which was not the case with the lower concentration. Another difference was that the product resulting from the acylation of the

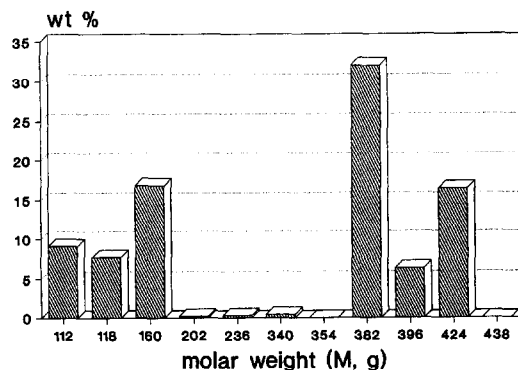


Fig. 6. Acylation of **1** (29 mmol) by **2** (5 mmol) over ZF520 at 333 K during 30 h. Solvent: **4**. Molecular weight distribution of the coke.

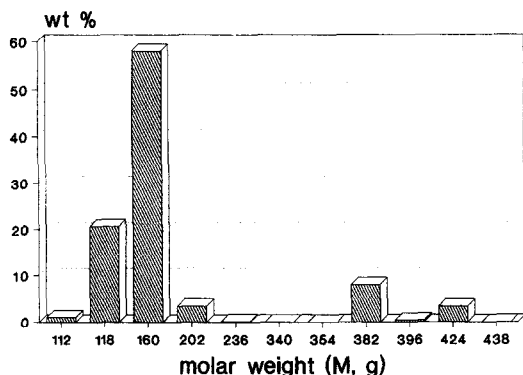


Fig. 7. Acylation of **1** (29 mmol) by **2** (58 mmol) at 333 K over ZF520 during 30 h. Solvent: **4**. Effect of the presence of **5** (14 mmol) on the composition of the coke.

benzofuran trimer ($M=396$) was found only when the concentration of **2** was low. This confirms that **2** inhibits the condensation of **1** through a Diels–Alder type reaction.

Effect of the presence of acetic acid

As we have seen above, **5** had little influence on the conversion of **1** into **3** but in its presence the total amount of coke deposited was greater, about twice that found without **5** (compare experiments 3 and 5, Table 2). However, **5** seemed to inhibit the formation of heavy products in the coke (compare Fig. 5b and Fig. 7): the major component contained in the coke was the main reaction product (**3**), a significant amount of substrate being also found. The compounds with $M=382$ and 424 were also found but in much smaller amounts (about four times less than without **5**). Hence it can be assumed that in the presence of **5** deactivation was mainly due to the retention of **3** in the zeolite.

Experiments without added solvent

The influence of the solvent was studied by comparing experiments in which **2** was used as the solvent to experiments with **4** as the solvent. When the reaction was carried out with **2** as the solvent, **1** and **2** were introduced at the same time.

With **2** as the solvent, the conversion of **1** was higher but the formation of coke was also more significant than with **4** as the solvent (compare experiments 3 and 6, Table 2). However, as can

be seen in Fig. 8, the adsorbed material contained essentially the reaction products. It contained a low percentage only of the compound with $M=382$. The composition of the coke was quite similar to the one obtained in the presence of **5**. Deactivation was essentially due to the inhibition by the product presumably through its irreversible adsorption as was the case when **5** was added. This again confirms that **2** inhibits the condensation of **1** and the formation of the two main series of heavy products (resulting from the acylation of the compounds with $M=340$ and $M=354$).

Effect of the Si/Al atomic ratio

All the zeolites contained as heavy compounds essentially those which could be considered as resulting from the acylation of a compound with $M=340$. Moreover, when the Si/Al ratio increased, the amount of heavy products deposited on the zeolite compared to the amount of reaction products retained in the structure increased (Fig. 9). In particular, LZY82 contained a large amount of **3** and of diacetylbenzofurans ($M=202$) but a very small amount of heavy products. This could be due partly to the fact that the conversion of **1** was also much lower than with the other zeolites. On the other hand, CBV760 compared to the other zeolites contained a very small amount of entrapped acylated benzofuran. One possible explanation is the larger size of the pores resulting from dealumination, which allows to form bigger molecules especially in CBV760.

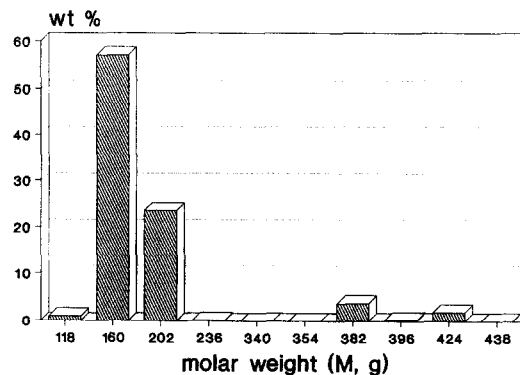


Fig. 8. Acylation of **1** (29 mmol) by **2** (371 mmol) over ZF520 at 333 K during 30 h, with **2** as the solvent. Molecular weight distribution of the coke.

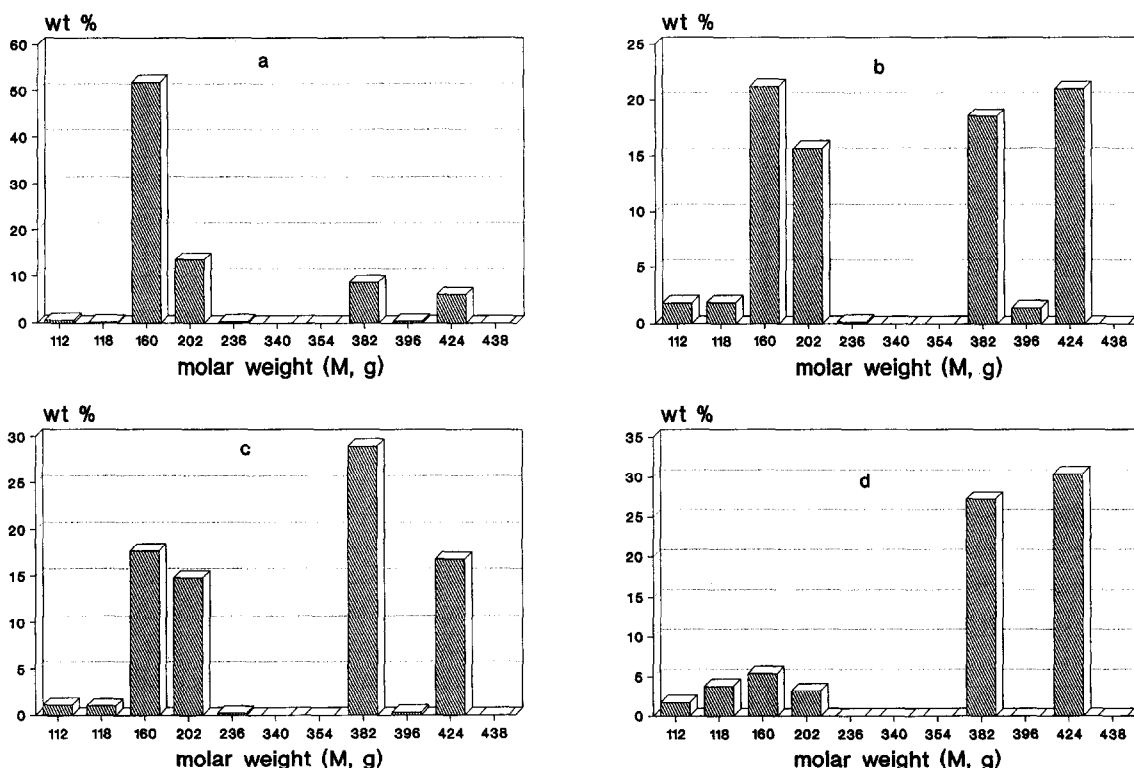


Fig. 9. Acylation of **1** (29 mmol) by **2** (58 mmol) at 333 K over Y zeolites during 30 h. Solvent: **4**. Molecular weight distribution of the coke. (a) LZY82, Si/Al=4.8; (b) CBV720, Si/Al=16; (c) ZF520, Si/Al=18; (d) CBV760, Si/Al=86.

Small molecules like **3** or diacylated benzofuran can plug the whole structure of LZY82 (and inhibit all kinds of reaction) more readily than in the case of the other zeolites. Another explanation could be that the diacylation or oligomerization would be easier on dealuminated zeolites because the acid sites are stronger.

4. Conclusion

The identification of the compounds present in the zeolites after reaction allows us to understand better how the catalyst functions, in particular how the reaction procedure affects the yield.

The low yield obtained when the benzofuran was introduced before the acylating agent could be due to the oligomerisation through a Diels–Alder type reaction of the substrate and the subsequent acylation of its dimer or trimer, which would give products entrapped in the zeolite, causing its rapid deactivation. This process was much

less effective when the acylating agent was introduced before and even less so when the concentration of this agent increased or when acetic acid was added to the reaction mixture. The differences in activity and in stability of the various zeolites can be explained by the differences in acidity and porosity, both of which can influence the nature of the compounds retained in the pore structure.

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References

- [1] Ng. Ph. Buu-Hoï, E. Bisagni, R. Royer and C. Routier, *J. Chem. Soc.*, (1957) 625–628.

- [2] T. Tomiyama, I. Tomiyama, T. Shirai, S. Wakabayashi, M. Futumara and S. Ichikawa, Jpn. Tokkyo Koho JP 03,261,778 [91,261,778]; C.A., 116 (1992) 151553x.
- [3] R.A. Sheldon, International Conference on Precision Process Technology. Perspective for Pollution Prevention, Delft, Netherlands, Kluwer Academic Publishers, Dordrecht, 1993, p. 125–138.
- [4] G. Pérot and M. Guisnet, International Conference on Precision Process Technology. Perspective for Pollution Prevention, Delft, Netherlands, Kluwer Academic Publishers, Dordrecht, 1993, p. 157–174.
- [5] G. Friedhoven, O. Immel and H.H. Schwartz, D.E. Pat. 2633458 (26.01.78); C.A., 88 (1978) 137904j.
- [6] B. Chiche, A. Finiels, C. Gauthier, P. Geneste, J. Graille and D. Pioch, J. Org. Chem., 51 (1986) 2128–2130.
- [7] W.F. Hoelderich, H. Lermer and M. Scharzmann, Ger. Offen. DOS 361 8964 (1987) BASF AG.
- [8] A. Finiels, A. Calmettes, P. Geneste and P. Moreau, Stud. Surf. Sci. Catal., 78 (1993) 595–600.
- [9] F. Richard, J. Drouillard, H. Carreyre, J.L. Lemberon and G. Pérot, Stud. Surf. Sci. Catal., 78 (1993) 601–606.
- [10] A. Cornelis, A. Gerstmans, P. Laszlo, A. Mathy and I. Zieba, Catal. Lett., 6 (1990) 103–109.
- [11] S. Fayed, M. Delmas and A. Gaset, J. Mol. Catal., 29 (1985) 19–31.
- [12] D.W. Breck and E.M. Flanigen, Molecular Sieves, Society of Chemical Industry, London, 1968, p. 47.
- [13] M. Guisnet and P. Magnoux, Appl. Catal., 54 (1989) 1–27.
- [14] D. Barthomeuf, Mater. Chem. Phys., 17 (1987) 49–71.
- [15] E.G. Derouane, J.M. André and A.A. Lucas, J. Catal., 110 (1988) 58.