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Zeolite-Catalyzed Acylation of Heterocyclic Compounds: Acylation of Benzofuran and 2-Methylbenzofuran in a Fixed Bed Reactor

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The acylation of benzofuran and of 2-methylbenzofuran by acetic anhydride was carried out over a Y zeolite (Si/Al atomic ratio = 16) in a dynamic flow reactor at 60°C, under atmospheric pressure. Deactivation was significant for benzofuran, but much less so for 2-methylbenzofuran with which high yields (about 100% conversion with 95% selectivity in 3-acetyl-2-methylbenzofuran) could be obtained. 2-Methylbenzofuran was about twice as reactive as benzofuran, the position 3 in 2-methylbenzofuran being at least two orders of magnitude more reactive than the position 3 in benzofuran. The difference in the aging process is attributed to a difference in the nature and the location of the irreversibly adsorbed material.

INTRODUCTION

Electrophilic aromatic substitution reactions are commonly carried out by using either protonic or Lewis acids in the liquid phase (1). Acylation reactions in particular require in most cases a stoichiometric amount of "catalyst" because carbonyl compounds (reactants as well as products) form stable complexes with Lewis acids such as $AlCl_3$ (2). One of the major drawbacks of this kind of chemistry is that it can cause much damage to the environment: the catalyst is not easy or impossible to recover, it is highly corrosive, and by hydrolysis it produces large amounts of corrosive by-products and salts (3–5). From this point of view, solid acid catalysts such as zeolites can offer definite advantages over soluble ones: they are easy to recover and produce no salts (4, 5). Moreover, continuous processes are easier to conceive using for instance fixed bed reactors. Several attempts have been made to use zeolites as catalysts in electrophilic aromatic substitution (6–10). Unfortunately there are very few examples up to now of zeolite-catalyzed reactions giving good yields in the field of functional compounds. This is mainly due to deactivation (10–13). One example is given here concerning benzofuran derivatives. At the present time, heterocyclic aromatic compounds such as benzofuran and related compounds are of interest in the field of pharmaceuticals (14, 15).

We found recently that 2-methylbenzofuran could be converted into 3-acetyl-2-methylbenzofuran (Scheme 1a) with about 100% yield in the presence of Y-zeolite at 60°C in the liquid phase (16). Deactivation was apparently much slower than in the case of benzofuran conversion into 2-acetylbenzofuran (Scheme 1b). With 2-methylbenzofuran the reaction was rapid enough and the catalyst stable enough to consider the possibility of carrying out the reaction conveniently at a low temperature in a fixed bed reactor.

The experiments reported in this article made it possible to measure more precisely the differences in reactivity of the two substrates, to understand better the aging process of the zeolite in the acylation of benzofuran and of 2-methylbenzofuran, and to show that the reaction was quite feasible under continuous conditions.

EXPERIMENTAL

Chemicals

Benzofuran (99.5%), 2-methylbenzofuran (96%), and chlorobenzene (99%) were purchased from Aldrich, and acetic anhydride (99%) from Janssen. They were used without further purification.

Catalyst

The unit cell formula of the commercial dealuminated Y-zeolite (CBV 720, CONTEKA) used in this study was $Na_{0.3}H_{11}Al_{11.3}Si_{180.7}O_{384}$ with 2.4 extraframework aluminum per unit cell. Knowing the composition of the zeolite and its framework Si/Al ratio, it was possible to obtain the unit cell formula. The composition of the zeolite was determined by chemical analysis (CNRS, Service Central d'Analyse, 69390 Vernaison, France). The framework Si/Al atomic ratio was deduced from the unit cell parameter (determined by X-ray diffraction, ASTM method D3942-80) using the equation given by Breck and Flanigen (17). The BET surface area (nitrogen adsorption measured at

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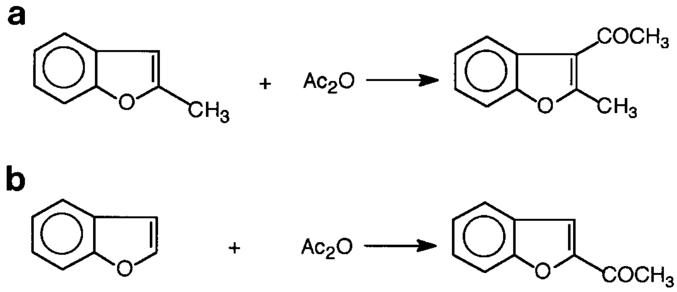


SCHEME 1. Acylation of (a) 2-methylbenzofuran into 3-acetyl-2-methylbenzofuran and (b) benzofuran into 2-acetyl-benzofuran.

$P/P_0 = 0.03$) was 780 $m^2 \cdot g^{-1}$ and its pore volume was 0.34 $cm^3 \cdot g^{-1}$. The ratio of the number of Brønsted acid sites to the Lewis acid sites determined by IR spectra of adsorbed pyridine was 4.7.

Procedure

The zeolite was pelletized and crushed so as to obtain particles with 0.2–0.4 mm diameter. The sample (250 mg in standard experiments) was calcined at 500°C in a pretreatment flow reactor (PR, Fig. 1) for 14 h under dry air flow. To avoid exposure to ambient atmosphere, the catalyst was then transferred while hot (by overturning the system under nitrogen flow) into the low temperature thermostated glass reactor (R, Fig. 1). The reactor had an internal diameter of 6 mm so that the catalyst bed was about 3 cm thick under standard conditions. The catalyst was maintained under dry nitrogen flow until reaction temperature (60°C) was reached. The reactant mixture (7.1 mol % benzofuran in acetic anhydride and 6.2 mol % of 2-methylbenzofuran in acetic anhydride under standard conditions) was introduced with a syringe pump at a flow rate of 3.6 $cm^3 \cdot h^{-1}$. The product mixture was condensed at the reactor outlet and the samples were analyzed periodically by gas liquid chromatography.

Chromatographic Analysis

The samples were analyzed with a Varian 3400 chromatograph equipped with a BP1 capillary column (length, 30 m; diameter, 0.25 mm; film thickness, 0.25 μm). The oven temperature was programmed from 70 to 230 °C (5°C per min) and maintained for 10 min at 230°C. The products were identified by adding aliquots of commercial compounds and by GC/MS analysis (Finnigan INCOS 500). The main products were isolated (see below) and identified by the usual techniques. Quantitative analysis was made possible by calibration with mixtures made from commercial compounds. Under the conditions specified above the calibration coefficients with respect to the substrates were as given in Table 1.

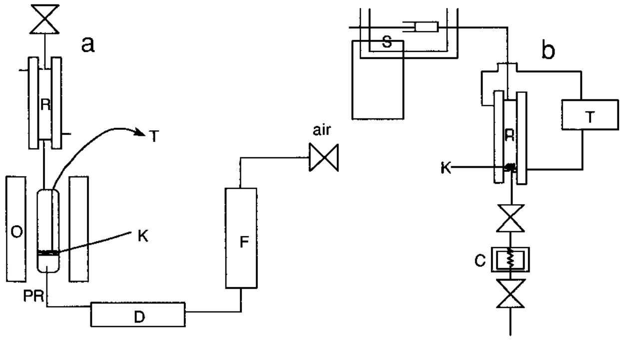


FIG. 1. Experimental system for pretreatment of the catalyst and continuous flow reaction. (a) Catalyst pretreatment: F, flowmeter; D. desicant; O. oven; PR, pretreatment reactor; K, catalyst; T, thermocouple. (b) Reaction: R, thermostated glass reactor; S, syringe; C, cooling system; T, thermostat; K, catalyst.

Separation and Identification of the Main Products

To verify the identification of the main products and the yield of the reaction as well as the quantitative gas chromatographic analysis, the product mixture obtained in two separate standard experiments (160 min for benzofuran and 120 min for 2-methylbenzofuran) were treated as follows. The reaction mixture (9.6 cm^3 for benzofuran and 7.2 cm^3 for 2-methylbenzofuran) was treated with an aqueous $NaHCO_3$ solution (0.7 $mol \cdot dm^{-3}$, 50 cm^3) to eliminate the unreacted acetic anhydride and acetic acid. The aqueous layer was extracted with CH_2Cl_2 (twice, 20 cm^3). The combined organic fractions were dried over anhydrous Na_2SO_4 and CH_2Cl_2 was eliminated using rotary evaporator. The products 2-acetylbenzofuran or 3-acetyl-2-methylbenzofuran were then recovered by flash chromatography (silicagel, cyclohexane/ethylacetate, 95 : 5). After elimination of the solvent, the reaction products were obtained in 26% (2-acetylbenzofuran from benzofuran), and 49% (3-acetyl-2-methylbenzofuran from 2-methylbenzofuran) yields. The gas chromatographic

TABLE 1

Calibration Coefficients with Respect to the Substrates

Substrate	Benzofuran	2-Methyl benzofuran	AcOH	Ac_2O	Monoacylated products	Diacylated products	Triacylated products
Benzofuran	1	—	7.3	3.4	0.80	0.67	0.57
2-Methylbenzofuran	—	1	8.2	3.8	0.82	0.69	0.60

analysis of the crude mixtures obtained from benzofuran and 2-methylbenzofuran gave yields of 27 and 55%, respectively.

The products were characterized by ^{1}H NMR (Bruker 200 MHz) and IR (Nicolet Magna 750 FTIR). The ^{1}H NMR spectrum of 2-acetylbenzofuran was identical to the one available in the literature (18), while that of 3-acetyl-2-methylbenzofuran was CD_2Cl_2, δ (ppm) = 2.55 (s, 3H); 2.7 (s, 3H); 7.23 (m, 3H); 7.8 (m, 1H). It could be noticed in particular that the signal at $\delta = 6.2$ ppm (1H) in the spectrum of 2-methylbenzofuran corresponding to the vinylic hydrogen in position 3 actually did not exist in the spectrum of 3-acetyl-methylbenzofuran, which indicated that acylation did occur in position 3. The IR spectra of the obtained 2-acetylbenzofuran and of a commercial sample were identical (main absorption bands: 1561 cm^{-1} (ν(C=C)); 1691 cm^{-1} (ν(C=O)). That of 3-acetyl-2-methylbenzofuran showed the main absorption bands at 1569 cm^{-1} (ν(C=C)) and 1678 cm^{-1} (ν(C=O)).

Coke Extraction

The extraction of the carbonaceous compounds deposited in the zeolites was carried out according to the procedure described by Guisnet and Magnoux (19). At the end of the reaction, the zeolite was recovered after having been left under nitrogen flow for another hour. The catalyst was then dissolved and stirred for 1 h in 10 cm^3 of a 40% aqueous solution of HF. No transformation of the carbonaceous compounds was caused. The organic layer was filtered, insoluble coke (graphitic particles) if any was weighted. The aqueous layer was then extracted with 20 cm^3 of CH_2Cl_2 and neutralized with $NaHCO_3$. The extraction process was carried out three times. The residue obtained by evaporation of the solvent was weighted and analyzed by GC/MS. The coke percentage was taken as the weight of residue × 100/weight of zeolite.

RESULTS

Activity, Stability, Reproducibility, and Regeneration

Both benzofuran and 2-methylbenzofuran were unreactive in the absence of a catalyst. Figure 2 shows the results of the acylation of benzofuran (Fig. 2a) and of 2-methylbenzofuran (Fig. 2b). The two substrates have a quite different behavior. The conversion of benzofuran decreases rapidly when time-on-stream increases, while that of 2-methylbenzofuran decreases more slowly and almost linearly. Moreover, the experiments are perfectly reproducible as shown with 250 mg and 60 mg of catalyst in the case of benzofuran and of 2-methylbenzofuran. In addition Fig. 2 shows that the activity of the catalyst can be totally recovered in both cases by a treatment under dry air for 12 h at 500°C (regenerated samples).

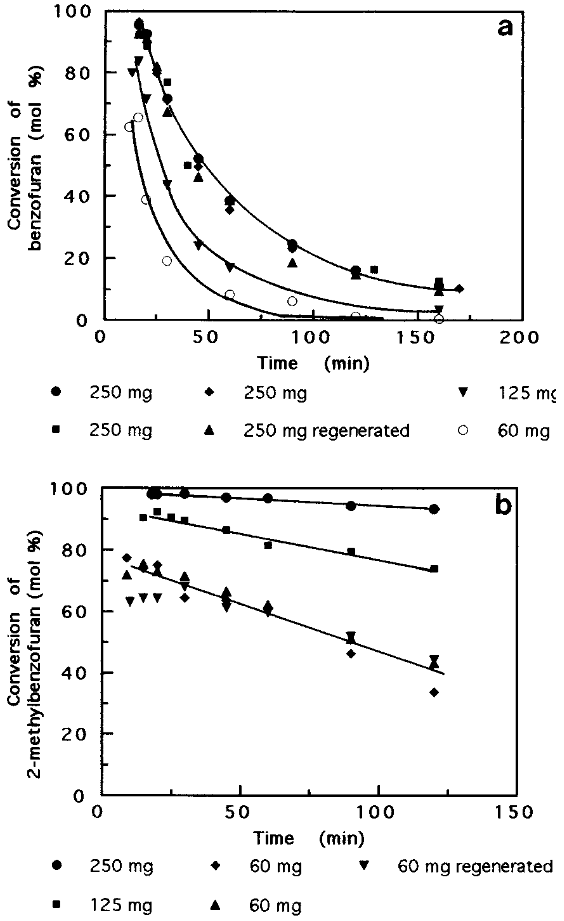


FIG. 2. Acylation of (a) benzofuran and (b) 2-methylbenzofuran on Y-zeolite at 60°C under atmospheric pressure. Effect of time-on-stream on the conversion. Reactants: benzofuran, 7.6 mol% in acetic anhydride (3.6 cm$^3 \cdot$ h^{-1}); 2-methylbenzofuran, 6.4 mol% in acetic anhydride (3.6 cm$^3 \cdot$ h^{-1}).

Reactivity

The results in Fig. 2 seem to imply that on the fresh catalyst both substrates have approximately the same reactivity. The difference in conversion which becomes very large when time-on-stream increases is probably due to a difference in deactivation.

Figure 3 shows the results obtained by reacting the substrates successively on two different samples of the catalyst in two different sequences. In Fig. 3a, benzofuran was made to react first and one could observe, as expected, the decrease in conversion as in Fig. 2a. After 2 h of reaction, 2-methylbenzofuran was substituted for benzofuran. Under these conditions the conversion of 2-methylbenzofuran was much lower than in Fig. 2b after the same time-on-stream and was only about twice that of benzofuran. In the experiment represented in Fig. 3b 2-methylbenzofuran was made to react first (sequence 1). Its conversion was about the same as in Fig. 2b under the same conditions. However, when ben-

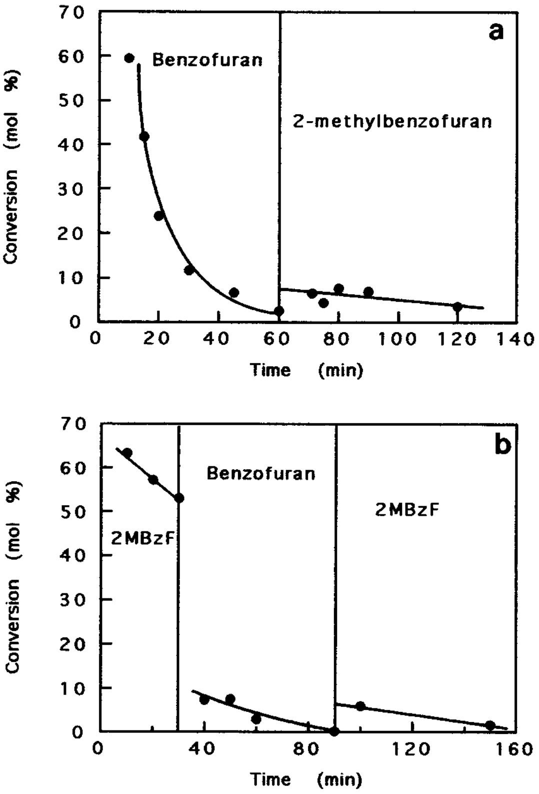


FIG. 3. (a) Benzofuran acylation followed by 2-methylbenzofuran acylation on the same sample of Y-zeolite (60 mg) at 60°C under atmospheric pressure (flow rates as in legend for Fig. 2). Effect of time-on-stream on the conversion. (b) Sequential acylation of 2-methylbenzofuran (2MBzF) and of benzofuran on the same sample of Y-zeolite at 60°C under atmospheric pressure. Effect of time-on-stream on the conversion.

zofuran was substituted for 2-methylbenzofuran (sequence 2), a very low conversion was obtained, about the same as the one which would have been obtained after 40 min on stream with benzofuran. When 2-methylbenzofuran was introduced again after benzofuran (sequence 3), its conversion was much lower than in sequence 1 but was about the same (with respect to the conversion of benzofuran) as in the experiment represented in Fig. 3a.

Irreversibly Adsorbed Material

Table 2 shows that after 2 h on stream with either of the two substrates irreversibly adsorbed material remained in large amounts on the catalyst recovered after reaction. Actually, the material obtained after dissolution of the zeolite in aqueous HF (19) and the treatment indicated in the Experimental section contained a few wt% of the reactants. With benzofuran, a significant amount of heavy products was also found, which was not the case with 2-methylbenzofuran. However, the main components found in the irreversibly adsorbed material were the reaction products themselves.

Product Distribution—Reaction Scheme

Effect of aging and of contact time. The product distribution was examined as a function of the conversion rate. Product distributions at various conversion rates could be obtained as a consequence of deactivation which occurred as time-on-stream increased and/or by changing the contact time by the use of different flow rates or varying the amount of catalyst.

Figure 2a shows the effect of the amount of catalyst and of time-on-stream in the case of benzofuran. The effect of the changes in conversion rate obtained (either through deactivation or by changing contact time) on the product distribution is shown in Fig. 4. With 2-methylbenzofuran, experiments were also carried out with various amounts of catalyst at a given flow rate of reactant (Fig. 2b). Figure 5 shows the effect of the conversion rate on the product distribution obtained by the acylation of 2-methylbenzofuran. It can be seen that the product distribution did not depend on the aging of the catalyst: the points (representing the proportions of the products) obtained with various quantities of catalyst are all on the same curves regardless of the aging of the samples.

Effect of the acetic anhydride/substrate molar ratio. Figure 6 shows that by increasing the acetic anhydride/substrate molar ratio the conversion with both substrates increases. By decreasing the acetic anhydride/substrate molar ratio the selectivity in the desired product for a conversion rate of the substrate of about 20% improves (Fig. 7).

Reactivity of the primary products. The reactivity of the major primary products in the presence of acetic anhydride was examined in both cases under the same reaction con-

TABLE 2

Irreversibly Adsorbed Material after 2 h on Stream

		Main components (wt%)				
Substrate	wt% in the zeolite	Reactants	Monoacylated	Diacylated	Triacylated	Other heavy products
Benzofuran	21.0	3.2	69.5	14.0	2.0	11.3
2-Methylbenzofuran	24.2	5.3	83.6	8.0	2.4	0.7

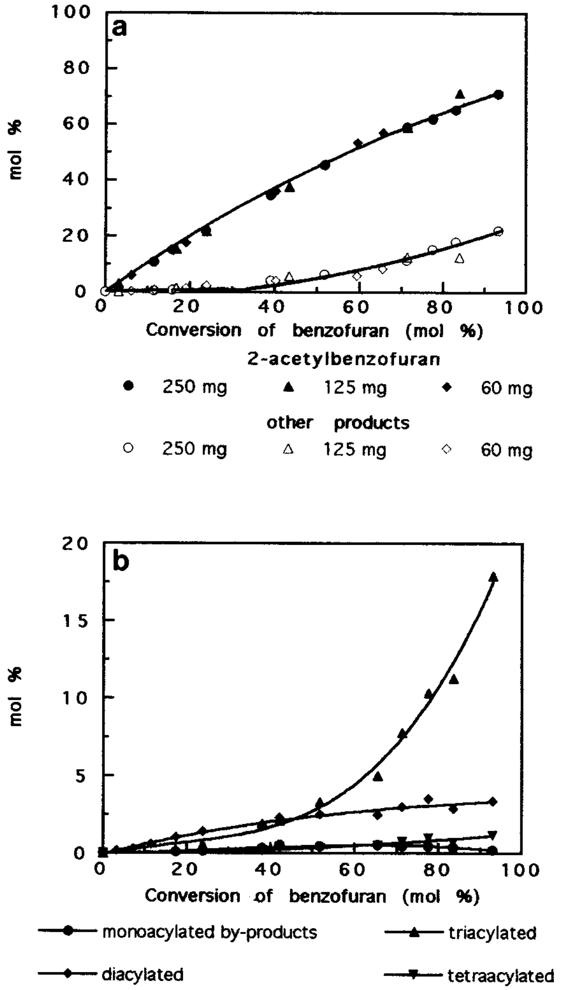


FIG. 4. Acylation of benzofuran on Y-zeolite at 60°C under atmospheric pressure. Effect of the conversion on (a) the total product distribution and (b) the distribution of the minor products.

ditions as those for benzofuran and 2-methylbenzofuran. Figure 8 shows that deactivation occurred both with 2-acetylbenzofuran and with 3-acetyl-2-methylbenzofuran as reactants. 2-Acetylbenzofuran was at least four times more reactive than 3-acetyl-2-methylbenzofuran.

Figure 9 shows the product distribution obtained from 2-acetylbenzofuran (the products which were only present in trace amounts were not considered). At a conversion below 10% a single product (diacetylbenzofuran) was formed. At a higher conversion it disappeared to give principally one of the triacylated products. Up to now it has not been possible to identify precisely the major product (diacetylbenzofuran) formed initially on the basis of GC/MS analysis. It can be suspected to be 2,3-diacetylbenzofuran.

As shown in Fig. 10 3-acetyl-2-methylbenzofuran gave only traces of the diacylated compounds and gave a triacylated methylbenzofuran as major product.

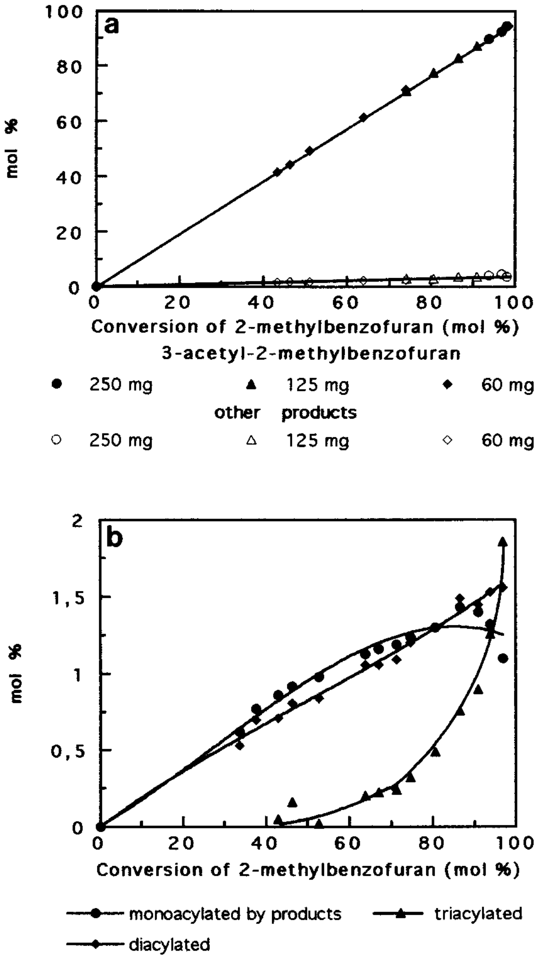


FIG. 5. Acylation of 2-methylbenzofuran on Y-zeolite at 60°C under atmospheric pressure. Effect of the conversion on (a) the total product distribution and (b) the distribution of the minor products.

DISCUSSION

Catalyst activity

As was the case in a batch reactor (10, 16), we show here that deactivation was much more pronounced with benzofuran than with 2-methylbenzofuran. Moreover, the aging process with the two substrates was not the same: activity loss was exponential with benzofuran but more or less linear with 2-methylbenzofuran. However, total reactivation under oxidizing conditions was also possible.

The difference in the deactivation process between the two substrates is not easy to understand for the moment. Actually the amount of irreversibly adsorbed material was about the same and was even slightly larger in the case of 2-methylbenzofuran with which the deactivation was slower. The compounds found in the irreversibly adsorbed material were mainly the acylation and diacylation products, save for the heavier products found with benzofuran as substrate.

The quantity of acylation and diacylation products

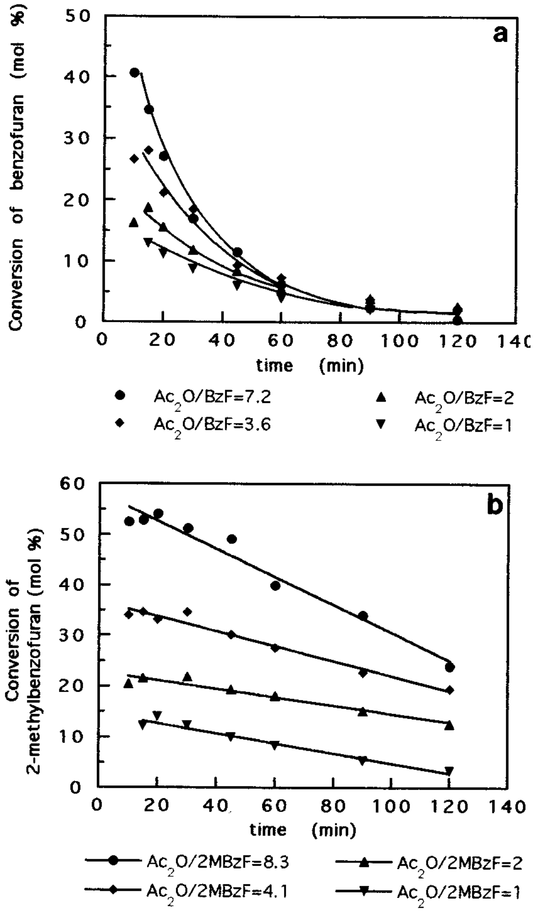


FIG. 6. Acylation of (a) benzofuran and (b) 2-methylbenzofuran on Y-zeolite at 60°C under atmospheric pressure. Effect of the acetic anhydride/substrate molar ratio on the conversion. BzF, benzofuran; 2MBzF, 2-methylbenzofuran.

correspond to about 7.5 × 10^{20} and 8.4 × 10^{20} molecule · g^{-1} with benzofuran and 2-methylbenzofuran, respectively, which means slightly over one molecule of retained product per acid site (according to its unit cell formula the zeolite contains 5.7 × 10^{20} sites · g^{-1}, see Table 1). Taking into account the fact that both substrates lead to similar amounts of irreversibly adsorbed material with much less deactivation in the case of 2-methylbenzofuran, it can be concluded that if these compounds were responsible for deactivation, entrapped acetyl- or diacetyl-2-methylbenzofuran would be much less toxic to Y-zeolite than entrapped acetyl- or diacetylbenzofuran, either because of their structure or of their location. The reason for this is not clear and further studies will be necessary to verify this hypothesis. Moreover, since the loss in activity is very small with 2-methylbenzofuran even with 24 wt% of adsorbed material we could consider that in this case most of the activity resides on the outer surface of the zeolite crystals (even with the fresh catalyst).

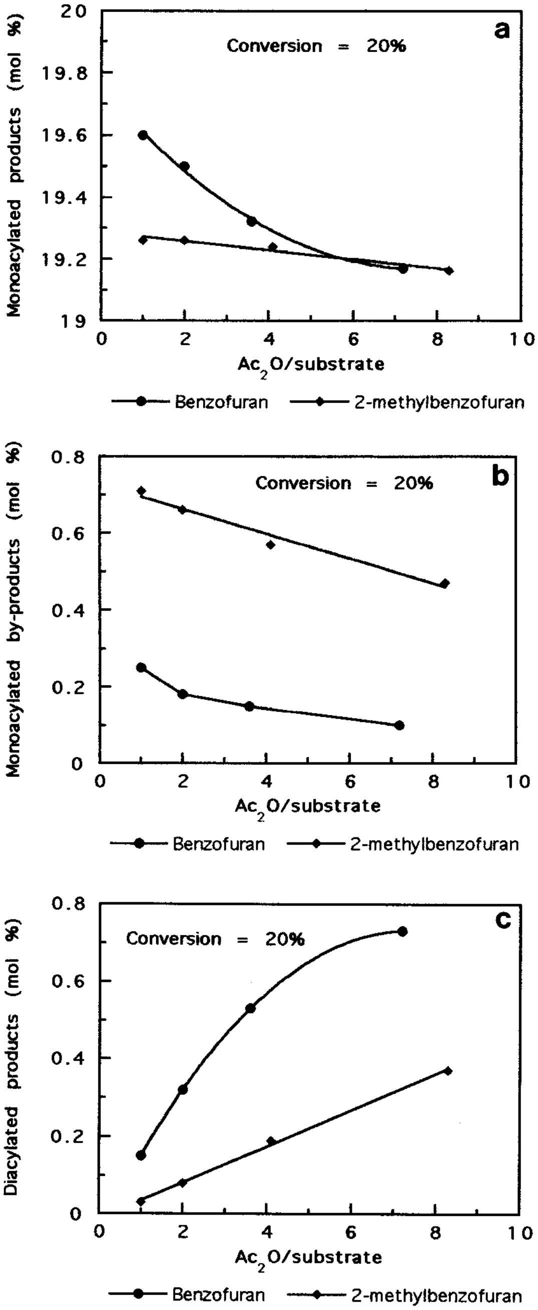


FIG. 7. Acylation of benzofuran and of 2-methylbenzofuran on Y-zeolite at 60°C under atmospheric pressure. Effect of the acetic anhydride/substrate molar ratio on the conversion into (a) the main product, (b) the monoacylated by-products and (c) the diacylated by-products at 20% conversion.

It seems more realistic, however, to assume that deactivation is caused mainly by the heavier compounds found in larger amounts with benzofuran than with 2-methylbenzofuran. These compounds found in much larger amounts when the acylation was carried out in a batch reactor were identified as acylated benzofuran trimers (16) and can indeed be considered as the actual cause for deactivation. Therefore, the difference in deactivation between

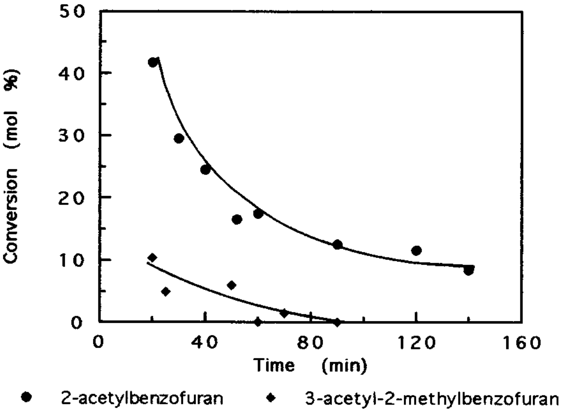


FIG. 8. Acylation of 2-acetylbenzofuran and of 3-acetyl-2-methylbenzofuran with acetic anhydride on Y-zeolite (60°C, atmospheric pressure). Effect of time-on-stream on the conversion.

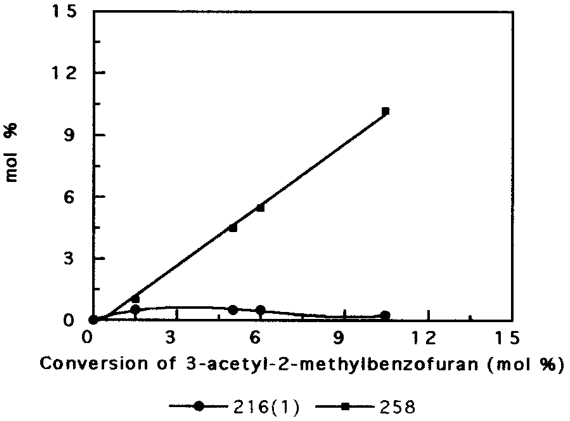


FIG. 10. Acylation of 3-acetyl-2-methylbenzofuran with acetic anhydride (60°C, atmospheric pressure). Effect of the conversion on the distribution of the main products represented according to their mass numbers. 216, diacetylated product; 258, triacetylated product.

benzofuran and 2-methylbenzofuran can be ascribed to a lesser tendency for the latter to form polymeric species, as found in the presence of Lewis acids (20).

Reaction Schemes and Mechanism

Deactivation made it difficult to compare reactivities of the two substrates. If we consider conversion rates at time-on-stream close to zero it seems that benzofuran and 2-methylbenzofuran have approximately the same reactivity (Figure 2) although with benzofuran because of the rapid deactivation the reactivity is difficult to estimate. Actually Fig. 3a shows that if 2-methylbenzofuran is allowed to react on a catalyst which has been previously deactivated with benzofuran as substrate, its conversion is roughly double that of benzofuran. The difference in reactivity was approximately the same in a batch reactor (16) and consistent with the results obtained with traditional catalysts (20). This is confirmed by the results in Fig. 3b (compare sequences 2 and 3) which show, moreover, that whereas 2-methylbenzofuran causes a very slow deactivation of its own transformation (sequence 1), it is much more toxic regarding benzofuran transformation and causes about the same deactivation as benzofuran itself during the same time-on-stream (sequence 2). If we compare sequences 1 and 3 in Fig. 3b, it can be seen that sequence 2 with benzofuran causes a severe deactivation of the catalyst with respect to 2-methylbenzofuran although this deactivation is not apparent with its own transformation.

As can be seen from Figs. 4 and 5 the reaction is highly selective in both cases. Benzofuran leads to 2-acetylbenzofuran and 2-methylbenzofuran leads to 3-acetyl-2-methylbenzofuran. As already indicated (10), the reaction involves the activation of the acylating agent on the protonic sites of the zeolite followed by the transfer of an acylium ion from (I) to the substrate to give the Wheland complex (II) (Scheme 2).

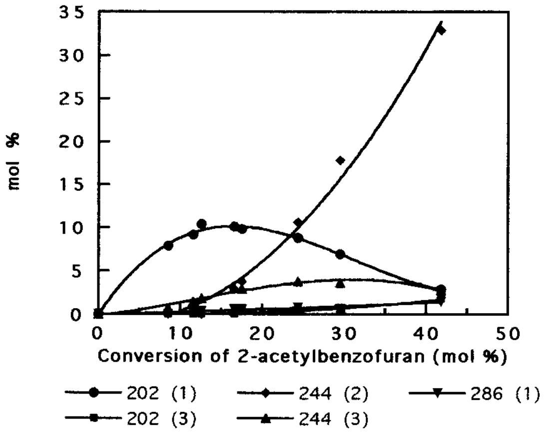
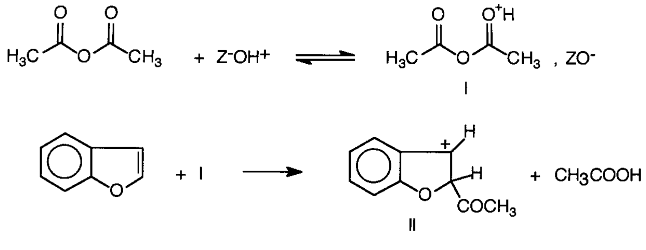
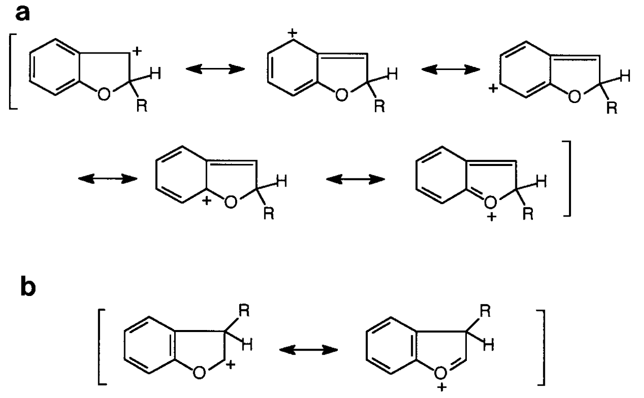


FIG. 9. Acylation of 2-acetylbenzofuran with acetic anhydride on Y-zeolite (60°C, atmospheric pressure). Effect of the conversion on the distribution of the main products represented according to their mass numbers. 202, diacetylated products; 244, triacetylated products; 286, tetraacetylated product. The numbers in parentheses represent the order of elution of the isomers in gas chromatography.



SCHEME 2. Activation of acetic anhydride on a zeolite protonic site.



SCHEME 3. Mesomeric forms in the Wheland intermediates resulting from the electrophilic attack at position (a) 2 or (b) 3 in benzofuran.

Position 2 in benzofuran is more reactive than position 3 because of the better stabilization of the corresponding Wheland complex (Scheme 3). The electrophilic attack at position 2 leads to five resonance structures (Scheme 3a) whereas attack at position 3 leads only to two (Scheme 3b).

In 2-methylbenzofuran the only position available for electrophilic substitution is position 3. The corresponding Wheland complex is more stable than with benzofuran because of the donor effect of the methyl group which stabilizes partly the cationic charge. 2-Methylbenzofuran is about twice as reactive as benzofuran and the reaction takes place exclusively at position 3 in 2-methylbenzofuran while benzofuran gives only trace amounts of 3-acetylbenzofuran. This indicates that the position 3 in 2-methylbenzofuran is at least two orders of magnitude more reactive than in benzofuran, as was found also in a batch reactor (16).

The difference in reactivity of the primary products (Fig. 8) explains also why the acylation of 2-methylbenzofuran is much more selective than that of benzofuran.

CONCLUSION

Both benzofuran and 2-methylbenzofuran can be acylated by acetic anhydride in the presence of Y-zeolite under mild conditions. However, 2-methylbenzofuran is more reactive than benzofuran, its 3-position being at least two orders of magnitude more reactive than in benzofuran. The other positions available in 2-methylbenzofuran are much less reactive as shown by the results obtained with the primary product, which explains that a high yield (about 95%) in 3-acetyl-2-methylbenzofuran can be obtained.

Moreover, 2-methylbenzofuran deactivates the catalyst much less than benzofuran. Although this phenomenon is not yet understood it makes it possible to carry out the reaction conveniently in a flow reactor.

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