# A Lewis Acid Site-Activated Reaction in Zeolites: Thiophene Acylation by Butyryl Chloride

## Yu. Isaev and J. J. Fripiat[1]

*Department of Chemistry and Laboratory for Surface Studies, University of Wisconsin—Milwaukee, P.O. Box 413, Milwaukee, Wisconsin 53201*

The acylation of thiophene by butyryl chloride has been studied in the liquid phase in the presence of 12 catalysts: HZSM-5, H-mordenite, and HY (ultrastable Y) with various framework Si/Al ratios, various numbers of Brønsted and Lewis sites, and various amounts of nonframework aluminum. The numbers of Brønsted and Lewis acid sites were obtained by FT-IR using chemisorbed ammonia, as described elsewhere. There is a correlation between the initial rates of reaction and the number of Lewis acid sites, whereas there is no correlation between the initial rates and the number of Brønsted sites. The correlation with the number of Lewis sites may be considered significant, since it expands on more than one order of magnitude. Poisoning of the catalyst probably results from the oligomerization on butyryl chloride. No carboxylic acid has been detected in the course of the reaction. No attempt has been made to determine the nature of the poisoning reaction.    © 1999 Academic Press

## INTRODUCTION

The acylation of aromatic molecules by acid chlorides RCOCl is a classic example of an electrophilic substitution catalyzed by Lewis acids. A sustained attention to the possibility of replacing the environmentally, unfriendly inorganic chlorides (such as $AlCl_3$, $FeCl_3$ or $SnCl_4$) by H- or rare-earth metal-exchanged zeolites is evident in numerous papers and reviews (1–5).

The main accent in those publications is on the yield in acylated products and less on the nature of the acid sites catalyzing the reaction. However, the influence of the porosity and of the hydrophobicity on the acylation reaction has also been studied (6–8), as has the influence of the dealumination of the zeolite (8–14). Boreskova *et al.* (15) assumed that the reaction took place on Lewis sites, while Corma *et al.* (8) in 1989 suggested the intervention of protonic acidity on the basis of the activity of partially sodium-exchanged HY zeolites. Interestingly, Corma *et al.* (8) observed that HZMS-5 calcined at 550°C has a very low activity despite a large intrinsic Brønsted acidity. On calcination at that temperature the content of nonframework

aluminum (NFAl) in HZSM-5 is low and the number of Lewis sites is small (18), while with HY and H-mordenite (16–18) the content of NFAl and number of Lewis sites are much larger.

At the time, restriction due to the molecular traffic in the porous system in these zeolites, compared with that in the Y or $\beta$ molecular sieves, was invoked by Corma *et al.* as a possible cause explaining the very low activity of HZSM-5. Since, as will be shown here, HZSM-5 becomes much more active when steaming brings about NFAl in the porous structure, while decreasing the number of Brønsted sites, the role of Lewis acidity has to be reconsidered.

Based on the study of acylation of benzofuran by acetic acid on Y-zeolites with framework (Si/Al) ratios between 4.8 and 86, Richard, Carreyre, and Pérot (11–13) observed a maximum activity for a ratio close to 15 and, simultaneously, and not surprisingly, a maximum in the coke formation. They concluded that the maximum activity results from a compromise between the number and the strength of protonic acid sites.

Gaare and Akporiaye (14), in the study of the Friedel–Crafts acylation of anisole by acetyl chloride on dealuminated Y-zeolite, observed an increase in the yield of the *p*-substituted product as the Al content of the lattice decreased. The increase in activity was attributed to the increase in hydrophobicity of the more siliceous lattice.

We must confess that we do not understand why hydrophobicity would represent an asset in reactions occurring without production of water. In addition, none of the referred papers has given the number of Brønsted or Lewis acid sites per gram of catalyst, which should be done as a prerequisite to the discussion on their respective influences, as should the heat of water adsorption be measured when referring to hydrophobicity.

The goal of the present contribution is to study the nature of the catalytic acid sites in the acylation of aromatics (thiophene and toluene) with acyl chloride (butyryl) in a solution (chlorobenzene) at ~100°C on different zeolites. The activities of steamed HZSM-5, H-mordenite, ultrastable Y, and fluorinated and dealuminated USY with different Si/Al ratios and Brønsted and Lewis site contents were compared.

[1] To whom correspondence should be addressed.

257

It will be shown that the initial rates correlate well with the number of Lewis sites and not with the number of Brønsted sites. The increased hydrophobicity which could be expected from the increase in the Si/Al framework ratio may play a role, if no nonframework Al is formed.

The yield in acylated products is generally two orders of magnitude higher than the number of Lewis sites, showing that the catalytic reaction is not stoichiometric in the consumption of the sites.

## EXPERIMENTAL

### Materials

The initial mordenite and USY zeolites are commercial PQ products with Si/Al ratios of 5.3 and 4.9, respectively. ZSM-5 is a commercial product of Angarskneftorgsynthesis Company. Toluene, thiophene, butyryl chloride, nitrobenzene, and chlorobenzene of analytical purity were purchased from VWR Scientific and used without further purification.

Fluorinated USY zeolites were prepared according to Panov *et al.* (19) in calcining USY impregnated with $NH_4F$. This treatment increases the framework Si/Al NMR ratio and reduces the number of Brønsted and Lewis sites. Without fluorination an increase in the number of Lewis sites results from an increase in that ratio. It was suggested that the substitution of OH by F on the NFAl decreases the probability of forming coordinately unsaturated Al (19).

The steaming of ZSM-5 was carried out in the quartz reactor. The sample was heated up to the temperatures shown in Table 2 at the rate of $2°C/min$ in oxygen and exposed to a flow of oxygen coming through water kept at $80°C$. At various lengths of time the steam was exchanged with the flow of dry oxygen and the sample was cooled down.

### Characterization of Materials

All catalysts were characterized by X-ray diffraction. XRD spectra were obtained by using a Scintag X-ray diffractometer (Cu$K\alpha$ radiation) and a scan rate of $5°/min$. The full sorption, $N_2$ adsorption, and desorption measurements were performed on an automated physisorption instrument (Omnisorp 100, Coulter Corp.). The Si/Al ratio in the modified zeolites was obtained from $^{29}Si$ NMR data, as described previously (16–18).

All the physical characterizations (XRD and $N_2$ porosity measurements) confirm that the modifications brought about by the dealumination treatments were those expected (19, 20) and that they did not deeply alter the lattice structure.

The measurements of the acidity of these zeolites were carried out as described previously (18), with FT-IR spectroscopy using $NH_3$ as a probe molecule. The FT-IR spectra were recorded on zeolites having chemisorbed $NH_3$ and outgassed at five different temperatures in the interval 115–350°C for 30 min. With knowledge of the extinction coefficients of the $NH_4^+$ and $NH_3$ bending modes and the integrated intensities, the absolute numbers of Brønsted or Lewis sites remaining at increasing temperatures were determined. At 115°C under vacuum, it is considered that all physically adsorbed species are removed. The number of Brønsted sites is obtained by fitting $NH_4^+$ data with a Langmuir desorption isobar. Since the heat of chemisorption of ammonia on Lewis sites can be described by a Freundlich isotherm, and consequently, $\ln n_{ads} = a + b/T$, the concept of site saturation is meaningless. It has been suggested that at 115°C the corresponding amount of chemisorbed $NH_3$ represents the amount of Lewis sites, because it is adsorbed with a differential heat equal to or larger than 100 kJ/mol, up to $\sim$200 kJ/mol (21). The physical adsorption energy and the energy of most hydrogen bonds is much lower than 100 kJ/mol.

The accuracy or the number of Brønsted and Lewis sites determined in that way and shown in Table 1 can be estimated to be about 10%. The sum of these two populations compared well with the ASTM test operated on samples outgassed at 115°C (18). The characteristics of the Lewis acidity will be commented on later.

In support of the accuracy of the FT-IR data, it is worth mentioning the very good correlation found between the absolute numbers of acetone and $NH_3$ adsorbed on Brønsted sites and the calculated number of protonic sites (22).

Thus, the results shown in Table 1 provide a safe basis for assigning the catalytic activity to either one of the possible acid sites. In Fig. 2 the errors corresponding to the determination of the Lewis sites are indicated for the three top values. For the others these errors correspond approximately to the thickness of the symbols.

### Catalytic Activity Measurements

*Catalyst activation.* The zeolite was heated in the flow of dry oxygen up to 150°C for 2 h and kept for 1 h at this temperature. The temperature was then increased to 250°C over 2 h and kept at this temperature for 1 h. Finally, the catalyst was heated to 450°C over 4 h and kept at this temperature for 2 h.

*Acylation process.* The reaction was carried out under the atmosphere of dry argon in a glass flask with a condenser. The mixture of $10^{-2}$ mol thiophene and of $10^{-2}$ mol butyryl chloride in 50 ml chlorobenzene was heated to 100°C. Nitrobenzene ($8.8 \times 10^{-3}$ mol) was used as the internal standard to follow the changes in the concentrations. The pretreated zeolite (0.15 g for the study of thiophene) was added to the stirred solution, carefully preventing its contact with atmospheric moisture. Samples were analyzed periodically by GC (Perkin-Elmer 8500,. TC-detector) using a $6 \times \frac{1}{8}$-in. packed column (10% OV-101 on

Chromosorb W-HP, 80/100). It should be emphasized that no carboxylic acid has been detected with GC/MS. Blank tests, without catalyst, at the same temperature have shown no reaction in the acylation of either toluene or thiophene.

### Analytical Treatment of the Experimental Data

Let $Y$ be the yield (%) in acylated product. If $C_A^{(t)}$ and $C_A^0$ are the concentrations in thiophene (Th) at time $t$ and time $t = 0$, respectively, we define the initial rate as

$$\left(\frac{dY}{dt}\right)_{t\to 0} = 100\, d\left(1 - \frac{C_A^{(t)}}{C_A^0}\right) \Big/ dt.$$

It is observed that the consumption of thiophene from the liquid phase matches the formation of 2-butyryl thiophene (2-BTh) very well .

On the opposite, the consumption of butyryl chloride is always higher than the yield in 2-BTh. Oligomerization of butyryl chloride probably occurs and this contributes to the poisoning of the catalyst.

For practical purposes, the initial rate of acylation is obtained from the linear regression of $Y$ versus time for a short time. The standard deviation ($R^2$) is usually better than 0.9 for at least five experimental points, and the error on the initial rate is that on the slope of the regression.

Since this contribution deals solely with the initial rates and the nature of the acid sites catalyzing the acylation reaction, we did not try to analyze the catalyst as to the nature of the coke formed during the reaction. Also, we did not try to measure the adsorption of reagents or reaction products by the zeolites. Such studies have been performed by Richard *et al.* (12, 13).

### RESULTS

#### Acylation of Toluene

Preliminary experiments were performed in the acylation of toluene with butyryl chloride (BC) to define the

**TABLE 1**

**Numbers of Brønsted and Lewis Sites in the Catalysts Used in This Work (mmol/g)**

| Catalyst | Brønsted sites | Lewis sites | NMR, Si/Al |
|---|---|---|---|
| 1. HZSM-5 (initial) | 0.81 | 0 | 16 |
| 2. HZSM-5 steamed for 60 min at 550°C | 0.81 | 0 | ~16 |
| 3. HZSM-5 steamed for 15 min at 600°C | 0.71 | 0 | 17.4 |
| 4. HZSM-5 steamed for 30 min at 600°C | 0.28 | 0.11 | 36.4 |
| 5. HZSM-5 steamed for 45 min at 600°C | 0.07 | 0.13 | 40.5 |
| 6. HZSM-5 steamed for 75 min at 600°C | 0.2 | 0.12 | 34.7 |
| 7. HZSM-5 steamed for 120 min at 600°C | 0.1 | 0.16 | n/a |
| 8. HZSM-5 steamed at 700°C | 0.06 | 0.17 | n/a |
| 9. H-mordenite | 0.82 | 0.21 | n/a |
| 10. USY initial | 1.42 | 1.43 | 4.9 |
| 11. USY1.5F | 0.83 | 1.0 | 6.6 |
| 12. USY3F | 0.42 | 0.88 | 12.1 |
| 13. USY5F | 0.62 | 0.78 | 14 |

experimental conditions. Although butyryl chloride is an active acylation reagent (7), the yield of the reaction never exceeded ~30% on USY, USY1.5F, and USY5F catalysts, which, as shown later, are the most active catalysts. In these catalysts, the numbers of Brønsted and Lewis sites are fortuitously close to one another and, thus, at this preliminary stage of the study the activity cannot be assigned to either kind of site (Table 1). The initial USY with the larger number of Brønsted and/or Lewis sites is the most active. As shown in Fig. 1, the reaction slows down earlier on USY then it does for USY5F which contains the lowest number of Brønsted and/or Lewis sites.

The interpretation of these observations is simple, if we admit that a poisoning reaction occurs more rapidly on the
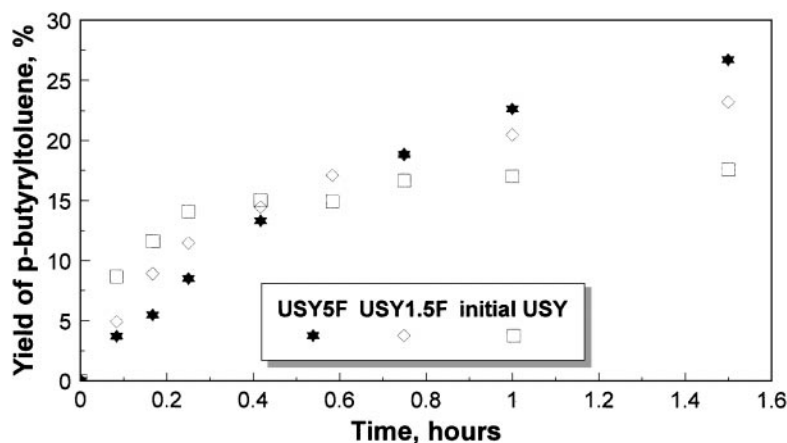


**FIG. 1.** Acylation of toluene at 100°C versus reaction time, catalyzed by USY, USY1.5F, and USY5F (see Table 1).

most active catalyst. As confirmed by GC/MS the product of the reaction is *p*-butyryltoluene; no other product is detectable in the liquid phase. However, deactivation of Y-zeolites has been reported for similar reactions (8, 11–13) and oligomerization of acetylchloride (25) has been suggested.

Additionally, we have found that when USY is used as catalyst at 110°C and for ~5 h the yields of *p*-butyryltoluene increase quasi-linearly with the weight of catalyst. The yield was 21% with 1 g of catalyst, 9% with 0.5 g of catalyst, and ~4% with 0.25 g catalyst. The reaction of thiophene being less easily poisoned, the complete set of 12 catalysts shown in Table 1 was studied under the experimental conditions detailed earlier and in the presence of (0.15 g) catalyst.

*Acylation of Thiophene*

There are several examples of the use of zeolites as catalysts for the acylation of aromatic heterocycles (11–13, 24). The reaction has an almost quantitative yield and high selectivity. As said before, the equality between the amount of thiophene consumed and the amount of 2-BTh as well as a larger than expected consumption of BC are the two general characteristics of the reaction. In Fig. 2 are represented a few examples of the evolution of the yield Y with time.

It is not a simple matter to evaluate the extent of the secondary reaction. BC can be adsorbed by the zeolite and we do not know the amount of 2-BTh remaining in the catalyst. A very rough estimate of the extent of the polymerization reaction is between 5 and 10% of the initial BC content for the majority of the reactions listed in Table 2. The initial rates of formation of 2-BTh are given in Table 2.

The initial ZSM-5, which does not contain Lewis sites in measurable amounts, has very low activity in the acylation of thiophene. Mordenite is much more active. The highest activity was observed in the presence of USY with the maximum Lewis site content. Those results indicate an increase in the acylation rate with the number of Lewis sites, irrespective of the pore size. Differences in the structure of the catalyst might additionally affect the catalytic activity of the zeolite. It has been shown (20) that steaming of ZSM-5 for different times at increasing temperatures up to 800°C and fluorination of USY do not appreciably modify the pore structure.

As shown in Fig. 3, the initial rates of acylation increase with increasing number of Lewis sites. Even if one considers that the 12 catalysts distribute themselves into five groups (no Lewis site, HZSM-5 with slightly increasing content in Lewis sites, H-mordenite, fluorinated USY, and initial USY), the trend is clear. Starting ZSM-5 and ZSM-5 steamed for 15 min have the lowest rates of acylation. In
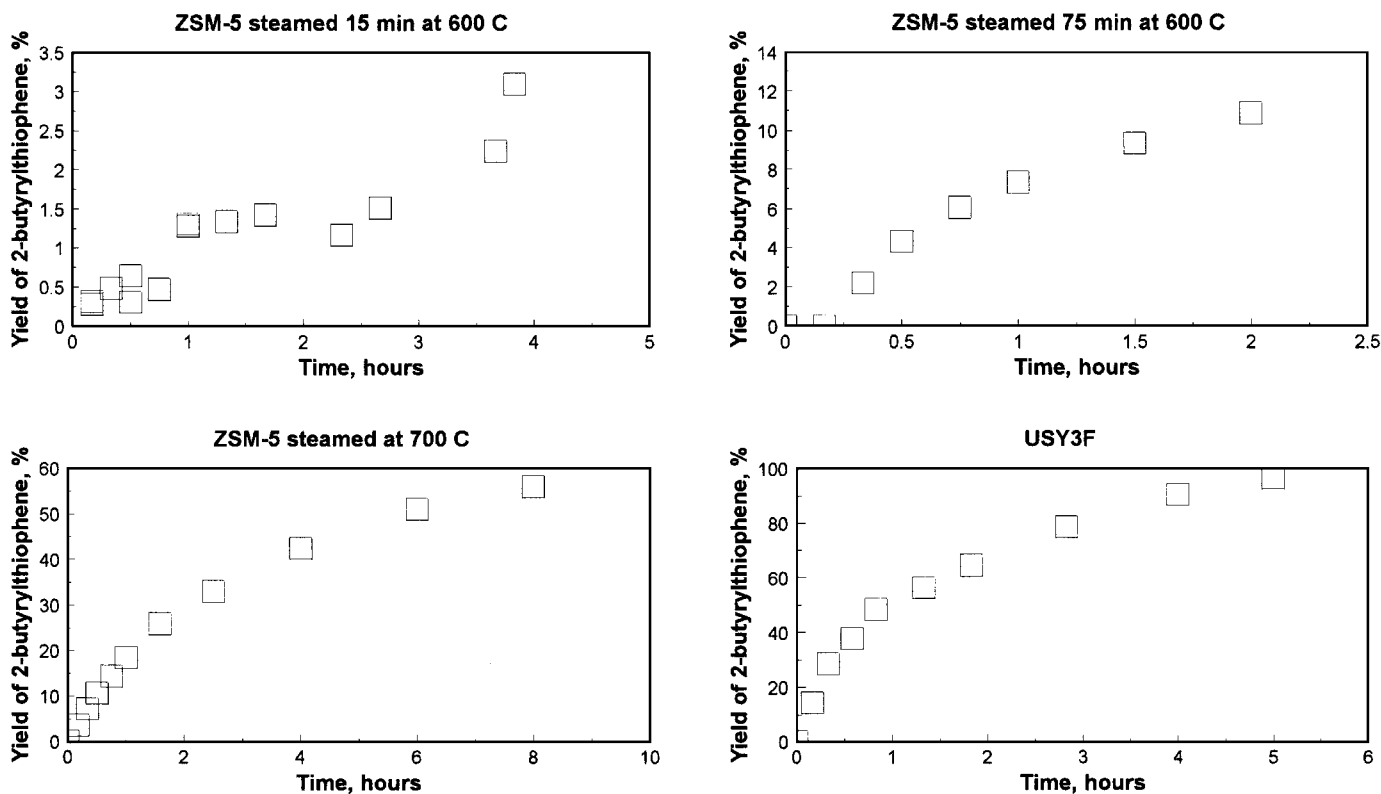


**FIG. 2.** Yield (%) of the acylation of thiophene versus reaction time.

## TABLE 2

**Parameters of the Acylation Reaction of Thiophene with Butyryl Chloride at 110°C Listed by Order of Increasing Content of Lewis Acid Sites (see Table 1)**

| Catalyst | Lewis acid sites (mmol/g) | $dY(\%)/dt,$ $t \to 0$ |
|---|---|---|
| 1. Initial HZSM-5, st.[a] | 0 | $0.9 \pm 0.5$ |
| 2. HZSM-5 steamed for 60 min at 550°C, st. | 0 | $0.5 \pm 0.1$ |
| 3. HZSM-5 steamed for 15 min at 600°C, st. | 0 | $0.6 \pm 0.1$ |
| 4. HZSM-5 steamed for 30 min at 600°C, st. | 0.11 | $8.4 \pm 1.1$ |
| 6. HZSM-5 steamed for 75 min at 600°C, st. | 0.12 | $7.6 \pm 0.5$ |
| 5. HZSM-5 steamed for 45 min at 600°C, st. | 0.13 | $10.1 \pm 0.9$ |
| 7. HZSM-5 steamed for 120 min at 600°C, st. | 0.16 | $14.6 \pm 1.3$ |
| 8. HZSM-5 steamed at 700°C, st. | 0.17 | $16.3 \pm 0.9$ |
| 9. H-mordenite, st. | 0.21 | $28.3 \pm 1.8$ |
| 13. USY5F, n.st. | 0.78 | $76.4 \pm 18.4$ |
| 12. USY3F, n.st. | 0.88 | $63.5 \pm 4.4$ |
| 10. USY, n.st. | 1.43 | $91.0 \pm 13.2$ |

[a] st., stoichiometric mixture; n.st., mixture of 2 butyryl chloride for 1 thiophene.

samples steamed for 30–75 min the rate is 3–10 times higher. ZSM-5 steamed at 700°C has maximal activity. The change in activity in the set of fluorinated zeolites shows the same tendency. The most active catalyst in this row is the initial USY.

The dependence with respect to the number of Lewis sites is clear for the 12 catalysts that were studied, while the variation with respect to the number of Brønsted sites is incoherent. The same initial experimental rates are plotted versus the Brønsted acid site content in Fig. 4. The activity decreases with an increase in the number of Brønsted sites for the HZSM-5 samples, while it increases with that number for the USY, USY3F, and USY5F catalysts in which the numbers of Lewis and Brønsted sites vary in the same way. H-mordenite and the initial HZSM-5 have the same number of Brønsted sites, but the initial rate of the reaction is about 25 times larger on H-mordenite than in HZSM-5, in good correlation with the difference between their content of Lewis sites. As far as the activity of HZSM-5 is concerned, the explanation presented by Corma *et al.* (8) deals with the hydrophobicity of the lattice. Still, the initial rate of reaction is multiplied by a factor of 10 after calcination at 700°C, as compared with that of HZSM-5, calcined at 600°C for 15 min.

In conclusion, assigning the activity of acid zeolites to Lewis activity fits the experimental observation satisfactorily. Still, among the remaining questions is the role of external or internal surfaces: Does reaction take place in the whole volume of the catalyst or only on the external surface? Two USY catalysts with different particle sizes were compared. One is composed of granules between 28 and 35 mesh and the other of granules larger than 60 mesh. Both those catalysts exhibited the same activity, suggesting that the process does not take place only on the external surface. However, the conclusion would be valid only if we had compared identical catalysts with different crystal sizes. We did not have such materials and we doubt that they can be prepared.

## DISCUSSION

Recently (25), the state of the acylating reagent acetyl chloride was studied by $^{13}$C NMR on protonic and metal oxide-exchanged Y and ZSM-5. Besides signals attributable to the adsorbed reagent, which are close in position to those observed in liquid acetyl chloride, a strong signal is observed near 183 ppm which could be assigned to an acetate-like structure resulting from the reaction of an acylium $R-C\equiv O^+$ ion with a lattice oxygen. This signal is observed
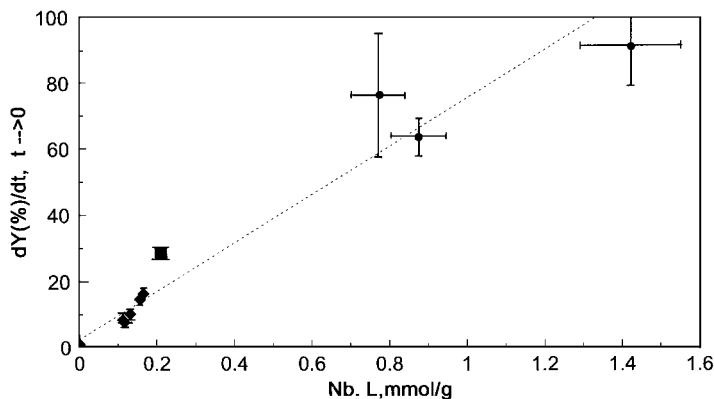


**FIG. 3.** Initial rates of thiophene acylation at 110°C versus the content of Lewis sites. The error bars are estimated as explained in the text. ◆, HZSM-5; ■, mordenite; ●, USY.
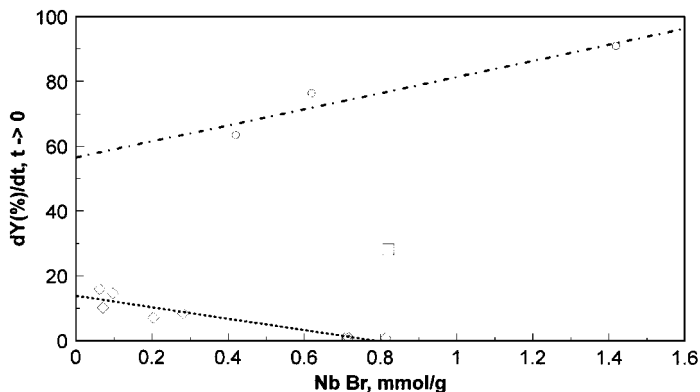
**FIG. 4.** Initial rates of thiophene acylation at 110°C versus the content of Brønsted sites. The lines are shown to outline the incoherent behavior. The error bars on the rates would be the same as in Fig. 3. The error bars on the content of Brønsted sites (not shown) should be smaller by a factor of at least 2 than those on the Lewis sites.

for alkali and alkali-earth exchanged Y-zeolite as well as for HZSM-5. Both forms play a role in the acylation of toluene and according to the authors of this study, Bosáček *et al.* (25), these observations are "in agreement with the role of donor–acceptor complexes between acylium ion precursors and Lewis acids."

Thus, a direct correlation between the number of Lewis acid sites and the initial rate of reaction of BC with thiophene is not unexpected. Indeed, such a correlation derived from the results in Table 2 and shown in Fig. 3 strongly suggests that the difference in reactivity of the different zeolites is due principally to their Lewis acid site contents, and much less to differences between their lattices. In addition, there is an apparent lack of correlation with the density in Brønsted sites (Fig. 4).

This does not mean that the Brønsted sites have no role. The acidic bridging OH could well act as adsorption sites as shown in the condensation of acetone (26). Also, the nature of the catalytic sites for BC oligomerization reactions is open to speculation, since no information pertaining to this area is available so far. It cannot be excluded that Brønsted sites are involved in the oligomerization reaction.

Our conclusion on the overwhelming role of Lewis acidity in acylation contradicts the opinion of Corma *et al.* (8), who by a series of experiments with Y and HZSM-5 concluded that the active sites are the Brønsted sites. They, indeed, observed an excellent correlation between the initial rate of formation of 1-(4-methoxy phenyl)-2 phenylethane and the degree of $Na^+$, $NH_4^+$ exchange on three Y-zeolites, namely, exchanged at 100, 50, and 21%. It was assumed that the number of protonic sites is a linear function of this exchange. However, this assumption would be correct only if no NFAl and silicon were formed during the calcination at 550°C for 3 h performed after drying the exchanged zeolite.

Unfortunately, HY-zeolites are easily dealuminated at temperatures as low as 400°C, and it may be suggested that the amount of NFAl and number of Lewis sites increases af-

ter calcination with the extent of Na–H exchange. As early as 1982, it was shown that Na–NH₄Y exchanged at 70% and calcined at 400°C underwent about 50% dealumination (27).

The number of Lewis sites is an intricate function of the NFAl content, the activation temperature, the length of treatment, the dryness of the medium in which activation is performed, etc. It has also been shown (18) (i) that the degree of dispersion of the Lewis sites, defined as the ratio of the number of Lewis sites to the number of NFAl, fluctuates considerably according to the nature of the zeolites, and (ii) that the strength of the Lewis sites, estimated from the vibration frequency of the $NH_3$, $\nu_2$ symmetrical bending mode, is larger in dealuminated HZSM-5 and H-mordenite than in USY.

Thus, it is not surprising that the linearity of the regression shown in Fig. 3 is far from perfect. On the opposite, the spread of the strength of the Brønsted sites is smaller as estimated from the spread of the heat of $NH_3$ chemisorption (28). Therefore, the dispersion of the results shown in Fig. 4 is not likely to be explained by this spread. As for the hydrophobicity of materials, recent results by Wakabayashi *et al.* (29) show that water adsorbs preferentially on Lewis sites in HZSM-5. Therefore, a dealuminated HZSM-5 would be more hydrophilic than the starting material.

## REFERENCES

1. Hölderich, W. F., and van Bekkum, H., *in* "Introduction to Zeolite Science and Practice" (H. van Bekkum, E. M. Flanigan, and

J. C. Jansen, Eds.), Studies in Surface Science and Catalysis, Vol. 58, p. 631. Elsevier, Amsterdam, 1991.

2. Van Bekkum, H., Hoefmagel, A. J., van Hoten, M. A., Gunnewegh, E. A., Vogt, A. H. G., and Kouwenhoven, H. W., *in* "Zeolites and Microporous Crystals," p. 379. Elsevier, Amsterdam, 1994.

3. Sonawane, H. R., Pol, A. V., and Moghe, P. P., *Tetrahedron Lett.* **35**, 8877 (1994).

4. Gunnewegh, E. A., Downing, R. S., and van Bekkum, H., *in* "Zeolites: A Refined Tool for Designing Catalytic Sites," p. 447. Elsevier, Amsterdam, 1995.

5. Wang, Q. L., Ma, Y., Ji, X., Yan, H., and Qin, Q., *J. Chem. Soc. Chem. Commun.*, 2307 (1995).

6. Chiche, B., Finiels, A., Gauthier, C., and Geneste, P., *J. Org. Chem.* **51**, 2128 (1986).

7. Chiche, B., Finiels, A., Gauthier, C., and Geneste, P., *J. Mol. Catal.* **42**, 229 (1987).

8. Corma, A., Climent, M. J., Garsia, H., and Primo, J., *Appl. Catal.* **49**, 109 (1989).

9. Gauthier, C., Chiche, B., Finiels, A., and Geneste, P., *J. Mol. Catal.* **50**, 219 (1989).

10. Fang, R., Harwey, G., Konwenhoven, H. W., and Prins, R., *Appl. Catal. A* **130**, 67 (1995).

11. Richard, F., Drouillard, J., Carreyre, H., Lemberton, L., and Pérot, G., *in* "Heterogeneous Catalysis and Fine Chemicals III" (M. Guisnet *et al.*, Eds.), Studies in Surface Science and Catalysis, Vol. 78, p. 601. Elsevier, Amsterdam, 1993.

12. Richard, F., Carreyre, H., and Pérot, G., *J. Mol. Catal. A* **103**, 51 (1995).

13. Richard, F., Carreyre, H., and Pérot, G., *J. Catal.* **159**, 427 (1996).

14. Gaare, K., and Akporiaye, D., *J. Mol. Catal.* **109**, 177 (1996).

15. Boreskova, E. G., Lugin, V. I., and Topchieva, K. V., *Kinet. Catal. (USSR)* **5**, 991 (1964).

16. Coster, D., Blumenfeld, A. L., and Fripiat, J. J., *J. Phys. Chem.* **98**, 6201 (1994).

17. Blumenfeld, A. L., and Fripiat, J. J., *Top. Catal.* **4**, 119 (1997).

18. Yin, F., Blumenfeld, A. L., Gruver, V., and Fripiat, J. J., *J. Phys. Chem. B* **101**, 1824 (1997).

19. Panov, A. G., Gruver, V., and Fripiat, J. J., *J. Catal.* **168**, 321 (1997).

20. Hong, Y., and Fripiat, J. J., *Microporous Mater.* **4**, 323 (1995).

21. Auroux, A., Muscas, M., Coster, D. J., and Fripiat, J. J., *Catal. Lett.* **28**, 179 (1994).

22. Panov, A. G., and Fripiat, J. J., *Langmuir* **14**, 3788 (1998).

23. Connors, K. A., "Chemical Kinetics. The Study of Reaction Rates in Solutions." VCH, Weinheim/New York, 1990.

24. Finiels, A., Calmettes, A., Geneste, P., and Moreau, P., *in* "Heterogeneous Catalysis and Fine Chemicals III" (M. Guisnet *et al.*, Eds.), Studies in Surface Science and Catalysis, Vol. 78, p. 595. Elsevier, Amsterdam, 1993.

25. Bosáček, V., Gunnewegh, E. A., and van Bekkum, H., *Catal. Lett.* **39**, 57 (1996).

26. Panov, A. G., and Fripiat, J. J., *J. Catal.* **178**, 188 (1998).

27. Thomas, J. M., and Klinowsky, J., *Adv. Catal.* **33**, 199 (1985).

28. Spiekwak, B. E., Handy, B. E., Sharma, S. B., and Dumesic, J. A., *Catal. Lett.* **23**, 204 (1994).

29. Wakabayashi, F., Kondo, J. N., Domen, K., and Hirose, C., *Catal. Lett.* **38**, 15 (1998).