

Acidic Degradation of Zeolite Catalysts in the Course of Aromatic Chlorination Using Sulfuryl Chloride

DIANO ANTENUCCI,* LIONEL DELAUDE,[†] ANDRÉ-MATHIEU FRANSOLET,*
and PIERRE LASZLO^{1,†}

*Laboratoire de Minéralogie, Institut de Minéralogie (B18); and [†]Laboratoire de Chimie Fine aux Interfaces, Institut de Chimie Organique (B6), Université de Liège, Sart-Tilman par 4000 Liège, Belgium

Received September 14, 1990; revised August 28, 1991

The structural changes of two faujasite-type zeolites in the course of aromatic chlorinations by sulfuryl chloride, SO_2Cl_2 , were investigated by X-ray powder diffraction. Both catalysts examined, the NaX zeolite, which promotes catenary side-chain chlorination, and the ZF520 zeolite, which promotes nuclear electrophilic chlorination, are strongly altered in the acidic reaction medium (hydrochloric acid and sulfur dioxide are evolved continually as the reaction proceeds). In the presence of residual humidity, progressive dealumination of the ZF520 catalyst occurs without destruction of the zeolite framework. It gives rise to the formation of an alum type structure, for which the molecular formula $(\text{H}_3\text{O})\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ has been suggested. Rapid degradation of the NaX zeolite is accompanied by the formation of sodium chloride and of the sodium aluminium sulfate hexahydrate, $\text{NaAl}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$. These compounds indeed catalyze the side-chain chlorination of toluene by SO_2Cl_2 . Under water exclusion, structural degradation of both zeolites is slowed down and formation of hydrated sulfates is prevented; however, the efficiency of the catalysts is also reduced. © 1992 Academic Press, Inc.

INTRODUCTION

In a companion study, we have shown how to effect at will either nuclear or side-chain chlorination of aromatic hydrocarbons (1). Both are reactions of considerable industrial interest. The source of chlorine was sulfuryl chloride, for reasons of convenience in university laboratories. The catalysts were zeolites of faujasite-type structure. We chose a Brønsted acidic zeolite with a high (Si/Al) ratio for the nuclear chlorination, the ZF520 (Si/Al = 20). Conversely, since the side-chain chlorination proceeds by a radical pathway, we elected a faujasite with a (Si/Al) ratio close to unity, the NaX (Si/Al = 1.25), that would maximize the relative number of silyloxy radicals upon thermal or photochemical activation.

The results were gratifying: high yields

and outstanding selectivities were obtained (1). They posed a conceptual problem: Why did the nature of the catalyst alter product distribution in such a radical manner? If the reactions were under thermodynamic control, these findings would be extremely puzzling. Hence, there were two possible explanations, viz., the reactions were under kinetic rather than thermodynamic control, or the zeolite catalysts were not true, regenerable catalysts.

The second possibility was pertinent: it implies a steady drop in catalytic activity of the ZF520 zeolite with the number of runs for which it was used. This suggested an alteration of the chemical structure, presumably due to the hydrochloric acid by-product attacking the aluminosilicate. If this were the case, one would expect the other faujasite catalyst, the NaX zeolite, to exhibit comparable shortcomings. However, the activity of NaX remained apparently intact at the very high initial level after a dozen

¹ To whom correspondence should be addressed.

consecutive reactions. In order to solve this paradox, we launched the structural study reported in this paper.

EXPERIMENTAL

Materials

Sulfuryl chloride was freshly distilled under a slow stream of nitrogen before use, until a colorless fraction (b.p. 69–70°C) was obtained. Toluene (99%, Janssen) was used either without any further purification or after distillation over sodium. Zeolite powder NaX (13×) was purchased from Aldrich; zeolite ZF520 was a gift from Zeocat (Montoir de Bretagne). Under normal conditions, both solids were used without any particular activation (see Table 1 for compositions determined by wet chemical analysis). Before control experiments under anhydrous conditions, they were dried for 1 night in a vacuum oven at 170°C and 5 torr. The sample of natural tamarugite came from the collections of the Mineralogy Institute, University of Liège.

Zeolite-Catalyzed Chlorination of Toluene

A suspension of NaX or ZF520 zeolite (1 g) in toluene (50 ml, 0.47 mol) and sulfuryl chloride (10 ml, 0.12 mol) was refluxed for 30 min. When anhydrous reagents and catalysts were used, a calcium chloride tube was applied to the reflux condenser. Reactions in the presence of the ZF520 catalyst were performed in the dark. Irradiation by a 40-W "cold white" fluorescent tube placed 10 cm away from the Pyrex reaction flask was applied when using the NaX catalyst. After

TABLE 1
Chemical Compositions of the NaX
and ZF520 Zeolites

Zeolite	Composition (wt%)				
	SiO ₂	Al ₂ O ₃	Na ₂ O	H ₂ O	Total
NaX	36.40	25.63	15.94	21.98	99.55
ZF520	86.25	4.40	0.08	9.47	100.20

TABLE 2
Crystallochemical Data for the NaX
and ZF520 Zeolites

Zeolite	Cations for 384 oxygens per unit cell			Unit cell constant (nm)
	Si ⁴⁺	Al ³⁺	Na ⁺	
NaX	92.785	98.603	101.053	2.4995(2)
ZF520	183.581	11.147	0.232	2.4292(3)

reaction, the catalyst was filtered off, washed with 2 portions of toluene (5 ml each) and quickly air-dried before another use. Filtrate composition was determined by GC using 1,4-dichlorobenzene as internal standard.

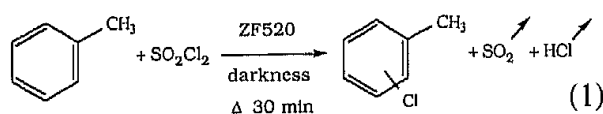
X-Ray Diffraction

Chlorination catalysts were studied at various stages during consecutive runs. After separation from the reaction mixture, they were dried for 1 night in an oven (80°C) and crushed in a mortar. The solid phase identifications were carried out by X-ray diffraction using a Philips PW1390 diffractometer equipped with monochromatized FeK α radiation. The samples were run twice with a scanning speed of $\frac{1}{2}^{\circ}$ 2 θ /min. For the second run, the powder was remounted with an admixture of Pb(NO₃)₂ as internal standard. The *d* values corrected by this procedure served to refine the unit-cell parameters with the least-squares refinement program of Appleman and Evans (2) (see Table 2).

RESULTS AND DISCUSSION

ZF520 Zeolite and Nuclear Chlorination

Nuclear chlorination takes place when toluene is refluxed with sulfuryl chloride in the presence of the ZF520 zeolite.



The activity of the catalyst decreases pro-

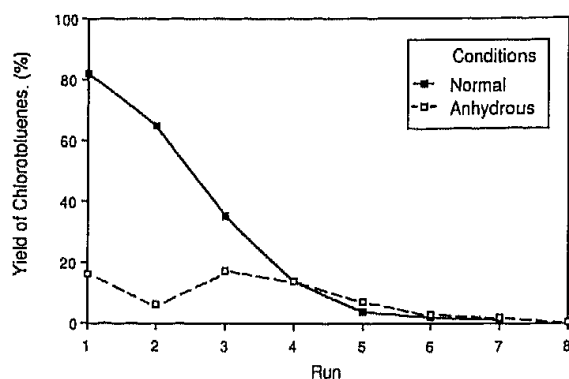


FIG. 1. Recycling of the ZF520 catalyst in consecutive chlorinations of toluene under normal and anhydrous conditions.

gressively during consecutive reactions: conversion of toluene into chlorotoluenes is achieved to the extent of 82% with a fresh sample of ZF520 zeolite but the same catalyst is no longer active after six consecutive reactions (Fig. 1) (1). X-ray powder diffractograms of the starting material and of the spent catalyst are compared in Fig. 2. Although the relative intensities of diffraction peaks are modified when recycling the catalyst, the faujasite-type structure is preserved. Cell dimensions of the starting and of the spent ZF520 catalysts, however, are altered. After four runs, the lattice constant a contracts from (2.4292 ± 0.0003) nm to (2.4248 ± 0.0003) nm. This agrees with the replacement of Al–O linkages (bond length 0.169 nm) by Si–O linkages (0.161 nm) stemming from dealumination (3, 4). Extraction of aluminum from the zeolitic framework is well known to occur under a wide range of conditions (5–9). The hydrochloric acid evolved during the chlorination and the sulfuric acid produced in the presence of residual humidity (no special care was taken to totally exclude water from the zeolite, from the aromatic hydrocarbon, or from the atmosphere) obviously promote the dealumination of the ZF520 zeolite.

The powder spectrum also reveals the presence of additional peaks in the spent catalyst (Fig. 2B). They can be attributed to a sulfate with an alum-type structure, $A^+B^{3+}(SO_4)_2 \cdot 12H_2O$. The cubic cell a pa-

rameter for this supplementary phase (1.2230 ± 0.0004) nm) is closely related to that reported by Wyckoff for the natural mineral tschermigite, $(NH_4)Al(SO_4)_2 \cdot 12H_2O$ (10). Yet we cannot assert the existence of such a compound in a reaction medium that contains no nitrogen source other than atmospheric dinitrogen. From a crystallochemical point of view, the alums $A^+B^{3+}(SO_4)_2 \cdot 12H_2O$ display highly variable compositions with $A^+ = K^+, TI^+, Na^+, Rb^+, Cs^+, (NH_4)^+, (NH_3OH)^+, (H_2NNH_3)^+, (CH_3NH_3)^+$ and $B^{3+} = Al^{3+}, Cr^{3+}, Ga^{3+}, Fe^{3+}, Rh^{3+}$ (11–14). Since the sodium content of the ZF520 zeolite is very low (cf. Table 1) and no other above-mentioned A^+ cations are present, we suggest the possible presence of some hydronium ions in the alum phase. As far as we know, this composition, $(H_3O)Al(SO_4)_2 \cdot 12H_2O$, has not been reported in the alum group. It is reminiscent of some sulfates of the alunite group $A^+(B^{3+})_3(SO_4)_2(OH)_6$, where partial substitution of K^+ or Na^+ by $(H_3O)^+$ ions in the A^+ site can be accomplished in the laboratory (15).

Another noteworthy feature is the a dimension of the alum structure phase, approximately two times smaller than the ZF520 a parameter. These geometrical relationships do not exclude an epitaxial overgrowth of the alum phase on the zeolite. However, we have no further arguments for such a crystal intergrowth.

Evidently, X-ray data suggest the intervention of zeolite acidic aluminate groups in the ZF520-catalyzed aromatic electrophilic chlorinations by sulfonyl chloride (16–19). However, the fresh catalyst is a pure sodium form (cf. Table 1), which should not contain significant amounts of Lewis or of Brønsted sites. Yet these sites may form as a result of the attack of HCl and/or SO_2 in the presence of small amounts of water. One would then expect an initial increase of activity followed by a decrease because of catalyst degradation. Actually, as shown in Fig. 3, the activity goes through a marked maximum with reaction time. This agrees with the ap-

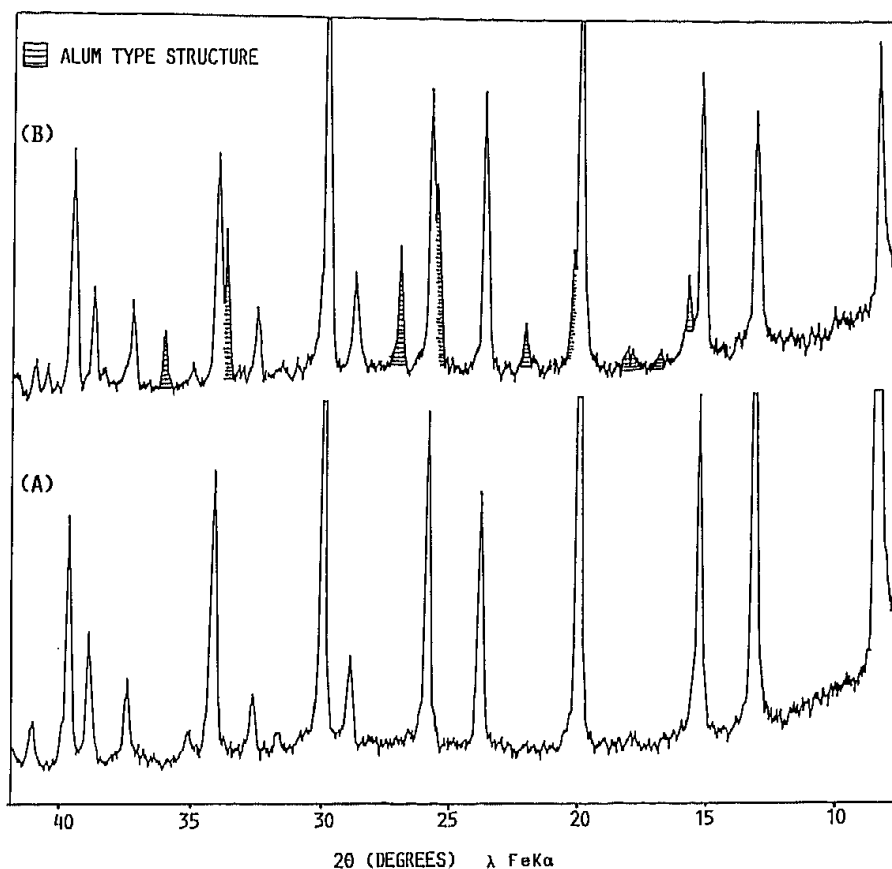


FIG. 2. X-ray powder diffractograms of (A) fresh ZF520 zeolite and (B) after four consecutive chlorinations under normal conditions.

pearance of Brønsted or Lewis acidic centers. Their subsequent extraction from the zeolite framework can be held responsible for the drop in catalytic activity after 6 min of reaction, assuming that the alum phase is devoid of acidic properties. Such a deactiva-

tion has already been reported by van Bekkum *et al.* for brominations of halobenzenes in the presence of Y-type zeolites (20). These authors suppressed the acidic leaching due to the hydrobromic acid liberated during the reaction by adding sodium hydrogen carbonate and KA zeolite (to absorb the water formed). In our case, attempts to preserve the high initial activity of the ZF520 zeolite by adding anhydrous sodium acetate, sodium carbonate, or sodium phosphate to the reaction mixture all failed. Concomitant introduction of A-type molecular sieves was not envisaged, as they would promote side-chain chlorination (1).

In view of the conclusion that residual water plays a leading part in the catalytic process, it was relevant to carry out the chlorination under strictly anhydrous conditions. Exclusion of water was achieved by working with dried reagents and zeolite cat-

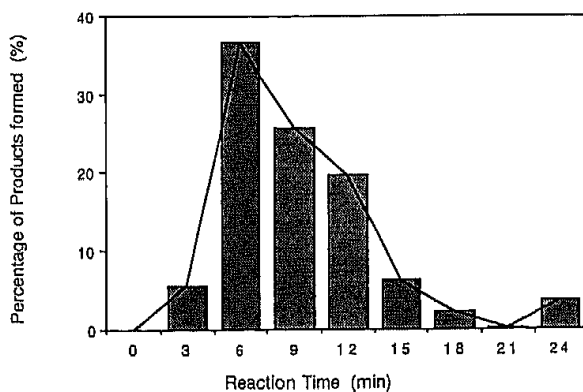


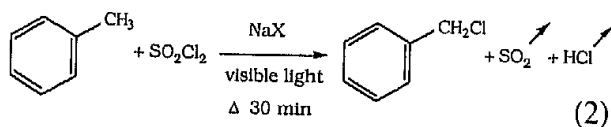
FIG. 3. Time course of the chlorination of toluene in the presence of ZF520 zeolite under normal conditions.

alyst under a moisture-free atmosphere (CaCl_2 tube). This leads to a dramatic yield lowering: while an initial 82% yield of chlorotoluenes is obtained under normal conditions, only 16% of products are formed during a first run under anhydrous conditions. Recycling of the catalyst further reduces its activity and no more reaction occurs after eight runs (Fig. 1). Obviously, the presence of H_2O , together with HCl and SO_2 , is required to allow the formation of acidic centers from the starting zeolite material.

In the absence of water, structural degradation of the ZF520 faujasite during successive chlorinations is slowed down. This can be deduced from a crystallographical analysis of the spent catalyst: comparison of X-ray powder diffractograms of the starting material and of a four times reused sample shows no significant differences. The lattice constant a contraction is 0.0031 nm, while it was 0.0044 nm after the same number of runs under normal conditions. Further investigations were performed after nine successive runs under water exclusion: the lattice constant a then contracts from 2.4292 ± 0.0003 nm to 2.4239 ± 0.0003 nm and small additional peaks characteristic of the already mentioned alum-type sulfate $(\text{H}_3\text{O})\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ emerge in the spectrum, symptomatic of a very slow dealumination. Exposure of the solid to atmospheric humidity during the work-up between two successive runs is a likely cause for these slight alterations.

NaX Zeolite and Side-Chain Chlorination

Side-chain chlorination takes place when toluene is refluxed with sulfuryl chloride in the presence of visible light and of highly aluminated zeolites, as the NaX faujasite.



The prowess of the catalyst remains intact, even after 10 consecutive runs. Yields of benzyl chloride vary between 70 and 76%

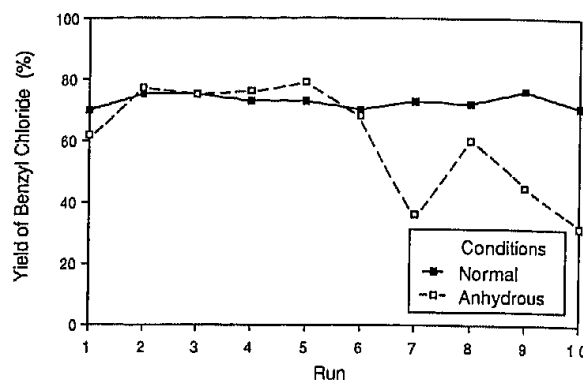


FIG. 4. Recycling of the NaX catalyst in consecutive chlorinations of toluene under normal and anhydrous conditions.

(Fig. 4) (1). The slight variations observed probably reflect the systematic errors in the weight of the reagents and in the chromatographic analysis of the product formed; they cannot be ascribed to a significant change in activity. X-ray powder diffractograms of the original NaX zeolite and of the spent catalysts indicate, however, that major structural changes occur during chlorination (Fig. 5). After 5 runs, the faujasite-type structure is almost totally broken down; only some residual diffraction peaks whose intensities are too weak for a reliable unit-cell measurement subsist (Fig. 5B). Simultaneously, two additional compounds appear: NaCl (halite) and $\text{NaAl}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, a monoclinic sulfate belonging to the krausite-tamarugite group, structurally different from the alums. This behavior becomes more evident after 10 runs (Fig. 5C). The appearance of sulfate and of chloride anions is consistent with the release of SO_2 and HCl as the reaction proceeds. As already discussed for the ZF520 degradation, these result from the lack of anhydrous conditions. Silica is probably accumulated in an amorphous form, not detected by X-ray diffraction.

Since structural alteration of the catalyst does not impede formation of benzyl chloride, the degradation products of the zeolite must be free-radical initiators as efficient as the original zeolite. In order to check this assertion, we have investigated the activity

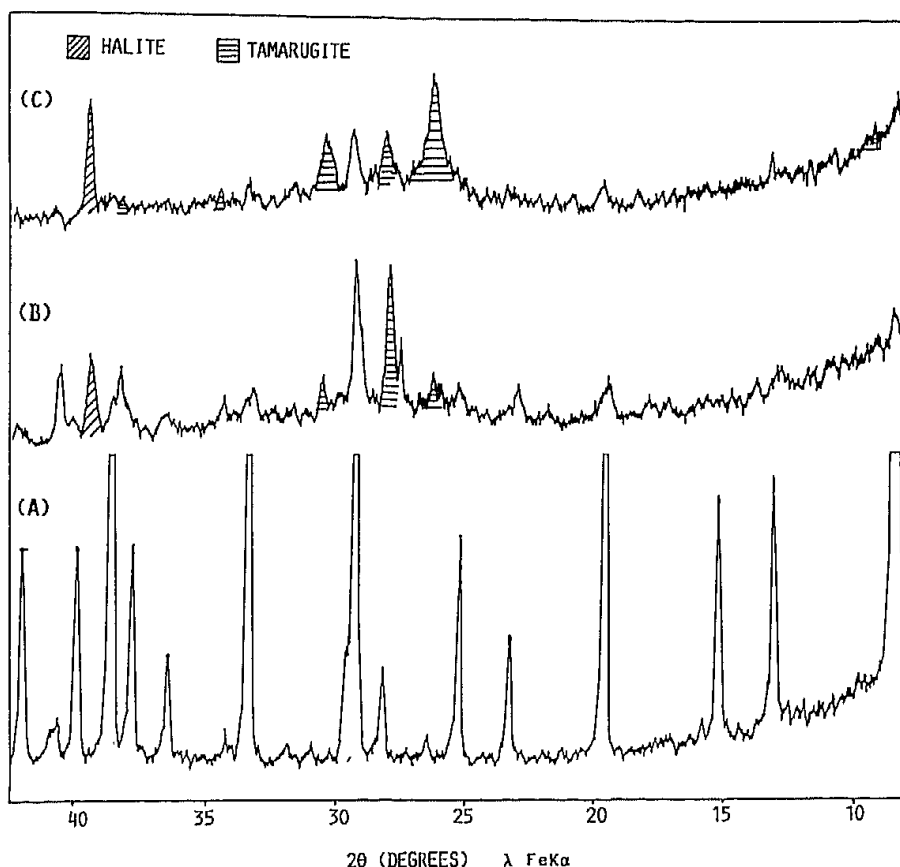


FIG. 5. X-ray powder diffractograms of (A) fresh NaX zeolite, (B) after 5 consecutive chlorinations, and (C) after 10 consecutive chlorinations under normal conditions.

of a mixture of natural tamarugite and of sodium chloride. Chlorination of toluene was chosen as test reaction. Control experiments in the presence of fresh NaX zeolite, in the presence of NaCl, and in the absence of any catalyst, were also performed. The results, gathered in Table 3, clearly indicate that the aluminosilicate zeolite framework plays no significant role in the chlorination of toluene and that the zeolite catalyst can

TABLE 3

Chlorination of Toluene (0.19 mol) by Sulfuryl Chloride (0.05 mol) under Reflux for 30 min in the Presence of Light from a 40-W Fluorescent Tube

Catalyst	Yield of benzyl chloride (%)
Zeolite NaX (0.4 g)	76
Tamarugite (0.18 g) + NaCl (0.32 g)	72
NaCl (0.4 g)	36
—	15

be replaced by a mixture of NaCl and of $\text{NaAl}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ without considerable yield lowering. The result obtained with sodium chloride alone is more surprising: in the presence of intense visible light, addition of salt to the reaction medium significantly favors the formation of benzyl chloride, thus indicating the generality of the initiation step.

Following the same procedure as with the ZF520 zeolite, complementary experiments were carried out with the NaX faujasite under anhydrous conditions. The yields of benzyl chloride obtained during 10 consecutive runs are depicted in Fig. 4. The absence of water has no significant influence upon radical initiation before the seventh run. Although we have no explanation for the abnormally low yield of this last reaction, it marks the beginning of a progressive deactivation of the catalyst, which is no longer active after 10 runs.

From a structural point of view, exclusion of water helps to prevent the degradation of faujasite: in contrast to the reactions effected in the presence of humidity, the zeolite framework subsists after 5 runs. Yet, the relative intensities of diffraction peaks are modified when recycling the catalyst. Halite (NaCl) also appears, while no evidence for the hydrated sulfate $\text{NaAl}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ can be found in the powder spectrum, even after 10 runs. At this stage, the faujasite-type structure has almost totally collapsed and been replaced with that of sodium chloride. The absence of tamarugite, which is a much better catalyst than sodium chloride alone (cf. Table 3), can be invoked to justify the progressive yield lowering during the last runs.

CONCLUSIONS

Both catalysts, ZF520 (nuclear chlorination) and NaX (side-chain chlorination), are markedly affected by the reaction conditions. Presumably, they are attacked by the hydrochloric and sulfuric acids formed by decomposition of sulfuryl chloride in the presence of residual humidity in the zeolite, in the solvent, and in the atmosphere. Dealumination of the ZF520 catalyst leads to an alum coexisting with barely altered faujasite. One would think that the alum phase is catalytically inactive and that the faujasite continues to serve as the catalyst, since the catalytic activity drops with the number of runs. The NaX zeolite catalyst degrades rapidly, as catenary chlorination proceeds into sodium chloride and hexahydrated sodium aluminium sulfate. Surprisingly, these degradation products are catalysts quite as efficient as the starting zeolite. Under careful exclusion of water, the degradation of both zeolites occurs more slowly and the formation of hydrated sulfate salts is prevented. Efficiencies of the catalysts are, however, moderately (NaX) or strongly (ZF520) affected.

We shall investigate next the potential of a number of aluminosilicate minerals, amor-

phous or well-crystallized, as catalysts for the free-radical chlorination of the side chain of aromatics.

ACKNOWLEDGMENTS

We thank J. M. Speetjens for the wet chemical analyses and Zeocat, Montoir de Bretagne (France) for the gift of the ZF520 zeolite. One of us (A.-M.F.) is grateful to FNRS, Belgium, for his position as Research Associate, and for Grants 1.5.009.88F and 1.5.017.89F.

REFERENCES

1. Delaude, L., and Laszlo, P., *J. Org. Chem.* **55**, 5260 (1990).
2. Appleman, D. E., and Evans, H. T., "Indexing and Least-Squares Refinement of Powder Diffraction Data. Report PB216188, U.S. Dept. of Commerce." National Technical Information Service, Springfield, 1973.
3. Anderson, M. W., and Klinowski, J., *J. Chem. Soc. Faraday Trans. 1* **82**, 1449 (1986).
4. Breck, D. W., "Zeolite Molecular Sieves—Structure, Chemistry, and Use," p. 104. Wiley, New York, 1974.
5. Barrer, R. M., and Makki, M. B., *Can. J. Chem.* **42**, 1481 (1964).
6. Kerr, G. T., in "Molecular Sieves" (W. M. Meier and J. B. Uytterhoeven, Eds.), Advances in Chemistry Series 121, Chap. 19, p. 219. American Chemical Society, Washington, DC, 1973.
7. Chen, N. Y., and Smith, F. A., *Inorg. Chem.* **15**, 295 (1976).
8. Anderson, M. W., Klinowski, J., and Xinsheng, L., *J. Chem. Soc. Chem. Commun.*, 1596 (1984).
9. Beyer, H. K., Belenykaja, I. M., Hange, F., Tielens, M., Grobet, P. J., and Jacobs, P. A., *J. Chem. Soc. Faraday Trans. 1* **81**, 2889 (1985).
10. Wyckoff, R. W. G., *Am. J. Sci.* **5**, 209 (1923).
11. Lipson, H., and Lodge, O., *Proc. R. Soc. London A* **151**, 347 (1935).
12. Klug, H. P., *J. Am. Chem. Soc.* **62**, 2992 (1940).
13. Klug, H. P., and Alexander, L., *J. Am. Chem. Soc.* **62**, 2999 (1940).
14. Klug, H. P., and Kieffer, G. L., *J. Am. Chem. Soc.* **65**, 2071 (1943).
15. Parker, R. L., *Am. Miner.* **47**, 127 (1962).
16. Jacobs, P. A., and Beyer, H. K., *J. Phys. Chem.* **83**, 1174 (1979).
17. Atkinson, D., and Curthoys, G., *Chem. Soc. Rev.* **8**, 475 (1980).
18. Haag, W. O., Lago, R. M., and Weisz, P. B., *Nature (London)* **309**, 589 (1984).
19. Dwyer, J., *Chem. Ind. (London)*, April 2, 258 (1984).
20. Wortel, T. M., Oudijn, D., Vleugel, C. J., Roelofsen, D. P., and van Bekkum, H., *J. Catal.* **60**, 110 (1979).