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# Dealumination of Zeolites[1]

## II. Kinetic Study of the Dealumination by Hydrothermal Treatment of a $NH_4NaY$ Zeolite

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The hydrothermal treatment of a $(NH_4)_{0.8}Na_{0.2}Y$ zeolite was carried out in a flow reactor in order to determine quantitatively the effect of the operating conditions (time, temperature, water pressure) on the dealumination of this zeolite. X-ray diffraction was used to follow the process of dealumination and to characterize the variations of the crystallinity. The enrichment of the outer surface in Al was measured by X-ray photoelectron spectroscopy (XPS). First the temperature of the zeolite was raised rapidly to the temperature chosen for the hydrothermal treatment (260 to 820°C) under nitrogen flow. During this rise in temperature there was a significant dealumination caused by water physically adsorbed or liberated by dehydroxylation. This dealumination is accompanied by a partial collapse of the zeolite framework. After the ceiling temperature was reached, the zeolite was submitted to a flow of water vapor. Two periods could be distinguished, namely an initial one in which dealumination was rapid, and a second one in which it was slow. Only the aluminum atoms with which $NH_4^+$ (and not $Na^+$) are associated could be extracted from the framework. For both periods the kinetic orders with respect to these aluminum atoms and to water are equal to 1; the apparent activation energy is about 20 kJ $mol^{-1}$ for the rapid dealumination and 70 for the slow process. The first period would correspond to the dealumination of the protonic zeolite and the second to that of the zeolite exchanged by cationic aluminum species. Under high water pressure (>50 kPa) there is a relationship between zeolite dealumination and subsequent migration of extra-framework aluminum species to the outer surface of the crystallites. However, these processes are independent. Indeed during the self-steaming of the zeolite, dealumination occurs without enrichment in Al of the outer surface.

### INTRODUCTION

The thermal and the catalytic stability of Y zeolites is considerably improved by dealumination (*1–3*). This dealumination is generally carried out through steaming at high temperatures of a $NH_4Y$ zeolite. Although this technique is currently used, there exist few quantitative data concerning the effect which the operating conditions (time of steaming, temperature, water pressure) have on the rate of dealumination. This technique causes the formation of extra-framework aluminum species which can migrate to the outer surface of the crystallites (*4–8*). We show here how the operating conditions determine the rate of dealumination of a $(NH_4)_{0.8}Na_{0.2}Y$ zeolite, the crystallinity of the dealuminated samples, and the rate of migration of the extra-framework species to the outer surface of the crystallites. The mechanism of dealumination is discussed on the basis of the kinetic data.

### EXPERIMENTAL

The dealumination was carried out by hydrothermal treatment of various samples of

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the same batch of $NH_4NaY$ zeolite ($(NH_4)_{48}Na_{14}Al_{62}Si_{130}O_{384}$) in a flow reactor under chosen operating conditions. The $NH_4NaY$ zeolite resulted from a double ion exchange of a NaY zeolite (chemical and framework atomic Si/Al ratio equal to 2.1, size of the crystallites ≈0.7 μm) under the following conditions: temperature 25°C, 10 $cm^3$ of 1.5 $M$ solution of $NH_4NO_3$ per gram of zeolite, duration 20 h. For the hydrothermal treatment, about 2 g of zeolite in the form of powder was used, the height of the bed being equal to 0.5 cm. While the temperature was increased to reach the treatment temperature (5 to 10 min) the zeolite was kept under nitrogen flow (170 $N$ $cm^3$ $h^{-1}$). Water (2 g $h^{-1}$) was introduced when the zeolite reached the treatment temperature (time zero). All the samples obtained were characterized by X-ray diffraction; the "crystallinity" $C_{RX}$ and the unit cell parameter $a_0$ were determined according to the ASTM methods D3906 and D3542, the $NH_4NaY$ sample being considered as reference. The number of aluminum atoms per unit cell was deduced from $a_0$ by using the equation proposed by Breck and Flanigen (*9*). The Al/Si ratio of the outer surface of the zeolite crystallites was determined by XPS analysis with an ISA RIBER spectrometer.

## RESULTS

Table 1 gives for all the dealuminated samples the formula of the unit cell, the number of extra-framework aluminum species per unit cell ($N_{EFAL}$), the percentage of dealumination, the atomic Al/Si ratio of the crystallite surface ($(Al/Si)_{XPS}$), and the crystallinity $C_{RX}$. The unit cell formula and $N_{EFAl}$ are determined from the chemical composition of the zeolite (% Al, % Si, % Na) and from $N_{Al}$, the number of aluminum per unit cell calculated from $a_0$ by using the equation proposed by Breck and Flanigen (*9*). For this determination it was supposed that the extra-framework species contain no silicon nor sodium atoms but only aluminum species. This is not quite true since there is a partial destruction of the zeolite during the increase in temperature under nitrogen flow (see below) and the extra-framework species thus formed obviously contain silicon atoms. With this supposition, the percentage of dealumination is equal to $100 \times N_{EFAl}/(N_{EFAL} + N_{Al})$.

### 1. *Effect of the Treatment Time*

The effect of the steaming time $t$ was studied at various temperatures (400, 500, 650, and 700°C) with a pressure of water vapor equal to 93.3 kPa. Moreover, at 650°C, two other values of water pressure (20 and 53 kPa) were used. Whatever the operating conditions, the percentage of dealumination increases rapidly with $t$ during the first 2–3 h of treatment, then more slowly (Fig. 1). The dealumination begins during the increase in temperature under nitrogen flow. At time zero the percentage of dealumination is equal to 1.6 at 400°C, 9.1 at 500°C, and 23.1 at 650°C (Table 1). A decrease in $C_{RX}$ is observed during the temperature increase; afterwards, $C_{RX}$ remains practically constant (at 400°C) or increases slightly and then remains constant (Fig. 1b).

The $(Al/Si)_{XPS}$ ratio of the dealuminated samples increases strongly with time. This atomic ratio passes from 0.34 for $NH_4NaY$ (which is lower than the framework Al/Si ratio : 0.48) to 1.16 after 40 h at 650°C under a water vapor pressure of 93 kPa. This value is about 10 times greater than the framework Al/Si ratio of this dealuminated sample (0.11). The increase in $(Al/Si)_{XPS}$ is particularly pronounced during the first 3 h (Fig. 2), i.e. during the period of rapid dealumination.

### 2. *Effect of the Temperature*

As shown in Fig. 1 the percentage of dealumination increases with the steaming temperature $T_S$. The effect of $T_S$ on the dealumination was studied over a larger range of temperature (from 260 to 820°C) for 3 h with a water pressure of 93.3 kPa. The dealumination begins at low temperature (Fig. 3). It is always accompanied by a loss of crystallinity. This loss of crystallinity becomes

TABLE 1

Conditions of Steaming and Characteristics of the Dealuminated Samples

| Operating conditions | | | Unit cell formula[a] | $N_{EFAL}$ | Deal. (%) | $(Al/Si)_{XPS}$ | $C_{RX}$[b]b |
|---|---|---|---|---|---|---|---|
| $T$(°C) | $P_{water}$ | $t$(h) | | | | | |
| 400 | 0 | 0 | $Na_{14.1}Al_{61.5}Si_{130.5}O_{384}$ | 1 | 1.6 | | 88 |
| 400 | 93.3 | 0.25 | $Na_{14.4}Al_{58.6}Si_{133.4}O_{384}$ | 5 | 7.9 | | 86 |
| 400 | 93.3 | 1 | $Na_{14.7}Al_{55.7}Si_{136.3}O_{384}$ | 9.3 | 14.3 | | 88 |
| 400 | 93.3 | 3 | $Na_{15.2}Al_{50.7}Si_{141.3}O_{384}$ | 16.7 | 24.8 | | 87 |
| 400 | 93.3 | 13 | $Na_{15.4}Al_{49.0}Si_{143.0}O_{384}$ | 19.2 | 28.1 | | 86 |
| 400 | 93.3 | 20 | $Na_{15.5}Al_{48.1}Si_{143.9}O_{384}$ | 20.5 | 30.0 | | 85 |
| 500 | 0 | 0 | $Na_{14.4}Al_{58.1}Si_{133.9}O_{384}$ | 5.8 | 9.1 | | 80 |
| 500 | 93.3 | 0.25 | $Na_{14.7}Al_{55.4}Si_{136.6}O_{384}$ | 9.3 | 14.4 | | 85 |
| 500 | | 1 | $Na_{15.2}Al_{50.6}Si_{141.4}O_{384}$ | 17.1 | 25.2 | | 87 |
| 500 | | 3 | $Na_{15.9}Al_{43.9}Si_{148.1}O_{384}$ | 26.7 | 37.8 | 0.6 | 88 |
| 500 | | 13 | $Na_{16.4}Al_{39.6}Si_{152.4}O_{384}$ | 33.1 | 45.5 | | 85 |
| 500 | | 20 | $Na_{16.6}Al_{37.4}Si_{154.6}O_{384}$ | 36.3 | 49.2 | | 85 |
| 650 | 0 | 0 | $Na_{15.1}Al_{51.5}Si_{140.5}O_{384}$ | 15.5 | 23.1 | 0.34 | 76 |
| 650 | 93.3 | 0.25 | $Na_{15.5}Al_{47.9}Si_{144.1}O_{384}$ | 20.8 | 30.3 | | 85 |
| 650 | | 1 | $Na_{16.1}Al_{41.3}Si_{150.7}O_{384}$ | 30.1 | 42.2 | 0.5 | 88 |
| 650 | | 2 | $Na_{16.8}Al_{35.9}Si_{156.1}O_{384}$ | 38.5 | 51.7 | 0.71 | 84 |
| 650 | | 3 | $Na_{17.0}Al_{34.0}Si_{158.0}O_{384}$ | 41.4 | 54.9 | 0.85 | 83 |
| 650 | | 4 | $Na_{17.1}Al_{32.5}Si_{159.5}O_{384}$ | 43.6 | 57.3 | | 83 |
| 650 | | 5 | $Na_{17.3}Al_{31.8}Si_{160.2}O_{384}$ | 44.6 | 58.4 | | 82 |
| 650 | | 8 | $Na_{17.6}Al_{29.1}Si_{162.9}O_{384}$ | 48.7 | 62.6 | 1.0 | 84 |
| 650 | | 13 | $Na_{18.1}Al_{24.4}Si_{167.6}O_{384}$ | 55.5 | 69.5 | | 83 |
| 650 | | 20 | $Na_{18.3}Al_{21.3}Si_{170.7}O_{384}$ | 60.1 | 73.8 | | 83 |
| 650 | | 40 | $Na_{18.5}Al_{18.9}Si_{173.1}O_{384}$ | 63.6 | 77 | 1.15 | 80 |
| 650 | | 65 | $Na_{18.7}Al_{18.0}Si_{174.0}O_{384}$ | 65 | 78.3 | | 81 |
| 700 | 93.3 | 3 | $Na_{17.5}Al_{29.7}Si_{162.3}O_{384}$ | 47.7 | 61.6 | 0.94 | 82 |
| 700 | | 13 | $Na_{18.5}Al_{20.4}Si_{171.6}O_{384}$ | 61.4 | 75.1 | | 80 |
| 260 | 93.3 | 3 | $Na_{14.2}Al_{60}Si_{132}O_{384}$ | 3 | 4.8 | | 96 |
| 300 | | | $Na_{14.7}Al_{55.9}Si_{136.1}O_{384}$ | 9 | 13.9 | | 97 |
| 450 | | | $Na_{15.7}Al_{46.5}Si_{145.5}O_{384}$ | 22.9 | 33 | | 87 |
| 600 | | | $Na_{16.7}Al_{36.8}Si_{155.2}O_{384}$ | 37.2 | 74 | | 84 |
| 760 | | | $Na_{18.4}Al_{21.2}Si_{170.8}O_{384}$ | 60.3 | 74 | | 54 |
| 800 | | | | | | | 10 |
| 820 | | | | | | | 0 |
| 650 | 0 | 3 | $Na_{15.9}Al_{44.4}Si_{147.6}O_{384}$ | 26 | 36.9 | 0.34 | 87 |
| | 9.33 | | $Na_{16.1}Al_{42.2}Si_{149.8}O_{384}$ | 29.2 | 40.9 | 0.37 | 85 |
| | 20.0 | | $Na_{16.3}Al_{40.7}Si_{151.3}O_{384}$ | 31.5 | 43.6 | 0.51 | 84 |
| | 33.3 | | $Na_{16.4}Al_{39.4}Si_{152.6}O_{384}$ | 33.4 | 45.9 | | 84 |
| | 53.3 | | $Na_{16.6}Al_{37.4}Si_{154.6}O_{384}$ | 36.3 | 49.3 | 0.73 | 83 |
| 650 | 20 | 7 | $Na_{16.5}Al_{39.2}Si_{152.8}O_{384}$ | 33.7 | 46.2 | | 84 |
| 650 | 20 | 13 | $Na_{16.7}Al_{36.6}Si_{155.4}O_{384}$ | 37.5 | 50.6 | | 84 |
| 650 | 53.3 | 10 | $Na_{17.3}Al_{31.3}Si_{160.7}O_{384}$ | 46.4 | 59.7 | | 83 |

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[a] The amount of protonic sites was not determined.

[b] Reference $NH_4NaY$.

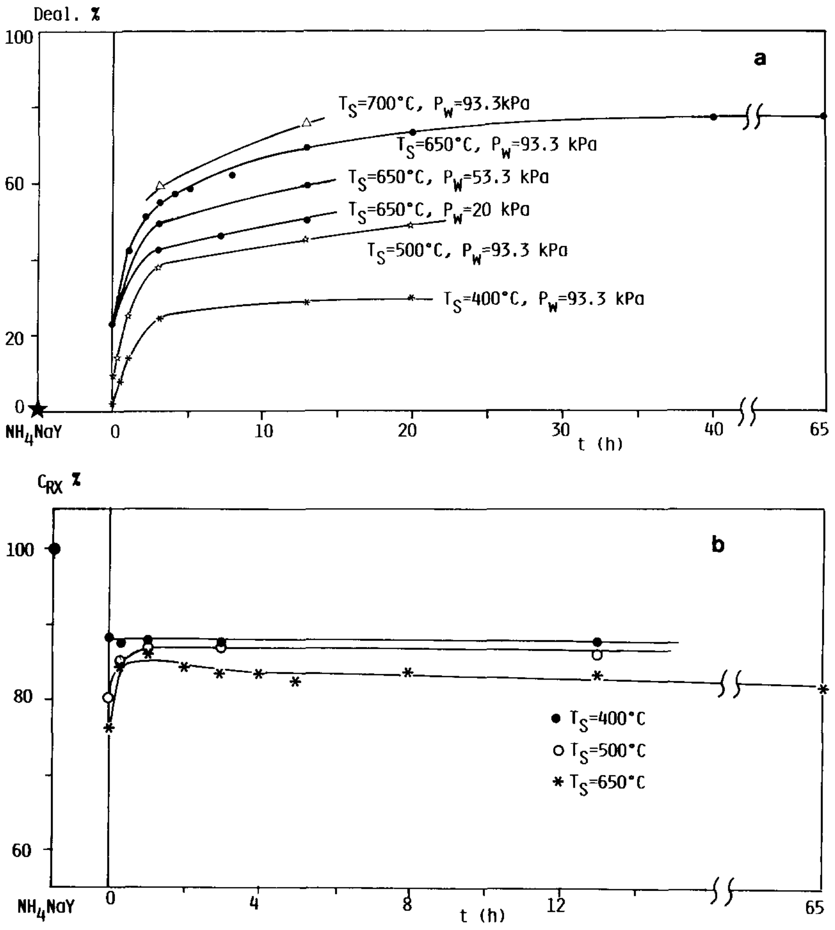


FIG. 1. (a) Percentage of dealumination of the Y zeolite (Deal., %) as a function of the hydrothermal treatment time ($t$, h) under various operating conditions: $T_S$, temperature; $P_w$, water pressure. (b) Crystallinity ($C_{RX}$, %) of the dealuminated samples as a function of the hydrothermal treatment time ($t$, h) at various temperatures, with a water pressure of 93.3 kPa.

very significant for $T_S$ above 700°C. The $(Al/Si)_{XPS}$ ratio is always greater than the total Al/Si ratio and than the framework Al/Si ratio. The higher $T_S$ the greater the difference (Fig. 4).

### 3. *Effect of the Water Vapor Pressure*

As shown in Fig. 1 the greater the water pressure ($P_w$) the higher the percentage of dealumination. The effect of $P_w$ on the dealumination was studied over a larger range of pressures (from 0 to 93.3 kPa) for 3 h at 650°C. The percentage of dealumination increases with $P_w$. It must be noted that for this temperature a very pronounced dealumination of the zeolite occurs before adding water (Fig. 5), a loss in crystallinity accompanying the dealumination. The addition of water causes a slight decrease of the crystallinity (Fig. 5). The $(Al/Si)_{XPS}$ ratio is practically the same for $NH_4NaY$ before and after a 3-h treatment under nitrogen flow (Fig. 6). On the other hand, under water flow, $(Al/Si)_{XPS}$ is greater than the framework Al/Si ratio. The higher $P_w$ the greater the difference between the ratios (Fig. 6).

## DISCUSSION

The effect of the operating conditions of the hydrothermal treatment on the dealumi-

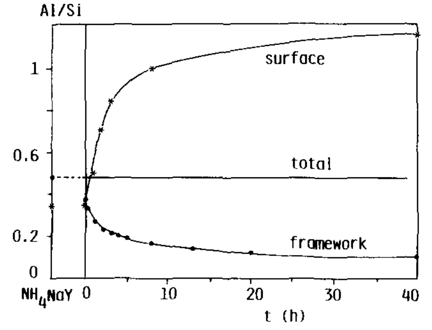


FIG. 2. Change of the atomic Al/Si ratios as functions of the hydrothermal treatment time ($t$, h).

nation of Y zeolites is now well known (*2, 4, 8, 10, 11*). However, practically no quantitative relation between the rate of dealumination and the operating parameters (time of treatment, temperature, pressure of water) has been reported in the literature. Nevertheless, we can quote the kinetic order with respect to the framework aluminum atoms as being found equal to 2 for Y zeolites by Martins *et al.* (*12*) and for ZSM-5 by Sano *et al.* (*13, 14*).

### *1. Kinetics of Dealumination*

*1.1. Effect of time.* An apparent order with respect to the aluminum atoms can be deduced from the effect of the treatment time $t$ on the composition of the unit cell. If the unit cell is considered as a reactor the following equation can be written:

$$-dN_{Al}/dt = k'(N_{Al})^{\alpha} \quad (1)$$

with $k'$ the apparent rate constant of dealumination for given values of $T_S$ and $P_w$. If the

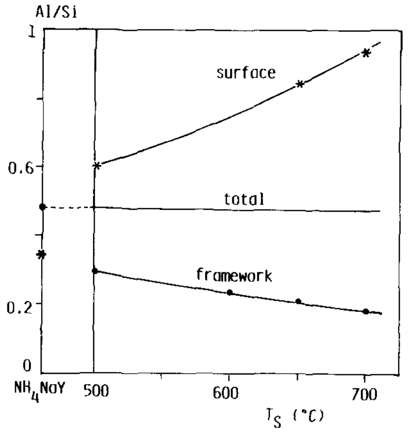


FIG. 4. Change of the atomic Al/Si ratios as functions of the temperature of a hydrothermal treatment ($T_S$, °C) of 3 h with a water pressure of 93.3 kPa.

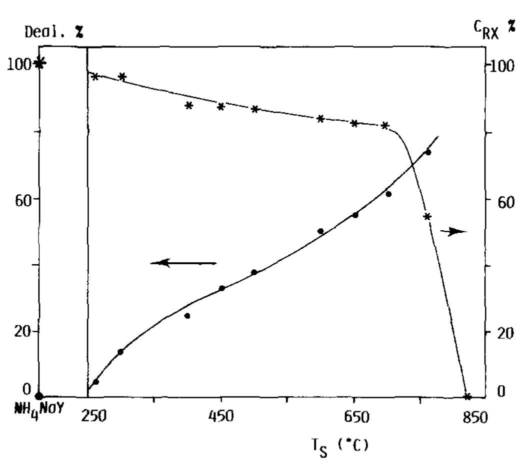


FIG. 3. Percentages of dealumination (Deal., %) and of crystallinity ($C_{RX}$, %) as functions of the temperature of a hydrothermal treatment ($T_S$, °C) of 3 h with a water pressure of 93.3 kPa.

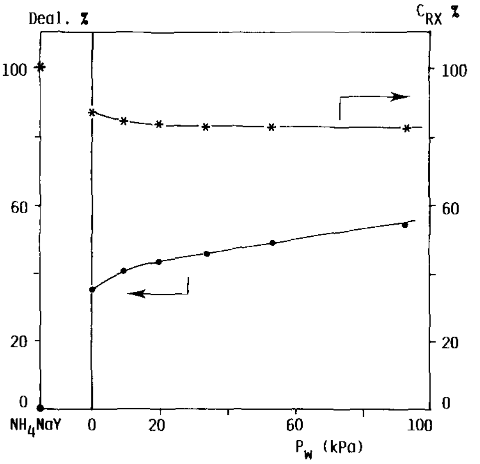


FIG. 5. Percentages of dealumination (Deal., %) and of crystallinity ($C_{RX}$, %) as functions of the water pressure ($P_w$, kPa) used for a hydrothermal treatment of 3 h at 650°C of the $NH_4NaY$ zeolite.

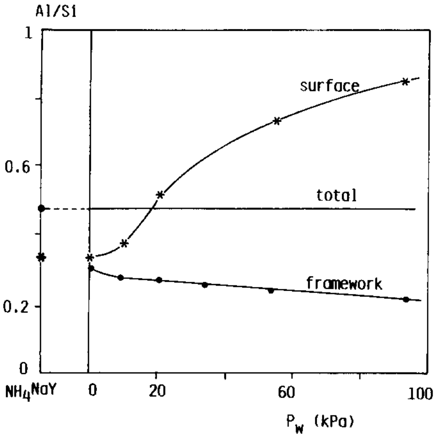


FIG. 6. Change of the atomic Al/Si ratio as a function of the water pressure ($P_w$, kPa) used for a hydrothermal treatment of 3 h at 650°C of the $NH_4NaY$ zeolite.

reaction order is equal to 2 there must exist a linear relation between $1/N_{Al}$ and $t$. Figure 7 shows that this is the case at least for 3 h $< t \leq 20$ h. For $t < 3$ h a quasi-linear relation is also obtained but the slope is considerably greater. Two periods of dealumination could therefore be distinguished, the initial period with rapid dealumination and the other with slow dealumination, the apparent kinetic order with respect to aluminum being equal to 2 for both periods.

However, this kinetic order of 2 is questionable. Indeed, only the aluminum atoms with which are associated $NH_4^+$ (and not $Na^+$) can be removed by hydrolysis (*1*, *10*, *15*). In agreement with this, the rate of dealumination at 650°C and 93.3 kPa becomes practically equal to zero after 40 h reaction (Fig. 1), i.e., when $N_{Al}$, the number of aluminum atoms per unit cell, is close to $N_{Na}$, the number of sodium atoms per unit cell. Therefore in Eq. (1), $N_{Al}$ must be replaced by $N_{Al}^* = N_{Al} - N_{Na}$.

$$-dN_{Al}^*/dt = k'(N_{Al}^*)^{\alpha}. \qquad (2)$$

With Eq. (2) the order with respect to aluminum is no longer equal to 2 but to 1. Indeed a linear relation is found between ln $(N_{Al}^*)$ and $t$ (Fig. 8) both for the period of rapid dealumination and for that of slow dealumination. This order of 1 is in good agreement with the observation by NMR that the removal of Al atoms from the zeolite framework proceeds step by step, with a transformation of Si($n$ Al) into Si($n$ − 1)Al) units (*10*, *16*).

*1.2. Effect of temperature.* The values of the apparent activation energy $E$ for the two periods of dealumination were calculated from the rate constants drawn from Fig. 8 for 400, 500, and 650°C. $E$ is 20 ± 2 kJ mol$^{-1}$ for the rapid dealumination and 70 ± 2 kJ mol$^{-1}$ for the slow dealumination (Fig. 9). $E$ was also estimated from the experiments carried out for 3 h at various treatment temperatures $T_s$ with $P_w$ = 93.3 kPa. The value of $k'$ used for this estimation was

$$k' = \ln((N_{Al}^*)_0/N_{Al}^*)/t \qquad (3)$$

with $(N_{Al}^*)_0$ the value of $N_{Al}^*$ for the zeolite after the increase in temperature under nitrogen flow. Only three values of $(N_{Al}^*)_0$ were experimentally obtained ($T_s$ = 400, 500, 650°C). The other values were estimated by extrapolation from the curve: $(N_{Al}^*)_0 = f(1/T_s)$. A value of $E$ equal to about 25 kJ mol$^{-1}$,

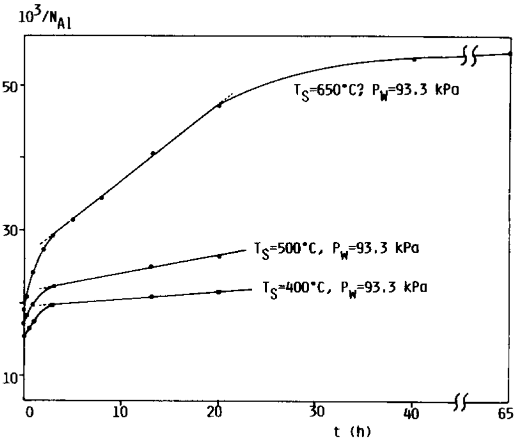


FIG. 7. Dealumination of the $NH_4NaY$ zeolite through hydrothermal treatment under various operating conditions. Checking of an apparent reaction order equal to 2 with respect to the framework aluminium atoms. $N_{Al}$, number of these atoms per unit cell, $t$(h) hydrothermal treatment time.

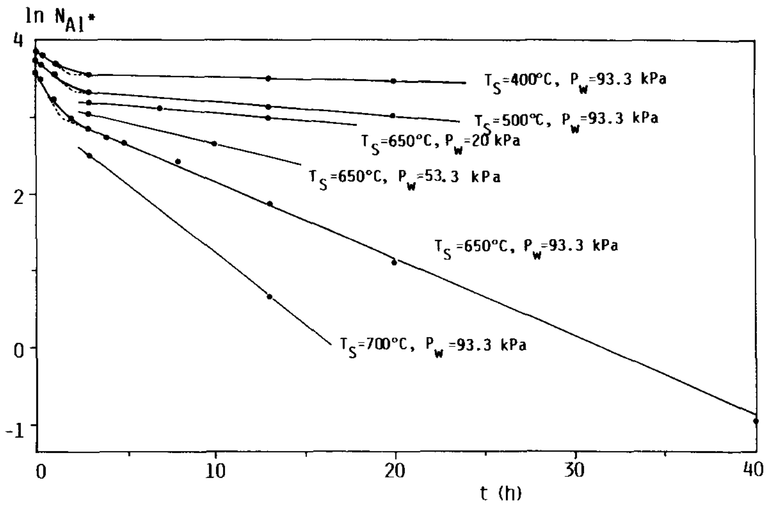


FIG. 8. Dealumination of the $NH_4NaY$ zeolite through hydrothermal treatment under various operating conditions. Checking of an apparent reaction order equal to 1 with respect to the framework aluminum atoms not associated with Na ions. $N^*_{Al}$, number of these atoms per unit cell; $t$(h), hydrothermal treatment time.

i.e., close to that determined for the rapid dealumination, was obtained.

*1.3. Effect of the water vapor pressure.* Figure 10 shows that the apparent order with respect to water is 1 for the period of slow dealumination at 650°C. The $k'$ values used for this determination are drawn from the curves of Fig. 8 corresponding to the experiments with different values of water pressure $P_w$ for $T \geq 3$ h.

An approximate value of the order with respect to water can also be obtained for the period of rapid dealumination from experiments carried out for 3 h at 650°C with different values of $P_w$. The values of the reaction

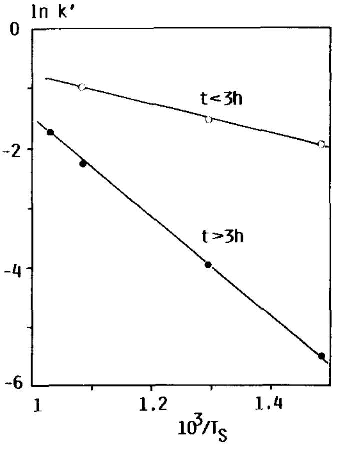


FIG. 9. Effect of the temperature of hydrothermal treatment $T_S$ on the rate constant of dealumination ($k'$, $h^{-1}$) under a water pressure of 93 kPa. Determination of the apparent activation energy.

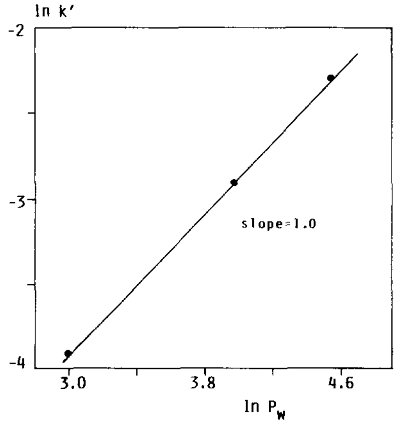


FIG. 10. Effect of the water pressure $P_w$ on the rate constant of dealumination at 650°C for times greater than 3 h ($k'$, $h^{-1}$). Determination of apparent reaction order with respect to water.

rate constant used for this determination are those obtained from Eq. (3). An order value of about 0.5 is found. This value is probably lower than the real value, the period of treatment (3 h) being intermediate between the periods of rapid and of slow dealumination.

*1.4. Kinetic equations.* The kinetic equations found for the dealumination under water flow are

Initial period:

$$\frac{-dN^*_{\mathrm{Al}}}{dt} = 0.6\, e_{\mathrm{Al}}^{-2400/T} N^*_{\mathrm{Al}} P_{\mathrm{w}}^{0.5}$$

after 3 h:

$$\frac{-dN^*_{\mathrm{Al}}}{dt} = 10.5\, e^{-8350/T} N^*_{\mathrm{Al}} P_{\mathrm{w}},$$

with $t$ expressed in hours and $P_{\mathrm{w}}$ in kPa. These equations differ slightly by the reaction orders with respect to water and by the values of the rate constants and of the apparent activation energies.

### *2. Migration of Extra-Framework Species to the Outer Surface*

XPS analysis shows a significant enrichment in aluminum of the outer surface of the zeolite crystallites during the treatment under water flow. This enrichment can be explained by the migration to the outer surface of extra-framework species rich in aluminum. There is a quasi proportionality between the $(\mathrm{Al/Si})_{\mathrm{XPS}}$ ratio and the percentage of dealumination calculated on the removable aluminum (not associated with sodium cations) of the samples treated at 650°C under a water pressure $P_{\mathrm{w}}$ of 93.3 kPa (Fig. 11). The values obtained for samples treated for 3 h under the same pressure $P_{\mathrm{w}}$ at 500 and 700°C or under $P_{\mathrm{w}} = 53.3$ kPa at 650°C follow the same relationship (Fig. 11). Under these conditions there is therefore a relationship between the zeolite dealumination and the subsequent migration to the surface of the extra-framework aluminum species (*4*, *8*). However, for values of $P_{\mathrm{w}}$ lower than 50 kPa, smaller values of $(\mathrm{Al/Si})_{\mathrm{XPS}}$ are obtained (Fig. 11), which shows that the migration of the aluminum extra-framework species is slower. Moreover, $(\mathrm{Al/Si})_{\mathrm{XPS}}$ of the sample treated without addition of water for 3 h at 650°C is equal to $(\mathrm{Al/Si})_{\mathrm{XPS}}$ of $\mathrm{NH_4NaY}$ (Fig. 11). Without addition of water (self-steaming) there is therefore no migration to the outer surface of aluminum species and this although the percentage of dealumination is a significant one (about 30%). This means that aluminum migrates as hydroxylated species. The same observations have been previously reported by Fleisch *et al.* (*4*) for the dealumination of REY.

### *3. Mechanism of Dealumination*

Our experiments show that after the increase in temperature under nitrogen two periods of dealumination can be distinguished: an initial one in which dealumination occurs rapidly with a reaction order with respect to water of about 0.5 and a second one with slower dealumination, the reaction order with respect to water being 1. For both periods the dealumination rate is proportional to the number of hydrolyzable aluminum atoms.

During the increase of temperature under nitrogen (self-steaming) a rapid dealumination of the zeolite occurs and there is a loss in crystallinity. The percentage of dealumination and the loss in crystallinity increase with the temperature chosen for the hydrothermal treatment $T_{\mathrm{s}}$. This is due not only to the temperature increase but also to the increase with $T_{\mathrm{s}}$ of the self-steaming time. What are the phenomena which occur during the period of self-steaming and the two other periods?

It is well known that dealumination through hydrothermal treatment consists of hydrolysis of Al–O bonds with formation of neutral and cationic aluminum species (*8*, *17*). Then the defect sites created by dealumination are filled by silicon atoms with a consequent stabilization of the zeolite framework.

*3.1. Period of self-steaming.* Reactions 1 to 4 (Fig. 12) can be proposed to explain the

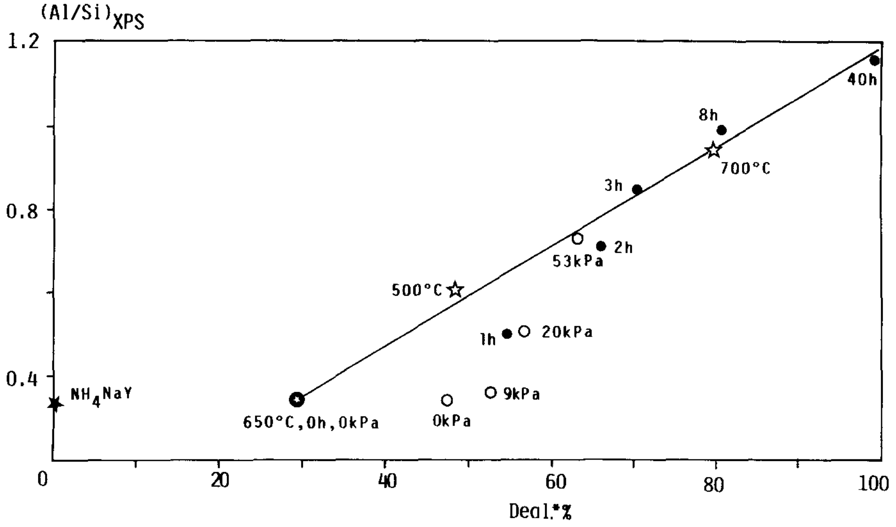


FIG. 11. Atomic Al/Si ratio of the outer surface of the zeolite crystallites ((Al/Si)$_{XPS}$) as a function of the percentage of dealumination calculated on the aluminum atoms not associated with Na ions (Deal.*, %). (●) $T_S$ = 650°C, $P_w$ = 93.3 kPa; (○) $T_S$ = 650°C, $t$ = 3 h, (☆) $t$ = 3 h, $P_w$ = 93.3 kPa.

dealumination of a $NH_4NaY$ zeolite during the period of self-steaming. Deammoniation (step 1) which begins at low temperature (*1, 23*) leads to a protonic zeolite in equilibrium with the hydroxyl form. Reactions 2 to 4 correspond to the hydrolysis of the various Si–O–Al bonds. However, the elimination of aluminum from the framework as well as the decrease in crystallinity could also be provoked by $NH_3$ liberated by zeolite deammoniation (*24*).

The following steps of the dealumination are the migration of the aluminum species generated by aluminum atoms extracted from the zeolite framework and the filling in by silicon atoms of the vacancies thus created, which leads to a stabilization of the framework (step 5). The loss in crystallinity

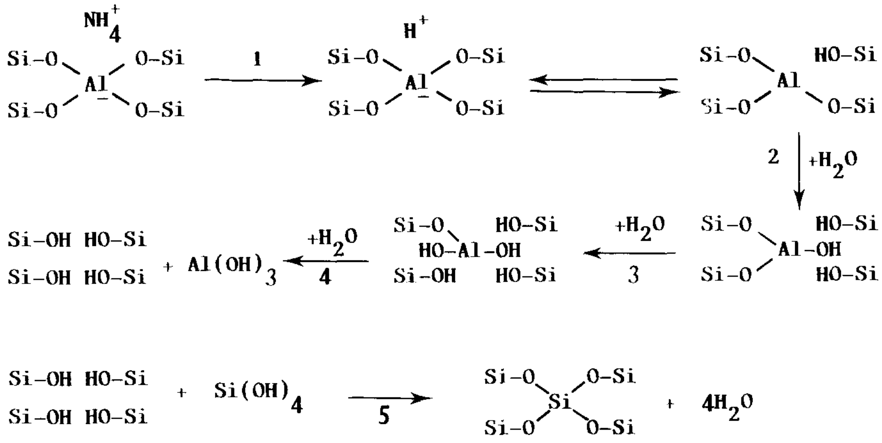


FIG. 12. Mechanism of dealumination of a $NH_4Y$ zeolite.

observed during the self-steaming means that the filling in of the defect sites by silicon (*25*, *26*) is slower than the dealumination process. Two reasons can be proposed to explain this observation:

(i) As the amount of water is relatively small, the migration of the silicic species, which like extra-framework aluminum species are hydroxylated species, occurs more slowly than the dealumination steps.

(ii) With the starting zeolite having no extra-framework silicic species, the stabilization of the zeolite framework cannot occur initially. Parts of the zeolite framework having undergone a pronounced dealumination have numerous defect sites and therefore collapse (*27*). This destruction of the framework is necessary to create the extra-framework silicic species necessary for the stabilization of the zeolite. It seems probable that the collapse of the framework occurs preferentially in the crystallite parts which are the richest in aluminum atoms.

It can be noted that a small increase in crystallinity is found during the first half hour of treatment under a water flow following the self-steaming. This can be explained both by an increase in the migration rate of the silicic species due to the presence of a large amount of water and by the large amount of silicic species created by the partial collapse of the framework during the self-steaming.

*3.2. Period of rapid dealumination under water vapor flow.* Steps 2 to 4 are probably responsible for the dealumination occurring during the first 3 h under water flow. Extraction of aluminum (step 4) is followed by the migration of aluminum species to the outer surface and by the filling in of the defect sites by silicon. Since $C_{RX}$ increases or remains constant during this period, the formation of hydroxylated silicon species, their migration, and the filling in of the defect sites (step 5) are more rapid than the dealumination. Therefore, the low value of the apparent activation energy is not due to limitations in the diffusion of water or of silicon species. On the other hand, there is a rapid increase in $(Al/Si)_{XPS}$, which shows that the migration of the aluminum species from the defect sites to the outer surface is rapid. The dealumination process is therefore limited by reactions 2 to 4. One molecule of water and one framework aluminum atom intervene in each of these elementary steps. If one of these reactions is the limiting step, the reaction orders must be 1 with respect to the aluminum atoms and to water. A value of 1 is actually found for the reaction order with respect to Al, but the value found for the reaction order with respect to water is apparently lower than 1. Imprecision concerning this latter value is probably responsible for this discrepancy.

*3.3. Period of slow dealumination under water vapor flow.* The dealumination being slower than during the previous period, the mechanism or at least the limiting step must be different from those proposed to explain the rapid dealumination. According to Fleisch *et al.* (*4*) the dealumination initially rapid could simply result from the unstable nature of Al-rich sites present on the starting zeolite. The same authors propose another explanation, namely that the rate of Al migration to the surface would be the limiting factor. This seems to be unlikely. Indeed, as shown here, dealumination can occur rapidly without migration of extra-framework aluminum species to the outer surface of the crystallites (see dealumination before time zero). Other explanations can be proposed:

(i) limitations to the diffusion of water caused by extra-framework species deposited on the outer surface or on the walls of the mesopores created by dealumination;

(ii) exchange of the zeolite by cationic extra-framework aluminum species, the dealumination of the exchanged zeolite being slower than that of the protonic zeolite.

This latter hypothesis is the most likely. Indeed it is well known that cationic extra-framework aluminum species are formed during dealumination. Moreover, the dealumination of cationic zeolites such as REY is slower than the dealumination of protonic

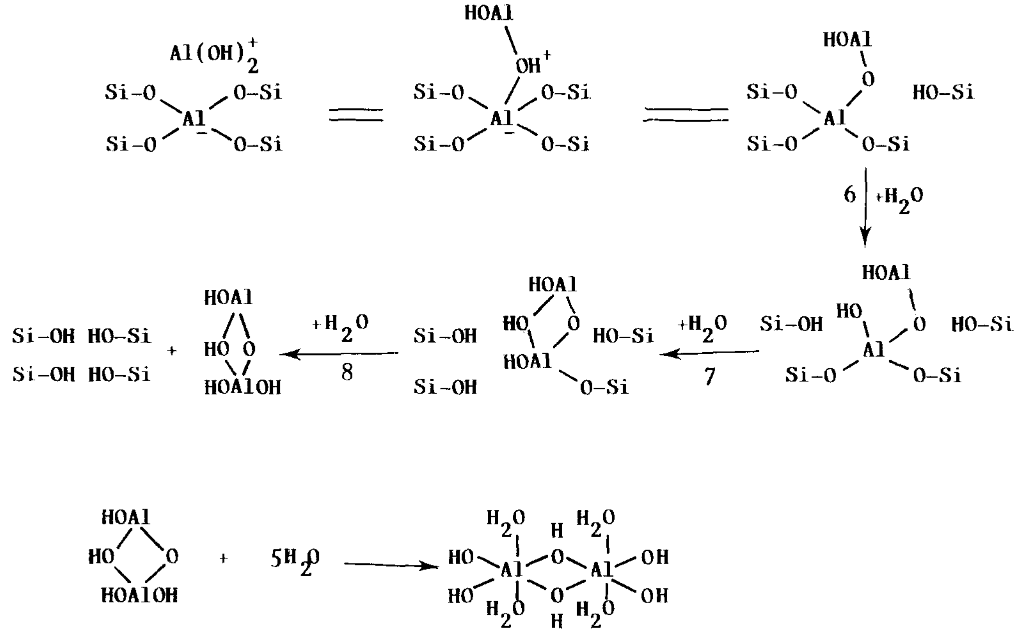
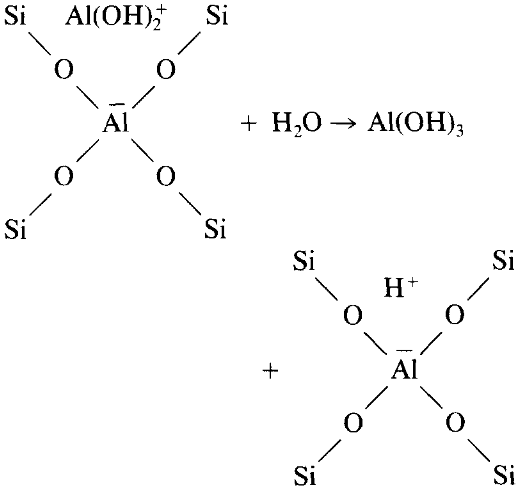


FIG. 13. Mechanism of dealumination of a Y zeolite exchanged by cationic aluminum species.

zeolites (*4*). The limiting step of the dealumination would be the formation of a protonic zeolite by hydrolysis of the zeolite exchanged by cationic aluminum species such as:



Another possibility could be that hydrolysis of Si–O–Al occurs directly on the zeolite exchanged by cationic aluminum species (Fig. 13). One of the steps of this hydrolysis would be the limiting step and would be slower than the limiting step of the dealumination of the protonic zeolite.

## CONCLUSION

After the rapid rise in temperature of the zeolite under nitrogen flow (self-steaming), two periods of dealimination can be distinguished. A rapid dealumination of $NH_4NaY$ occurs during the self-steaming under the effect of the water physically adsorbed or liberated by dehydroxylation and of $NH_3$ liberated by deammoniation. The filling in by silicon of the defect sites created by dealumination is slower than dealumination and therefore a partial collapse of the zeolite framework occurs. During the first period under water flow there is a rapid dealumination and a small increase in crystallinity due to the filling in of defect sites created during self-steaming. After 2–3 h of hydrothermal treatment the dealumination becomes slower. For both periods the kinetic orders with respect to water and to aluminum are equal to 1. The first period would correspond to the dealumination of a protonic Y zeolite and the second to that of the zeolite exchanged by cationic aluminum species. When the water pressure is equal to or higher than 50 kPa there is a relationship between the rates of dealumination and of migration of extra-framework aluminum species to the outer surface. However, during self-steaming, although dealumination is rapid, there is no enrichment in Al of the outer surface of the crystallites. The migrating aluminum species are therefore hydroxylated.

## REFERENCES

1. Mc Daniel, C. V., and Maher, P. K., *in* "Zeolite Chemistry and Catalysis" (J. A. Rabo, Ed.), ACS Monograph, Vol. 171 p. 285. Am. Chem. Soc., Washington, DC, 1976.
2. Scherzer, J., *in* "Catalytic Materials, Relationship between Structure and Reactivity" (E. G. Derouane, *et al.*, Eds.), ACS Symposium Series, Vol. 248, p. 157. Am. Chem. Soc., Washington, DC, 1984.
3. Corma, A., *in* "Zeolites: Facts, Figures, Future" (P. A. Jacobs and R. A. van Santen, Eds.), Studies in Surface Science and Catalysis, Vol. 49, p. 49. Elsevier, Amsterdam, 1989.
4. Fleisch, T. H., Meyers, B. L., Ray, G. J., Hall, J. B., and Marshall, C. L., *J. Catal.* **99,** 117 (1986).
5. Dwyer, J., Fitch, F. R., Guanlin Qin, and Vickerman, J. C., *J. Phys. Chem.* **86,** 4574 (1982).
6. Dwyer, J., Fitch, F. R., Machado, F., Guanlin Qin, Smith, S. M., and Vickerman, J. C., *J. Chem. Soc. Chem. Commun.*, 422 (1981).
7. Wichterlova, B., Novákova, J., Kubelkova, L., and Jírů, P., *in* "Proceedings, 5th International Conference on Zeolites" (L. V. C. Rees, Ed.), p. 373. Heyden, London, 1980.
8. Gross, Th., Lohse, U., Engelhardt, G., Richter, K. H., and Patjelova, V., *Zeolites* **4,** 25 (1984).
9. Breck, D. W., and Flanigen, E. M., "Molecular Sieves," p. 47. Society of Chemical Industry, London 1968.
10. Engelhardt, G., Lohse, U., Patzelova, V., Mäji, M., and Lippmaa, E., *Zeolites* **3,** 233 (1983).
11. Klinowski, J., Fyfe, C. A., and Gobbi, G. C., *J. Chem. Soc., Faraday Trans. 1* **81,** 3003 (1985).
12. Martins, R. L., Leite, A. C. B., Lan, Y. L., and De Costa, S. T., *in* "Zeolites for the Nineties" (J. C. Jansen *et al.*, Eds.), p. 75, 8th Int. Zeol. Conf., Amsterdam, 1989.
13. Sano, T., Suzuki, K., Okado, H. Fujisawa, K., Kawamura, K., Ikai, S., Hagiwara, H., and Takaya, H., *in* "Catalyst Deactivation" (B. Delmon *et al.*, Eds.), Studies in Surface Science and Catalysis, Vol. 34, p. 613. Elsevier, Amsterdam, 1987.
14. Sano, T., Suzuki, K., Shin, S., Hiroyuki, H., Takaya, H., *in* "Zeolites for the Nineties" (J. C. Jansen *et al.*, Eds.), p. 77, 8th Intern. Zeol. Conf., Amsterdam, 1989.
15. De Carvalho, A. P., Wang, Q. L., Giannetto, G., Cardoso, D., Brotas de Carvalho, M., Ramoa Ribeiro, F., Nagy, J. B., Asswad, J., Derouane, E. G., and Guisnet, M., *J. Chim. Phys.* **87,** 271 (1990).
16. Wang, Q. L., Doctorate thesis, No. 296, Univ. of Poitiers, 1989.
17. Maher, P. K., Hunter, F. D., and Scherzer, J., *in* "Molecular Sieve Zeolites-1" (R. F. Gould, Ed.), Adv. Chem. Ser., Vol. 101, p. 266. Am. Chem. Soc., Washington, DC, 1971.
18. Barrer, R. M., and Klinowski, J., *J. Chem. Soc., Faraday Trans. 1* **71,** 690 (1975).
19. Jacobs, P. A., and Uytterhoeven, J. B., *J. Chem. Soc., Faraday Trans. 1* **69,** 373 (1973).
20. Kerr, G. T., *J. Phys. Chem.* **71,** 4155 (1967).
21. Scherzer, J., and Humphries, A., *in* "Symposium on Advances in Zeolite Chemistry," Reprints, ACS Meeting, p. 520, Las Vegas, 1982.
22. Freude, D., Pfeifer, H., Staudte, B., *Zeolites* **3,** 171 (1983).
23. Kerr, G. T., *in* "Molecular Sieves" (W. M. Meier *et al.*, Eds.), ACS Adv. in Chem. Ser., Vol. 121, p. 219. Am. Chem. Soc., Washington, DC, 1974.
24. Briend-Faure, M., Cornu, O., Delafosse, D., Monque, R., and Pletre, M. J., *Appl. Catal.* **38,** 71.
25. Maxwell, I. E., Van Erp, W. A., Hays, G. R., Coupeurs, T., Huis, R., and Clague, A. D. H., *J. Chem. Soc. Chem. Commun.*, 523 (1982).
26. Klinowski, J., Thomas, J. M., Fyfe, C. A., and Gobbi, G. C., *Nature* (*London*) **296,** 533 (1982).
27. Lohse, W., and Mildebrath, M., *Z. Anorg. Allg. Chem.* **476,** 126 (1981).