Reaction of Na-A zeolite with molecular fluorine

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Abstract. NaA zeolite reacts rapidly with molecular fluorine at room temperature forming a mixture of amorphous material and of residual crystalline materials. The extent of the reaction depends on the gaseous pressure. The amorphous material contains fluorinated octahedral aluminum complex, sodium and silica. The crystalline fraction keeps the same unit cell parameter as the initial sample.

1. Introduction
At room temperature, gaseous F₂ extracts rapidly and almost quantitatively tetrahedrally coordinated aluminum from the lattice of acid, near-faujasite zeolite, HY (Si/Al ≈ 13). Fluoro-hydroxy-aluminum complexes of the type Al₃F (OH)₅₋(5+n)⁺ in which Al is octahedrally coordinated are formed in the zeolite cages. Under a molecular fluorine pressure of 300 torr and within 10 minutes, the dealumination of HY is nearly total at room temperature [1, 2]. However the crystallinity of the zeolite is unchanged as already observed by Lok et al. [3], Becker et al. [4] and Ghosh et al. [5].

Similar observations were carried out with H-ZSM-5 [2]. The structure remains intact while the Si/FAI ratio increases, from 27 to 233 or from 55.2 to 382. The terminal (dangling) SiOH’s in H-ZSM-5 are fluorinated also, while the extent of this reaction was negligible in HY. However, the formation of tetrahedral Al-F species was detected for fluorinated HY prepared through aqueous impregnation with NH₄F [6].

Panov et al. [7] found that the main effect of fluorination of ultrastable Y zeolite (USY) by ammonium fluoride is to increase the strength of the residual Brønsted sites. Hierarchical ZSM-5 is produced with a chemical treatment using mixed NH₄F/HF solutions without substantial changes in the number of sites [8-10]. HZSM-5 modified with aluminum fluoride shows that dealumination increase their activity and stability [11].

The introduction of fluorine with NH₄F in the beta zeolite framework generated higher amounts of stronger Bronsted acid sites while in the mordenite zeolite is observed a lower amount of acid centers. [10]. Terminal silanols and extra framework aluminum species like Al-OH were the result of the dealumination by acid leaching induced by (NH₄)₂SiF₆ [12].

Engelhardt and Michel [13] considered the dealumination of NaA as impossible, because the silica backbone was not maintained. This observation will be confirmed here although Fyfe et al [14] proved that the structurally analogous ZK-4 can be dealuminated completely by steaming.

As far as we are aware, the dealumination of NaA by molecular fluorine at room temperature has not been attempted. The comparison of the behaviors towards fluorine of the A and Y molecular sieves is interesting since, from the structural point of view, they differ only by the nature of the polyhedron joining the cubooctahedra, being a square prism in A and a pseudo-hexagonal prism in Y.

The difference of behavior of these two zeolites with respect to molecular fluorine will be analyzed and an explanation will be tentatively provided. Among the possible causes, the much higher Al content in NaA plays unquestionably a role since Al was proven to be a weak point of the zeolites lattices, previously studied.

On the opposite, in NaA, kinetic constraints could slow down the reaction, favoring the structural integrity. The van der Waals molecular diameter of F₂ is 2.7 Å and the windows in zeolite A have a
diameter of 4.1 Å. Our hope to dealuminate extensively NaA by \( \text{F}_2 \) was however unfulfilled. Considerable loss of surface area occurs by exposing NaA to \( \text{F}_2 \) at room temperature and even at 373 K. Dealumination of HY does not decrease noticeably the porous volume [15] but, in zeolite A the structure collapses.

2. Experimental
The Linde 4 Na-A zeolite (lot 94 1889020064) was outgassed (< 10\(^{-3}\) torr) at 200ºC for at least two hours in order to eliminate physisorbed \( \text{H}_2\text{O} \) and to minimize the formation of HF. After outgassing the zeolite at 300ºC, the temperature was lowered and dry \( \text{F}_2 \) (Air Products), purified on a NaF bed, was introduced under pressures between 50 and 600 torr in a stainless steel reactor. The fluorine absorption was followed volumetrically for about 20 minutes at 298K or at 343K. After 20 minutes, no pressure change was noticeable and the excess \( \text{F}_2 \) was evacuated. A good agreement was found between the fluorine content obtained volumetrically and by chemical analysis. The sample was kept in air until the X-ray diffraction pattern, the NMR and IR spectra were recorded.

The fluorine analyses were carried out by the potentiometric technique proposed by Bodkin [16]. The sample was melted with lithium tetraborate and metaborate. It was then dissolved in nitric acid (10 wt%), and the EMF of the solution was compared to those obtained from standard solutions of NaF in the same solvent. The standard error on F determination was 10%.

X-ray diffraction patterns were recorded with a D500 Siemens goniometer (Cu K\( \alpha_1 \), scanning speed of 2\(^{°}\)/min) and an internal standard (KCl) was mixed with the sample in order to get accurate spacing measurements. The strong KCl reflection line at 2\( \theta \) = 50\(^{°}\) corresponding to a spacing of 1.816 Å was taken as reference for calculating the spacings at 1.919, 1.895, 1.740, and 1.690 Å corresponding to the 540, 541, 550 and 720 reflections on the untreated sample. The average a\(_0\) was 24.594 Å, to be compared to 24.61 Å given by Gramlich and Meier [17] for the initial structure. The average error on a\(_0\), appreciated from the reproducibility of the numerical values, was ±0.02 Å.

It must be outlined that no evidence for the expected formation of cubic NaF has been found. The diatomic bond strength of NaF is 519 kJ vs. 663 kJ for Al-F [18]. Thus the latter is formed preferentially and residual Na probably combined with the amorphous silica formed in the dealumination process.

The one-pulse \(^{27}\text{Al} \) MAS NMR spectra were recorded under the following conditions: frequency: 130.3 MHz, spinning rate: 15.4 kHz, line broadening: 100 Hz, P1: \( \cong \pi/12 \) µs and 256 scans. For \(^{29}\text{Si} \), the conditions were as follows: frequency: 99.36 MHz, spinning rate: 9.4 kHz, line broadening: 20 Hz, P1: 3µs and a variable number of scans.

The IR spectra were obtained from 1% KBr pellets on a Nicolet 5SX fitted with a CsI optic.

3. Results and Discussion
Considering the low dissociation enthalpy of molecular fluorine, namely 156 kJ/mol, and the bond strength of AlF\(_3\) (663.3 kJ/mol), a dissociative absorption process was predictable, [19]. Indeed, the plot of the molecular fluorine uptake is linear respect to the square root of the pressure (torr). Pressure and temperature determine the maximum uptake (Figure 1).

The rate of fixation, very rapid during the first 100s, decreases exponentially with the advancement of the reaction. The fluorine contents of the solids after equilibration at different temperatures and pressures are shown in table 1. The experimental error is less than 10%.

The X-ray diffractograms at different degrees of dealumination, see figure 2 and table 1, have been analyzed from two different viewpoints:

- The degree of crystallinity, abbreviated as crystal, was determined by comparing the sum of the intensities of the 110, 300, 311 and 410 reflections with that of the initial NaA. In opposition to what had been observed for dealuminated HY, USY, and H-ZSM-5, the crystallinity of NaA is affected to the extent of the progress of the fluorination reaction.
- The cubic unit cell dimension $a_0$ has been measured from the 540, 541, 550 and 720 reflections. When the crystallinity is larger than 65%, $a_0$ remains within 0.02 Å the initial value. For crystallinity lower than 65%, it decreases towards 2.5 Å.

**Figure 1.** Fluorine uptake vs. the square root of the fluorine pressure at three temperatures.

**Figure 2.** X-ray diffractograms of NaA, original material or treated at 298K under fluorine pressure of, from top to bottom 100, 300 and 600 torr, respectively. The formation of an amorphous phase is evidenced by the “halo” near 20°.

**Table 1.** Fluorine content and crystallinity in the samples prepared under pressures between 50 and 600 torr at different temperature.

| Label | Initial Pressure (torr) | Temp. K | Fluor. a 10²⁰ Atom/g | Cristal. b % | $a_0$ c Å | FAl d 10²⁰ Atom/g | Relat. Abs. e at 552cm⁻¹ % |
|-------|------------------------|---------|----------------------|-------------|----------|------------------|-------------------------|
| Z4AF  | 600                    | 298     | 17                   | 41          | 24.49±0.02 | 1.4              | 5.7                     |
| Z4AF  | 300                    | 298     | 13                   | 65          | 24.59±0.02 | 3.0              | 7.2                     |
| Z4AF  | 100                    | 298     | 4.8                  | 92          | 24.58±0.02 | 9.1              | 9.1                     |
| Z4AF  | 50                     | 298     | 2.4                  | 99          | 24.58±0.02 | 13               | 9.9                     |
| Z4AF  | 600                    | 343     | 21                   | 28          | 24.49±0.025| na.              | 4.6                     |
| Z4AF  | 300                    | 343     | 13                   | 51          | 24.54±0.04 | na.              | 6.8                     |
| Z4AF  | 100                    | 343     | 5.1                  | 89          | 24.59±0.02 | na.              | 9.3                     |
| Z4AF  | 50                     | 343     | 1.5                  | 98          | 24.59±0.02 | na.              | 10.1                    |

aFluorine content; bcrystallinity; c cubic unit cell dimension; d framework Al content from the integrated areas of the NMR line at 64.2ppm and equ.(1); e relative absorbance FT-IR of the D-4R vibration at 552cm⁻¹ with respect to the absorbance of the Si-O stretching at about 1000cm⁻¹.
Thus, at any degree of advancement of the dealumination reaction, the solid may be considered as an intimate mixture of amorphous material and of crystalline NaA. In HY, [7], the unit cell dimension shrunken as Al-O bonds are replaced by shorter Si-O bonds but the degree of crystallinity is not affected. The $^{27}$Al MAS NMR spectra in figure 3 have been plotted by keeping constant the amplitude of the line at 64.4 ppm attributable to tetrahedral aluminum, belonging to the zeolite framework, hereafter called FAl. At the absolute scale, the integrated areas of the Al$^{IV}$ resonance at 64.4ppm are 4.2, 9.0 and 27.4 arbitrary units for Z4AF6, Z4AF3, Z4AF1, respectively, while it is 127.3 a.u. in the starting material. The difference between the total aluminum content (Al$^t$) and FAl is the non-framework aluminum, called NFAl$^{calc}$, not to be confused with the NFAl observed on the spectra of figure 3 as a broad asymmetric resonance near 5ppm. The upfield shift and tailing of this resonance, as NFAl increases, are in agreement with earlier observations [1, 2]. A similar shift, observed in these works, was attributed to the fluorination of the NFAl species.

Whereas it is possible to estimate the residual FAl content from the equation:

$$FAl = \frac{Al^t(FAl \text{ sample/FAl starting})}{Al^t-FAl}$$

NFAl cannot be obtained directly from the NMR spectra because the shift and the shape of an Al resonance line are dominated by the value of the quadrupolar interaction. For NFAl, the interaction is strong and depends on the nature of the samples because different octahedral fluoro-complexes are formed according to the availability of fluorine (Table 2). The quadrupolar interaction is considerably weaker and more constant for FAl [20].

**Figure 3.** $^{27}$Al MAS NMR spectra of NaA at three fluorine (Fl) contents, see table 1, namely Z4AF6: Fl=17, Z4AF3: Fl=13, and Z4AF1: Fl=4.8, $10^{20}$ atoms/g Z resonance.

**Figure 4.** $^{29}$Si MAS NMR spectra of the samples. From top to bottom, the number of scans has been increased in order to keep the signal to noise ratio comparable.
Another NMR observation supports also the existence of a mixture of amorphous (reacted), and crystalline (unreacted), materials. The $-90.2\pm0.1\text{ppm}$ $^{29}\text{Si}$ MAS NMR in the initial NaA line remains at that frequency at low residual degree of crystallinity as shown in figure 4. The consequences of the translocation of aluminum in the dealuminated samples, from tetrahedral to non-framework positions, is the formation of an envelope of broad Si resonances between -110 and -80 ppm as shown in the same figure.

### Table 2. NMR Characteristics of the six-fold coordinated NFAl.

| Sample Label | Crystallinity | Amplitude of the Al^{VI} resonance, a.u. | Chemical Shift of the Al^{VI} resonance, ppm. |
|--------------|---------------|-----------------------------------------|---------------------------------------------|
| Z4AF6        | 41            | 2.4                                     | 4.5                                         |
| Z4AF3        | 65            | 1.1                                     | 4.9                                         |
| Z4AF1        | 92            | 0.4                                     | 7.3                                         |
| Z4AF.5       | 99            | <0.1                                    | 10.6                                        |

Figure 5A shows that FAI decreases linearly as the fluorine content increases. While the variation of NFAl is apparently exponential. From the correlation coefficient of the regression between the fluorine content and FAI (0.975), the error on the estimate of FAI is probably less than 10%.

The key for understanding the behavior of NaA in molecular fluorine may be found, we believe, in figure 5B. The crystallinity, as defined above, and the intensity of the square prism vibration at 552 cm$^{-1}$ [21], decrease simultaneously with the fluorine content, and thus with NFAl$_{\text{calc.}}$, demonstrating the dependence of the stability on the double ring bridging the cubooctahedra. In HY, such a modification of the vibrational band of the hexagonal prism was not observed.

In HY, the specific surface area was not greatly affected by dealumination, while in NaA, the surface area, initially 760 m$^2$/g, is less than 300 m$^2$/g when the residual crystallinity is lower than 30%.

![Figure 5](image-url)

**Figure 5.** (A) Linear decrease of the FAI content, $10^{20}$ atoms/g zeolite from the integrated areas of the 64.4 ppm NMR line, with respect to the fluorine content, $10^{20}$ atoms/g. (B) Decrease of the crystallinity of the residual material and of the relative absorbance of the double 4 ring vibration at 552 cm$^{-1}$ with respect to NFAl$_{\text{calc.}}$, equ. (1), $10^{30}$ atoms/g zeolite.
4. Conclusions
The discussion has been focused on the different behaviors of NaA and HY towards dealumination by molecular fluorine. In both cases, the lattice aluminum is rapidly extracted and brought into non-lattice position where octahedral fluoro-complexes are formed. The structure and composition of these complexes are probably different according to the chemical characteristics of the host lattices. This aspect will not be discussed here.

The most striking difference is the presence, in NaA, of a crystalline phase mixed with an amorphous material. The amorphous material contains silicon, fluorine, residual sodium and octahedral aluminum.

The amount of crystalline material decreases as fluorination progresses, but its structure is unchanged. The arguments supporting this conclusion are the following:

- The maximum variation of the $a_o$ parameter is between 24.6 and 24.5 (table 1)
- The frequency of the residual Si resonance remains at -90.2ppm, thus the silicon environment ($1S_i/1Al$) remains unchanged.
- Two structural parameters, the crystallinity and the absorbance of the IR band assigned to the square double ring decrease simultaneously, (figure 4B). The amorphization could be a consequence of the catastrophic removal of the square prisms pillaring the cuboctahedra.

What is common with the behavior of the HY and H ZSM-5 is the linear decrease of the framework aluminum content with the amount of fixed fluorine and the simultaneous formation of octahedral fluorine-aluminum complexes.

5. References
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