

## DEALUMINATION OF NaX ZEOLITE WITH NITROSYL CHLORIDE

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### ABSTRACT

The interaction of nitrosyl chloride with NaX zeolite is described. The reactions observed in a static reactor and an i.r. cell using self-supporting wafers can be divided into two groups: at lower temperatures, an "ion-exchange" process takes place, the  $\text{Na}^+$  ions being "exchanged" for the nitrosonium cation stemming from the reactant; at elevated temperatures,  $\text{NOCl}$  or its surface intermediate, the  $\text{NO}_3^-$  ion, leads to dealumination of the zeolite. A probable mechanism is proposed for the reactions eventually leading to dealumination.

### INTRODUCTION

Since the first publications on "ultrastabilization" in 1966, an increasing number of papers have dealt with dealuminating procedures using different reactants and media, and with investigations of the various physical and chemical properties of the partly or completely dealuminated zeolitic samples [1-17].

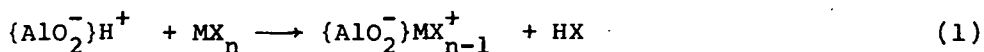
A few recent papers describe dealumination procedures in which volatile halogen-containing reactants are used and dealumination is carried out as a gas-solid reaction in the absence of water vapour [18,19].

Some years ago we performed experiments to decrease the aluminium content of zeolites using volatile reagents [20-22]. It turned out that a wide class of chemicals, e.g. volatile metal halides, oxyhalides, thiohalides, acid halides and even metal alcoholates and alkyls, are able to cause dealumination to various extents.

The reactions taking place between a zeolite and some agent from the above classes can be divided into two groups.

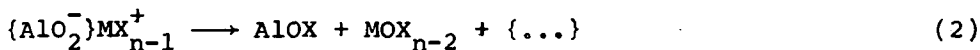
The first group involves transformations at ambient temperature or slightly above, where the agent interacts with the exchange cation, resulting in a neutral molecule (which, if non-volatile, remains in

the framework, or, if volatile, leaves it) and in a charged species derived from the agent itself:



where M is unspecified and X is a halide, alkoxy, alkyl, etc. group. The stability and life-span of the  $\text{MX}_{n-1}^+$  ion and its reactivity toward framework ions and extraneous reactants varies between very wide limits, depending mainly on the electronegativity of X.

The second group consists of surface reactions occurring at elevated temperatures between  $\text{MX}_{n-1}^+$  and the framework constituents. These transformations have the following common characteristics: one (or two) framework  $\text{O}^{2-}$  ion(s) from among the nearest neighbours of the aluminium leave(s) the lattice to join  $\text{MX}_{n-1}^+$ ; thereafter, provided X is of sufficient electronegativity (being for example some halide), the X species undergoes rearrangement, leading to the production of an aluminium-oxy-X cluster and an empty nest:



where the symbol  $\{\dots\}$  stands for a framework vacancy. As far as  $\text{MOX}_{n-2}$  is concerned, its chemical identity depends on the valency of M, i.e. on the value of n.

This paper presents recent results on the probable mechanism of dealumination using NOCl as reagent. With  $\text{M} \equiv \text{NO}$  and  $n = 1$ , NOCl does not follow in all details the scheme outlined previously, but exhibits a peculiar behaviour instead, which may turn out to be characteristic for this class of chemicals.

## EXPERIMENTAL

The zeolite used in the experiments was NaX (Union Carbide Co., Linde Div.), as supplied.

The dealumination reactions were carried out in a recirculatory flow reactor and in an i.r. cell.

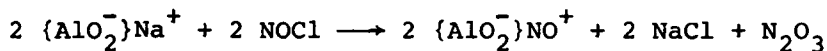
Both the gaseous products and the solids were analysed.

The surface reactions taking place upon the adsorption of NOCl were followed by i.r. spectroscopy, using self-supporting wafers of appr.  $10 \text{ mg} \cdot \text{cm}^{-2}$  thickness. The adsorptions of the gaseous products of the dealumination ( $\text{NO}_2$ , NO) were studied separately.

The KBr pressed pellet technique was used for determination of the spectra of the dealuminated zeolites in the structure-sensitive i.r. region.

## RESULTS

The gases released in the interaction of NaX zeolite with NOCl were determined in a recirculatory flow reactor. It was found that their molar ratio corresponded to  $\text{NOCl}:\text{NO}_2:\text{NO} = 2:1:1$ , suggesting an overall reaction in agreement with Eq. (1):



For investigation of the mechanisms of the reactions taking place between NaX and NOCl in situ, i.r. measurements were performed. Figure 1 shows the spectra recorded upon the adsorption of  $3 \cdot 10^2$  Pa NOCl on the pretreated (at 773 K in vacuum) NaX zeolite wafer. After the admission of NOCl at room temperature, three absorption bands appeared, at 2375, 2010 and  $1370 \text{ cm}^{-1}$ .

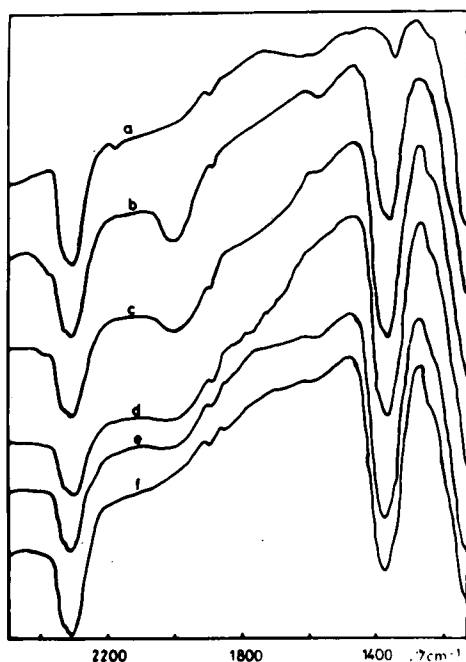


Fig. 1. Infrared spectra of adsorbed NOCl

- (a) pretreated NaX
- (b) at ambient temperature
- (c) 0,5 h at 373 K
- (d) 3 h at 373 K
- (e) 15 h at 373 K
- (f) 0,5 h at 373 K evacuated

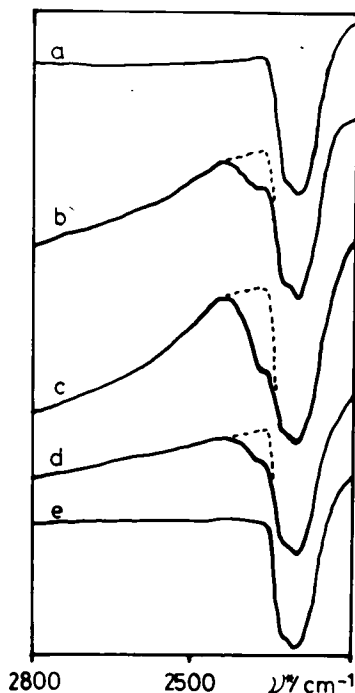


Fig. 2. Infrared spectra of adsorbed NOCl

- (a) pretreated NaX
- (b) at ambient temperature
- (c) 11 h at 273 K
- (d) 0,5 h at 373 K
- (e) 3 h at 373 K

After heat treatment at 373 K, the intensity of the band at  $2010\text{ cm}^{-1}$  decreased. Evacuation at the same temperature led to the complete disappearance of this band. It seems very likely that the absorption at  $2010\text{ cm}^{-1}$  is caused by adsorbed NOCl.

The nature of the shoulder at  $2375\text{ cm}^{-1}$  was studied in a separate experiment at higher NOCl pressures, for the frequency of this band overlaps with that of the  $\text{NO}^+$  ion [23]. The intensity of this band follows a maximum curve as a function of temperature (see Fig. 2), and therefore the species causing this band should be a reaction intermediate.

On elevation of the temperature, the band at  $1375\text{ cm}^{-1}$  (probably due to the  $\text{NO}_3^-$  ion in the zeolite structure [24]) decreases in intensity and two new bands appear, at  $1240$  and  $1630\text{ cm}^{-1}$ , assigned to  $\text{NO}_2^-$  ions formed in the framework and to adsorbed NO [25], respectively. Heat treatment at 673 K causes a shift in the frequency of the band at  $1630\text{ cm}^{-1}$  to  $1690\text{ cm}^{-1}$ , and following evacuation it disappears.

From the results of i.r. measurements and reactor experiments it can be concluded that the main gaseous products of the reactions are different nitrogen oxides. In order to assign the bands observed and to acquire a more detailed insight into the reactions taking place in the zeolite framework, separate experiments were carried out with  $\text{NO}_2$  and NO, under the same conditions as used with NOCl.

Figure 3 shows the spectra following the adsorption of  $4 \cdot 10^2\text{ Pa}$   $\text{NO}_2$  on NaX zeolite. At room temperature two absorption bands appear, at  $1915$  and  $1370\text{ cm}^{-1}$ . The former band is caused by sorbed  $\text{NO}_2$  [26] and the latter can be assigned to the  $\text{NO}_3^-$  ion. At higher temperatures two other bands develop, at  $1690$  and  $1245\text{ cm}^{-1}$ , while the intensity of the band at  $1370\text{ cm}^{-1}$  decreases. The band at  $1370\text{ cm}^{-1}$  has the same temperature-dependence as the nitrate band in the case of NOCl adsorption.

Figure 4 shows the absorption bands upon the adsorption of NO on NaX zeolite. The band positions at ambient temperature are  $1630$ ,  $1240$  and  $1690\text{ cm}^{-1}$ . It can be seen clearly that, as the temperature is raised the intensity of the band at  $1240\text{ cm}^{-1}$  (assigned to  $\text{NO}_2^-$  ions in the zeolite structure) increases, attains a maximum, and then decreases, provided the sample was exposed to heat treatment at 473 K or above. Simultaneously, the heating gives rise to two new bands, at  $1470$  and  $1410\text{ cm}^{-1}$ .

Figure 5 shows the spectrum of the NaX sample treated with NOCl in the structure-sensitive i.r. region. Comparison of this spectrum with that of the untreated specimen reveals two new absorption bands,

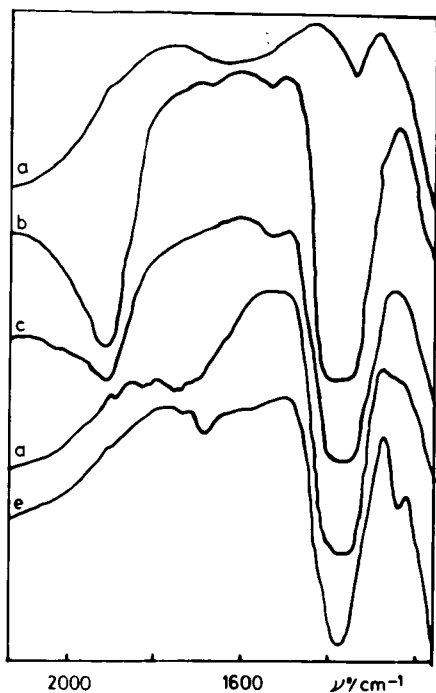


Fig. 3. Infrared spectra of adsorbed  $\text{NO}_2$

- (a) pretreated NaX
- (b) at ambient temperature
- (c) evacuated at ambient temperature
- (d) 0,5 h at 573 K
- (e) 0,5 h at 673 K

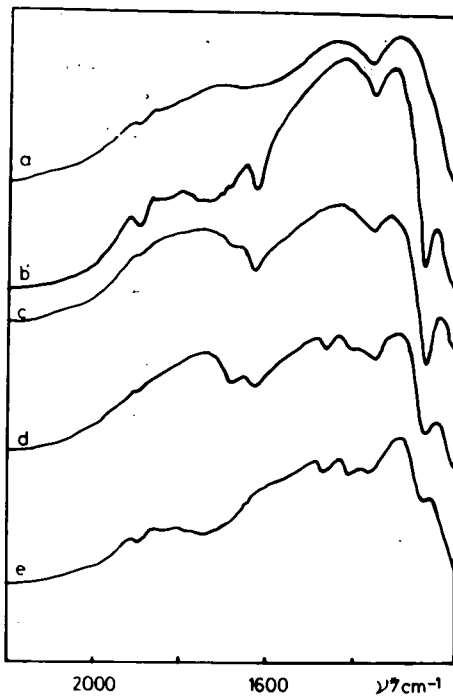


Fig. 4. Infrared spectra of adsorbed  $\text{NO}$

- (a) pretreated NaX
- (b) at ambient temperature
- (c) 15 h at 373 K
- (d) 15 h at 473 K
- (e) 3 h at 573 K

at 1390 and 860  $\text{cm}^{-1}$ . The spectrum of  $\text{NO}_3$  ions residing in the structure of an NaX sample prepared by the well-known salt occlusion technique exhibits the same characteristics (see Fig. 5, spectrum c).

## DISCUSSION

The wavenumbers and the assignments of the bands observed on the adsorption of  $\text{NOCl}$ ,  $\text{NO}_2$  and  $\text{NO}$  on NaX zeolite are listed in Table 1. The spectroscopic changes caused by prolonged adsorption and heat treatment are indicated.

The sequence of reactions taking place during the interaction of  $\text{NOCl}$  with NaX can be visualized as follows.

At 293 K and above the i.r. absorption developing at 2375  $\text{cm}^{-1}$  suggests the formation of  $\text{NO}^+$  cations, with the simultaneous formation

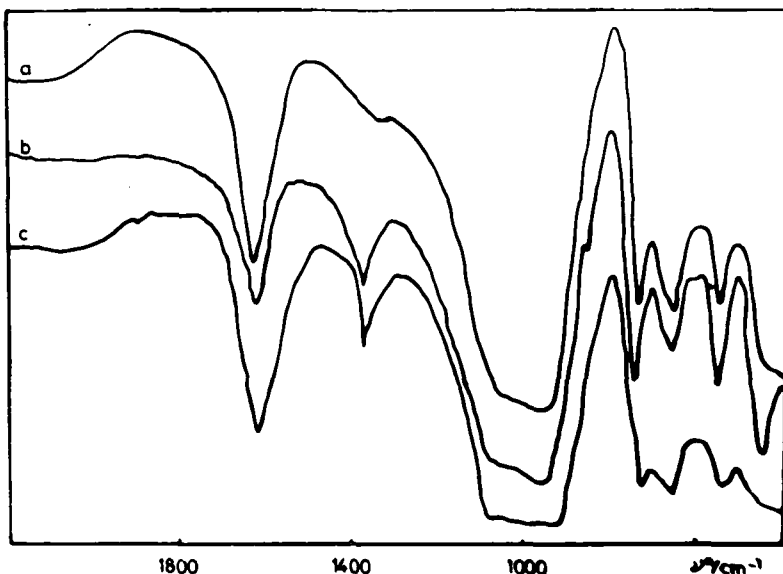
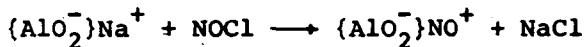


Fig. 5. Infrared spectra of NaX samples in the structure sensitive region

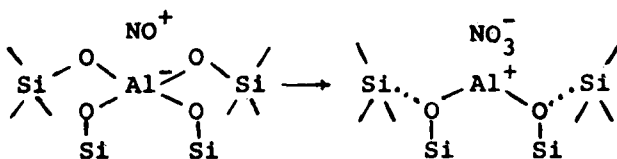
- (a) pretreated NaX
- (b) NaX treated with NOCl
- (c)  $\text{NaNO}_3$  occluded in NaX framework

of NaCl. It is believed that this reaction is similar to that described by Beattie for the interaction of NOCl and analcite [27]. It is essentially an "ion-exchange", where  $\text{Na}^+$  ions are substituted for the  $\text{NO}^+$  "ions" of NOCl in agreement with Eq. (1):



At 373 K the band intensity at  $2375 \text{ cm}^{-1}$  follows a maximum curve, indicating that  $\text{NO}^+$  is a surface intermediate and should therefore be involved in successive transformations.

The i.r. absorption at  $1370 \text{ cm}^{-1}$ , characteristic of the  $\text{NO}_3^-$  ion, provides evidence that the redox step

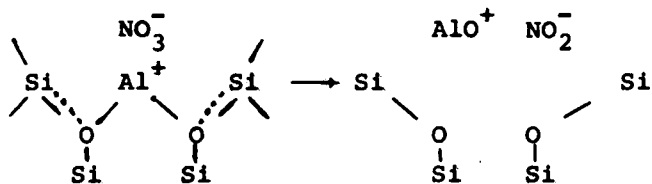


takes place during the elimination of two lattice  $\text{O}^{2-}$  ions and simultaneous oxidation of the trivalent nitrogen into the pentavalent state. The fate of the two electrons left behind is uncertain at present. After this step the aluminium is presumed to remain bound in the zeolitic lattice.

Table 1  
Assignment of the observed bands

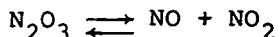
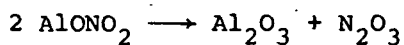
Adsorption of	Wavenumber /cm <sup>-1</sup>				
NOCl Assignment: Remarks:	2375 NO <sup>+</sup> ion maximum curve	2010 adsorbed NOCl decreases in time and with temp. rise	1630 adsorbed NO increases	1370 NO <sub>3</sub> <sup>-</sup> ion decreases	1240 NO <sub>2</sub> <sup>-</sup> ion maximum curve
NO <sub>2</sub> Assignment: Remarks:		1915 adsorbed NO <sub>2</sub> decreases	1690 adsorbed NO increases	1370 NO <sub>3</sub> <sup>-</sup> ion decreases	1245 NO <sub>2</sub> <sup>-</sup> ion increases
NO Assignment: Remarks:		1910 adsorbed NO <sub>2</sub> decreases	1630 adsorbed NO decreases under evacuation		1240 NO <sub>2</sub> <sup>-</sup> ion maximum curve

On elevation of the temperature up to 473 K, a strange reversal of the previous redox step takes place: the loosely bound aluminium leaves the lattice and the (Al<sup>+</sup>NO<sub>3</sub><sup>-</sup>) moiety rearranges by charge transfer into AlONO<sub>2</sub>, where the nitrogen is again present as a trivalent species:



The formation of NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> ions in the interaction of NOCl with NaX zeolite is corroborated by comparison of the spectra in Fig. 5. The ions reside as stable entities in the structure of the zeolite, unless the reaction temperature exceeds their decomposition temperature. On washing of the treated sample with distilled water, the NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> ions can be transferred into solution and their concentrations determined by classical analytical methods.

The formation of N<sub>2</sub>O<sub>3</sub> is due to the thermal decomposition of the AlONO<sub>2</sub> species:



The newly formed strained Si - O - Si linkages produce i.r. absorption at  $860 \text{ cm}^{-1}$ , as shown in Fig. 5. Similar bands could be observed in the case of mordenites dealuminated with phosgene [22].

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