DEALUMINATION OF ZEOLITES BY VOLATILE REAGENTS STRUCTURAL AND OTHER CONSEQUENCES

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On interacting with zeolites, volatile non-metal (and even metalloid and metal) halides exhibit excellent dealumination abilities at elevated temperatures. The dealuminated samples were investigated by ir, proton nmr, X-ray spectroscopy and in the cracking reaction of propane. A new ir absorption band was observed at 930 cm^{-1} in good correlation with degree of dealumination.

It is a well-established fact that the thermal and hydrothermal stabilities of zeolites and their catalytic activities in carboniogenic reactions depend to a large extent on the structural silicon to aluminium ratio. There are several reasons, both theoretical and practical, explaining why, since the pioneering work on ultrastabilization, an increasing number of publications deal with dealumination procedures and their various consequences. Until recently the investigations were restricted almost exclusively to two types: zeolite Y and mordenite.

Characterization of the dealuminated zeolitic specimens extends to structural questions and to the catalytic activity exhibited in selected test reactions [1—14]. A great deal of subtle structural information is nowadays becoming available from ^{29}Si and ^{27}Al n.m.r. investigations aimed at the precise determination of the coordination of framework Si and Al ions [15—19].

From among the different reagents leading to dealumination, acid halides (and in a broader sense metal and metalloid halides) deserve special attention, for framework Al usually reacts under the given conditions to form volatile $AlCl_3$, which can easily be removed from the structure [20].

This paper deals with the dealumination of zeolites using volatile halides as reagents, and with the characterization of the zeolitic specimens thus obtained.

Experimental

The zeolites used in the experiments were Na-mordenite (Norton Co.) and NaY (Union Carbide Co., Linde Div.) as supplied, and samples in which the Na$^+$ ions had been partially exchanged for NH$_4^+$ ions.

Most often the mordenite samples were dealuminated with phosgene.

A heated quartz tube-reactor was used to carry out the dealumination. The operations involved the following steps: the reactor was charged with a 2 g sample of

the zeolite (particle size 0.4—0.8 mm), which was ignited at 873 K during purging with a slow stream (3.33 10^{-3} cm^3 s^{-1}) of dried N$_2$; after pretreatment for 3 hr the temperature was adjusted to the set value, and a stream of phosgene was admixed to the N$_2$ in order to yield a gas mixture containing 20 vol % phosgene; after completion of the reaction, the (partially dealuminated) sample was heated for a further 1 hr in N$_2$ at 873 K to eliminate the adsorbed phosgene and AlCl$_3$.

The fall-out (consisting mainly of AlCl$_3$ and FeCl$_3$) was collected and analyzed.

The zeolite sample was washed free of Cl$^-$ ions and dried at 353 K. Its aluminium content was determined by means of the classical coagulation technique. For purposes of analytical comparison a few samples were dealuminated by extraction with cc. HCl. The dealumination procedure described by BEYER [21], making use of SiCl$_4$ and leading to the exchange of *framework* Al^{3+} ions for Si^{4+} ions, was also applied.

The ir spectra were determined with a Specord IR—75 spectrometer using the pressed KBr pellet technique (the pellets contained 11 wt % zeolite).

Crystallinity was checked with a Dron-3 X-ray diffractometer, taking the reflections, at $3° < 2\theta < 34°$.

The catalytic activities of the dealuminated mordenite samples were studied in the cracking reaction of propane, using a recirculatory flow reactor with gc analysis.

Results and discussion

It is a common experience that, irrespective of the specific reactant applied, the degree of dealumination depends sensitively on the reaction temperature (see Fig. 1). At higher temperatures the greater mobility causes an increasing number of framework oxygen ions to interact with the dealuminating reactant (see e.g. GEUSSE [22]). The highest degree of dealumination attained in the case of mordenite was 96% with a crystallinity retention of 81% (as estimated on the basis of the nine most intense X-ray reflections).

Although the picture is far from being definitive, the great number of different reactants applied warrant some generalization. For dealumination to occur it seems a necessary condition that the reactant be able to interact first with the zeolitic
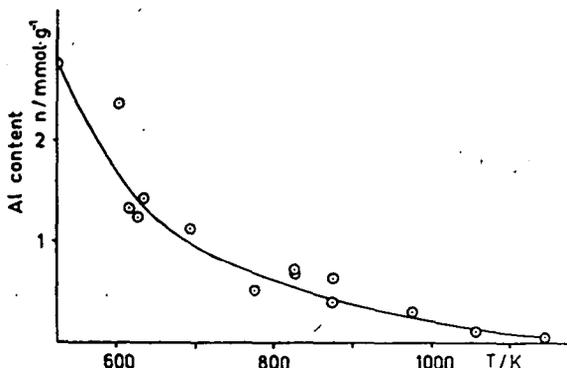
Fig. 1. Decrease of the aluminium content of the dealuminated samples as a function of reaction temperature

exchange ion; subsequently, the rest of the molecule eliminates a framework O^{2-} ion and at the same time shares the negatively charged constituents of the molecule with the Al^{3+} ion.

SiCl$_4$ can be regarded as an ideal reactant [loc. cit.] because the molecule is best suited *to get chemisorbed* on H-form zeolites at elevated temperatures (sieving effect may occur in the case of very narrow pores) under formation of HCl:

$$\{AlO_2^-\} \cdot H^+ + SiCl_4 \rightarrow HCl\uparrow + \{AlO_2^-\} \cdot SiCl_3^+;$$
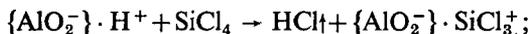
at still higher temperatures *exchange of framework cations* takes place and AlCl$_3$ will be set free:

$$\{AlO_2^-\} \cdot SiCl_3^+ \rightarrow AlCl_3\uparrow + \{SiO_2\}$$

Phosgene reacts similarly showing all the mechanistic details mentioned above: *chemisorption* under release of HCl:

$$\{AlO_2^-\}H^+ + COCl_2 \rightarrow HCl\uparrow + \{AlO_2^-\} \cdot COCl^+$$
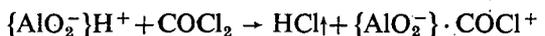
elimination of framework O^{2-} *ion:*

$$\{AlO_2^-\} \cdot COCl^+ \rightarrow CO_2\uparrow + AlOCl + \{...\},$$
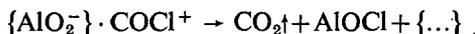
(where the symbol $\{...\}$ designates a so called empty nest). AlOCl reacts with another phosgene molecule fast forming AlCl$_3$ and CO$_2$.

If the reactant undergoes thermal dissociation at the temperature used for dealumination, the dissociation products are also able to effect a similar reaction [20]. (Nevertheless, it is not yet clear whether the success is due to a small amount of re-formed reactant.)

As far as the dealuminated zeolite itself is concerned, the following information has become available.

When the Al content of a Na-mordenite sample was reduced from the original 2.8 to 1.5 mmol Al^{3+} by dealumination, the sample hydrated and later evacuated at 673 K contained 1.92 protons/nest, as established, by proton n.m.r. investigations. This is merely half of the value to be expected on the basis of the mechanism put forward by BARRER for the extraction of Al^{3+} ions from mordenite with cc. HCl [25]. The dehydroxylation of the hydrated nests probably begins at or below 673 K and the low value found might be caused by this effect.

The crystallinity of (partially) dealuminated zeolite samples (determined as indicated earlier) was at least 90%. Only in a very few cases could crystallographic degradation be observed to reduce the crystallinity below 90%. In Fig. 2 the X-ray diffraction patterns of a few dealuminated samples are shown in the form of simplified line drawings. It is readily observed that dealumination brings about an unambiguous change in the diffraction patterns of the [200] and [202] faces: the intensity decreases in the former and increases in the latter case. Al^{3+} ions in the 1 and 2 positions in the mordenite framework are removed easily [1, 23], and therefore it may be conjectured that the changes in the X-ray patterns are caused primarily by removal of Al^{3+} ions from the 2 positions (apr. 25% of the total), followed by dissolution from the 1 positions. (This assumption must be proved by investigating the occupancy factor of the lattice).

Table I contains useful information on the framework vibrations of dealuminated zeolites. Dealumination with either phosgene or HCl brings about a shift to higher
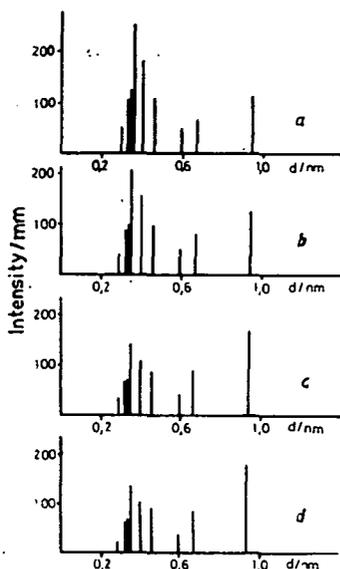
Fig. 2. Simplified X-ray patterns of the dealuminated samples (Aluminium contents of the samples in mmol g^{-1}: a) 2.78; b) 2.37; c) 1.42; d) 0.5.
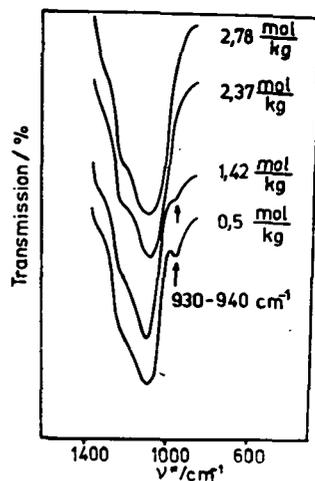
Fig. 3. I. r. spectra of the dealuminated mordenite samples (in the framework vibration region) exhibiting absorption at 930 cm^{-1}

Table I

Structural frequencies of the samples

Untreated mordenite Al content 2.8 mmol g^{-1}	Dealuminated with HCl Al content 1.3 mmol g^{-1}	Dealuminated with HCl Al content 1.0 mmol g^{-1}	Dealuminated with COCl$_2$ Al cont. 1.42 mmol g^{-1}	Dealuminated with COCl$_2$ Al cont. 0.5 mmol g^{-1}
452	450	450	450	450
555	566	566	565	566
571	581	586	581	586
623	641	645	650	656
714			720	
760	750	760	756	760
783	783	783	782	780
794	808	812	813	800
	920	930	950	960
1020	1045	1050	1080	1080

frequencies of those ir bands regarded by FLANIGEN as "structure-sensitive" [24]. The observed shifts (in cm^{-1}), 555→566, 623→656, 790→810, and 1020→1080, are in excellent agreement with the values published by BARTHOMEUF et al. [1]. Nevertheless, at higher degrees of dealumination a new absorption band could be observed at about 930 cm^{-1}, which showed a good correlation with the degree of dealumination (see Fig. 3). Its assignment is not at all simple. We attempted, unsuccessfully, to produce the absorption at 930 cm^{-1}:

a) By admixing amorphous Al_2O_3 and SiO_2 to the original sample [new absorption observed at 900 and 788 cm^{-1}, respectively].

b) By digesting H-mordenite in an ethereal solution of $AlCl_3$ or $SiCl_4$, followed by evacuation, hydrolysis and heat treatment [we observed the band at 710 cm^{-1} caused by "isolated TO_4 tetrahedra" [24]; its intensity was found to be proportional to the content of structural aluminium, explaining its complete absence from the ir spectra of dealuminated samples (see e.g. Fig. 4)].

On this basis it is felt that the absorption at 930 cm^{-1} is produced by new Si—O bonds formed following removal of the relevant AlO_2 units.
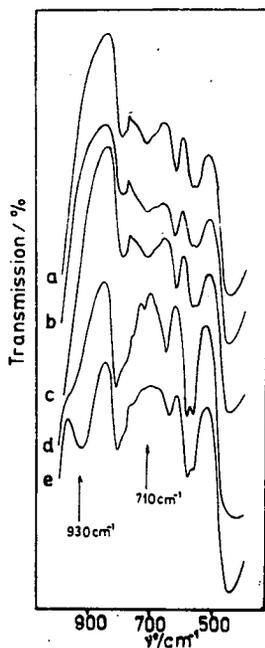
Fig. 4. I. r. spectra of the modified mordenite samples: a) untreated H-mordenite; b) $AlCl_3$ treated H-mordenite; c) $SiCl_4$ treated H-mordenite; d) H-mordenite dealuminated with $COCl_2$; e) H-mordenite dealuminated with cc. HCl
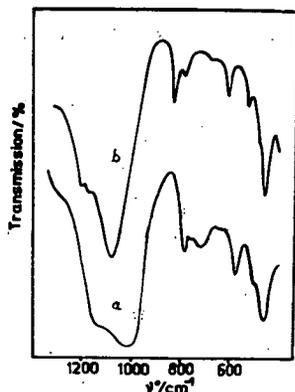
Fig. 5. I. r. spectra of HNaY (a) and HY dealuminated with $SiCl_4$ (b)

There is another very revealing experimental result which sheds light on the mechanism of dealumination and the stabilization process thereafter. If dealumination is carried out with Beyer's procedure, no new ir bands appear (see Fig. 5): the *exchange* of Al^{3+} for Si^{4+} ions is thermodynamically favoured and, as observed by KLINOWSKY [16], spontaneously results in a uniform structure of very high crystallinity. Of course, this is not true for reactants which dealuminate by *removal* (and not by *exchange*) of a structural element. Here, restoration of lattice order takes place with participation of building elements already present, which of necessity leads to some distortion of bond lengths and angles. (It is conceivable that $AlCl_3$, BCl_3, PCl_5 or some other compounds of Al, B and P which are not excluded from the zeolite interior by sieving effects, could also dealuminate by exchange.)
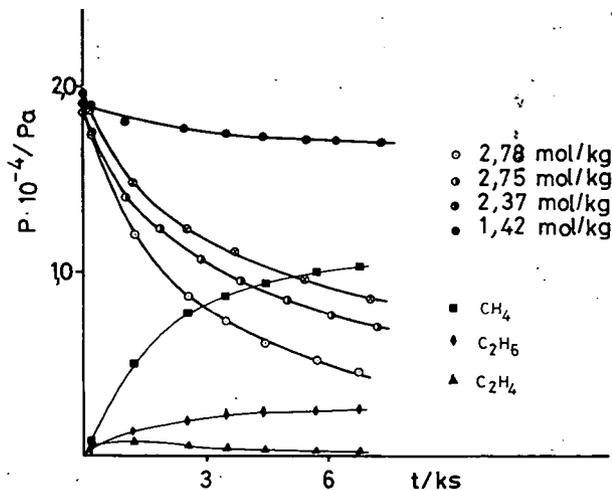
Fig. 6. Kinetic curves (pressure *vs.* time) in the propane cracking over partially dealuminated mordenite samples

Contrary to expectations (see e.g. BREMER ET AL. [7]), dealumination leads to a definite decrease in catalytic activity as can be inferred unambiguously from Fig. 6 on the example of propane cracking. Although no final explanation is yet available, it can be reasoned that the temperature of pretreatment (773 K) might be too high, causing dehydroxylation, or simply the differences in the cracking mechanisms of short and long chain hydrocarbons altered the general picture. It should not be forgotten that dealumination is surely *not a random process*, and catalysis may therefore turn out to be topologically sensitive over the dealuminated samples; in other words, shape selectivity on the catalyst side may accompany catalysis for these samples.

Summary

On interacting with zeolites, volatile non-metal (and even metalloid and metal) halides exhibit excellent dealumination abilities at elevated temperatures. In spite of the very peculiar behaviours observed in connection with different reactants, there

are a few phenomena which appear to be common and characteristic of these reactions.

For the dealumination to take place, it is a necessary condition that the reactant be able first to interact with the exchange ion (chemisorption); the rest of the molecule should be capable of extracting a framework O^{2-} ion (thermal and electrostatic interaction) and of neutralizing the positive charge by sharing some negatively charged species with the Al^{3+} ion.

The vacancies left behind after dealumination are able to undergo hydration in water, though dehydroxylation of the nests occurs at relatively low temperatures around 673 K.

As revealed by ir spectroscopy, the nests undergo some sort of rearrangement and stabilization, accompanied by the appearance of a new ir absorption band at 930 cm^{-1}. The intensity of this band and the degree of dealumination exhibit good correlation.

X-ray spectroscopy shows dealumination to be a selective process: in the case of mordenite, the Al^{3+} ions in positions 1 and 2 are preferentially removed.

The catalytic activity in the cracking of propane decreases monotonously with increasing dealumination, a fact deserving further attention.

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ДЕАЛЮМИНАЦИЯ ЗЕОЛИТОВ ЛЕТУЧИМИ РЕАГЕНТАМИ. СТРУКТУРНЫЕ И ДРУГИЕ ПОСЛЕДСТВИЯ

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Изучены структурные изменения в морденитах после деалюминации фосгеном. В ИК-спектрах деалюминированных образцов обнаружена неописанная еще в литературе новая полоса поглощения в области 930 см$^{-1}$. Появление новой полосы нами отпесена к Si—O колебаниям, возникающим в дефектных местах после удаления алюминия. Структурные свойства деалюминированных морденитов изучены методами рентгеновской диффракции и ЯМР спектроскопии, каталитическая активность — влиянием на скорость крекинга пропана.