

CALORIMETRIC INVESTIGATION OF THE EFFECT OF DEALUMINATION ON THE ACIDITY OF ZEOLITES

A. AUROUX, Y. BEN TAARIT

Institut de Recherches sur la Catalyse, Laboratoire Propre du C.N.R.S.  
Conventionné à l'Université Claude Bernard, Lyon I, 2, avenue Albert Einstein,  
69626 Villeurbanne, Cédex FRANCE.

ABSTRACT

Calorimetric investigation of  $\text{NH}_3$  adsorbed on a variety of dealuminated Y and mordenite zeolites showed a drastic change of the initial values and coverage dependence of differential heats of adsorption. These changes were interpreted in terms of the presence within the zeolite porous matrix of an alumina type phase which is behaving as an additional acidic component.

INTRODUCTION

Synthetic zeolites, particularly the faujasite and mordenite types, are well known and unrivalled materials as cracking catalysts (F.C.C.). As such they account, for the greatest consumption of zeolites. They have been used following exchange of the original  $\text{Na}^+$  ions for  $\text{NH}_4^+$  ions or rare earth cations. In the ammonium form, the  $\text{NH}_4^+$  decomposition needed to generate the acid centres was followed by an ultrastabilization treatment either prior to use or in situ, i.e. in the catalytic F.C.C. Reactor system. Ultrastabilization, in fact, is simply the result of the extraction of a significant part of framework aluminum ions by steam.

The practical conditions in which this treatment is performed, as well as the parameters that characterize the aluminum removal, such as the initial location of removed aluminum, the actual dealumination level, the fate of the extracted aluminum and, perhaps more importantly, the location and distribution of the residual aluminum ions within the lattice, primarily determine the catalytic performance of the resulting material, as well as its resistance to further hydrothermal aggression. Above all, the catalytic activity of zeolites is claimed to be closely related to its residual acidity, both qualitatively and quantitatively. The actual number of acid sites is usually associated with the actual number of framework aluminum ions. The strength of these sites, in turn, is dependent upon their location within the lattice. Last, but not least, the presence of extraframework species, particularly aluminum entities, may significantly alter the qualitative characteristics of the structural acid sites, or even generate a distinct and entirely different acidity pattern.

Our purpose in this work was to monitor the modifications of the zeolite acidity as a result of dealumination. Ammonia was chosen as the base molecule. The microcalorimetric method was used to investigate the adsorption of this probe molecule on a series of variously dealuminated samples.

#### EXPERIMENTAL AND MATERIALS

Differential heats of adsorption were determined using a SETARAM TIAN-CALVET type microcalorimeter associated with an automated volumetric equipment providing for simultaneous determination of the adsorption isotherm. The calorimeter temperature was set at 423 K. Ammonia adsorption was carried out under pressures not exceeding 133 Pa. Before adsorption the samples were evacuated overnight at 673 K.

The NaY starting material was supplied by LINDE Division of Union Carbide Corporation under the reference LZV 52. The Na Mordenite was supplied by Norton. It was ammonium exchanged, then heated to achieve ammonia removal. It was further steamed at temperatures in the 973-1163 K range and subsequently washed with N/10 HCl aqueous solution in order to remove (partially or totally) the extraframework aluminum species generated by steaming.

The Silicon-Aluminum ratio was determined both by chemical analysis (chemical ratio) and by using  $^{29}\text{Si}$  NMR<sup>(1)</sup> (Magnetic ratio). The former method accounted for the total aluminum content while the latter took into account the framework aluminum content, to the exclusion of any residual aluminum species still trapped within the zeolite porous matrix. Table 1 compares the Si/Al ratios obtained via both methods for samples used in this study.

#### RESULTS AND DISCUSSION

Y Zeolites. The differential heats of adsorption of ammonia on the starting HY sample (Si/Al=2.4) showed a characteristic dependence on the ammonia coverage (expressed by the volume of ammonia per mass unit of zeolite). This pattern (Fig.1a) exhibited a plateau that expanded over a large domain of coverage. The differential heats then declined progressively as the coverage increased. The initial heat characterizing the plateau was within  $137\text{-}140\text{ kJ.mol}^{-1}$ . This constant constancy over a broad coverage range is indicative of a uniform strength distribution within the structural acid sites of the HY starting material<sup>(2)</sup>. The irregular distribution among the weaker sites is in agreement with previous observations and could simply be due to the effect of coverage<sup>(3,4,5)</sup>.

Heat patterns displayed by dealuminated HY samples were at variance with that just described for HY in several respects : Samples whose "Chemical" Si/Al ratios were larger than the "magnetic" ratios displayed significantly

higher initial heats (up to  $180 \text{ kJ.mol}^{-1}$ ) than that measured for plain HY samples (Fig.1b,c,g). On the other hand the differential heat decreased almost linearly as the  $\text{NH}_3$  coverage increased. An inflexion point was noticeable when the heats were within  $140 \text{ kJ.mol}^{-1}$  (Fig.1b). At still higher coverages, the differential heat decreased abruptly to values around  $70 \text{ kJ.mol}^{-1}$ , well below the lowest values observed for the parent HY zeolite at much higher coverages.

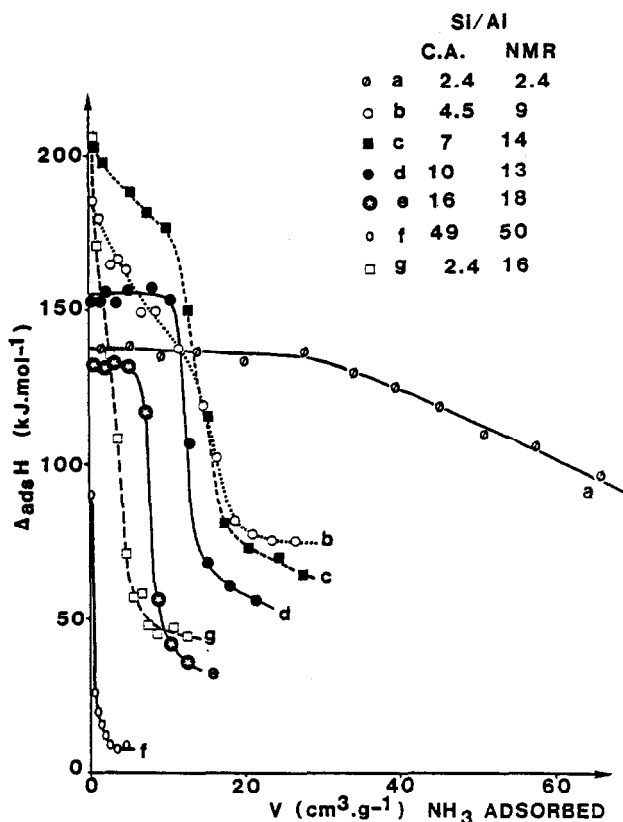


Fig.1 : Differential heats of ammonia adsorption over HY zeolites with various Al content as a function of coverage.

This behaviour clearly reveals a site strength heterogeneity in dealuminated zeolite samples where at least part of the extra-framework aluminum species had not been removed from the zeolite sample, as inferred from the contrasting "Chemical" and "Magnetic" aluminum contents. This result could be interpreted as an indication that the strength of the residual structural acid sites has been considerably enhanced as a result of the modification of their environment, since dealumination has probably resulted in a wide span of local

environments, thus giving rise to a broad strength distribution among the structural acid sites.

It could be argued, however, that the extra-framework aluminum species generated a new type of acidity both different in nature and stronger than the zeolitic acid sites. Since one is dealing with non-crystalline species, a wide variation in the related acidity should be expected, as their structure may vary from one location to the other. However ordered they might be, they would not match the long and short range ordered structure of zeolites.

In this respect results obtained with samples characterized by identical "Chemical" and "Magnetic" aluminum contents provide additional information with regard to the importance of the guest aluminum species: Samples subjected to moderate dealumination and quasi-quantitative removal of extra-framework aluminum displayed a homogeneous acid strength slightly, but significantly higher than that of the parent HY material (Fig.1d). The number of acid sites has of course been reduced in accordance with the dealumination level. This different behaviour may indicate that the residual structural acid sites remain essentially equivalent, even though alteration of their local environment inevitably resulted in a faint acid strength enhancement, well below that observed when guest aluminum species are present. Further dealumination generated samples characterized by similar thermograms (Fig.1e), though the plateau domain was restricted to lower coverages. Interestingly the initial differential heat measured also at the plateau was slightly below that of the parent HY. This trend to weakening and declining of the acidity was confirmed as dealumination was pursued up to Si/Al ratios of 50. The few residual sites, essentially structural in nature as inferred from their coincident "Chemical" and "Magnetic" Si/Al ratios, showed an affinity for ammonia well below that of HY (Fig.1f). This suggests that extreme dilution of the structural sites greatly depressed their strength. Thus it would appear that an optimum site density is a requisite for strong acidity.

It is noteworthy that the weakest sites are considerably affected as the heat of adsorption for extensively dealuminated samples did not exceed 10 kJ.per mole, well below the heats observed even for NaY zeolites. This might indicate a considerably reduced polar nature of the zeolite, thus rendering physisorption of  $\text{NH}_3$  even less energetic.

#### Mordenite type zeolite HM

When dealuminated samples were investigated, a quite similar behaviour was observed for these alumino-silicates. However the departure from constant values was less pronounced than in the case of faujasite (Fig.2). By contrast the

highest initial differential heats were naturally greater in the case of mordenite samples. This is consistent with the accepted view that mordenite zeolites are, in the main, stronger solid acids than faujasite.

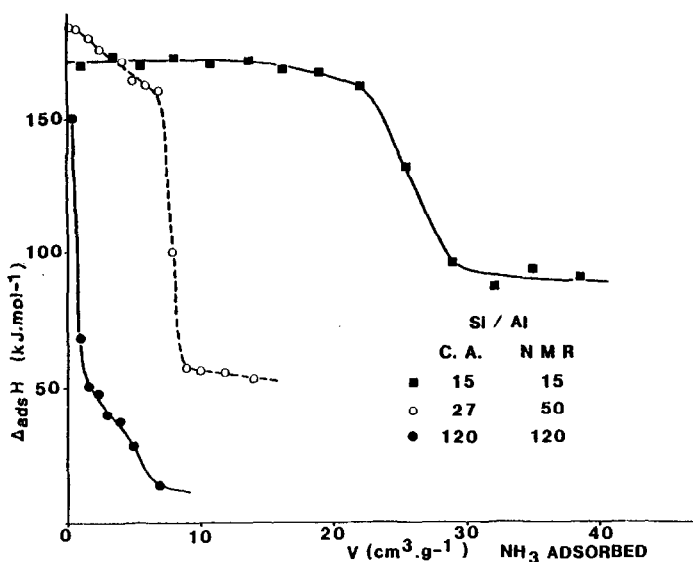
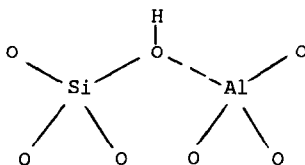


Fig.2 : Differential heats of ammonia adsorption over H Mordenites with various Al content determined by chemical analysis as a function of coverage.

In both cases, however, it appeared that the increase of the acid site strength is accompanied by a heterogeneous distribution, strengthwise, as a result of dealumination.

The concomittant occurrence of these two phenomena could be accounted for by two distinct hypotheses :

(i) It could be assumed that the acid sites are associated exclusively with the lattice aluminum ions. That is, only the so-called structural acidity is measured : these sites are usually depicted as :



The mobility of the hydrogen associated with the vicinal aluminum and silicon tetrahedra is obviously dependent on their local environment. In particular the occurrence of a second  $\text{AlO}_4^-$  tetrahedron would notably decrease such mobility through an additional electron flow into this structural  $\text{>SiOH}$  tetrahedron, whereas, removal of such a close neighbour would depress the electron flow and enhance the electrophilic character of the hydrogen. Removal of such  $\text{AlO}_4^-$  tetrahedra from a well-organized lattice might be supposed to introduce local perturbations generating an overall statistical disorder that would account for the fact the sites are heterogeneous until a proper dealumination level helps to establish a new long-range order in the residual aluminum tetrahedra. Further dealumination would again alter the newly reached local and long-range order.

(ii) It is equally conceivable that in spite of the changes in the local environment the acid strength should be affected only to a minor extent since the zeolite lattice is more of a covalent than an ionic nature, thus precluding large inductive effects from being felt beyond a limited number of bonds.

As a result of dealumination, extra-framework aluminum species are likely to form and resist mild acid washing. Such aluminum oxide type phases may, under specific treatments, generate acid centres different in nature from the structural acid sites<sup>(6)</sup>. Even washing with hydrochloric acid may well enhance the strength of such sites by partial chlorination of this guest "Alumina" phase. This would account for the higher values of the initial differential heats when such phases are present. Further phases so poorly organised with regard to the crystalline zeolite host can only generate acid sites with unevenly distributed strength. Interestingly enough, the first part of the thermograms for samples with these extra-phases closely matched those observed for pure  $\gamma$  alumina<sup>(7)</sup>.

We, in fact, strongly prefer this latter hypothesis, as it accounts perfectly for the concomitance of the two major phenomena caused by dealumination. Our choice is also corroborated by a number of additional observations and/or accounts which undoubtedly prove the occurrence of guest alumina-like phases following - and as a result of -dealumination under hydrothermal conditions. Indeed when "Chemical" and "Magnetic" aluminum contents coincide, that is when these guest phases are not present, the heterogeneous and strongly acid sites were not evidenced.

On the other hand, the existence of guest aluminum phases in steamed zeolites has been claimed by a number of authors<sup>(2,7,8)</sup>. Various methods have been used to determine their structure<sup>(8)</sup>. It was also demonstrated that these

aluminum oxide species could be located either inside the porous matrix or at the surface of the zeolite microcrystals. It could be anticipated that in this case the thermogram would be overlap of thermograms usually observed for pure  $\gamma$ -alumina and unmodified HY zeolite. This is what happened in this study. Our opinion that we are dealing with a composite acidity pattern is therefore reinforced.

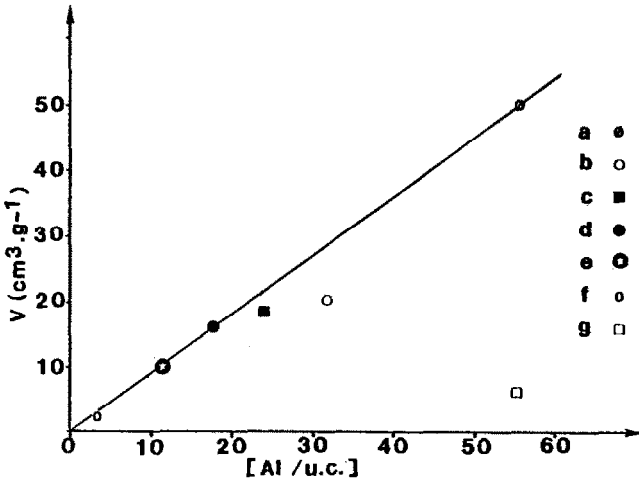


Fig.3 : Variation of the total number of acid sites of HY zeolites with various Al content as a function of the number of  $\text{AlO}_4$  per unit cell.

Finally, this study has emphasized the linear relation between the actual number of acid sites capable of neutralizing ammonia and the zeolite aluminum content (Fig.3). This linear relation holds good and is indeed, best, when the "Chemical" and "Magnetic" aluminum contents coincide. This is understandable, since only part of the extra-framework aluminum generates acid sites, as is the case for finely divided  $\gamma$  alumina.

#### CONCLUSIONS

Microcalorimetric investigation of the acidity of dealuminated zeolites showed that they are in fact composite materials associating the dealuminated zeolite lattice with a guest aluminum oxide phase. The lattice retained most of its acidic properties unchanged, though the number of acid sites was closely related to the residual aluminum tetrahedra. Slight enhancement of the acid strength was probably attributable to electronic perturbations resulting from larger separation of  $\text{AlO}_4$  tetrahedra. Isolated acid sites, however, seem to

retain only a weak acidity and the lattice became less and less polar. This is also in line with the "Hydrophobicity" of highly siliceous zeolites. The guest alumina-like component seemed to display the same acidic properties as  $\gamma$ -alumina : high acid strength and considerable heterogeneity of sites. The implication is that many adsorption as well as catalytic properties known for these zeolites should be drastically modified due to the occurrence of this phase whose own chemical, thermal and catalytic properties are so considerably different.

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