A dynamic assessment of MFI acidity using microcalorimetric techniques

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Abstract

The number and strength of the acid sites of a variety of NaHZSM-5 zeolites were measured as a function of the exchange level using NH_3 adsorption monitored by microcalorimetry. While the number of acid sites increased quasi linearly with the exchange level, the acid strength remained almost constant over a wide range of exchange levels then dramatically increased when 80% of the original Na^+ ions were removed. The removal of the residual Na^+ ions not only generated much stronger sites but resulted also in a general increase of the acid site population already present. This phenomenon, which is fairly similar to those encountered with faujasites and other acids, was interpreted in terms of remote perturbation of the acid centers structure by the very few residual Na^+ ions modifying significantly the TOT bond angles. In addition possible general cation redistribution induced by NH_3 adsorption may also affect the evolved heats of adsorption.

Keywords: Zeolite; Acidity; Microcalorimetry

1. Introduction

Earlier studies concerned with the investigation of the acidity of various zeolite structures showed an important heterogeneity of acid strength among the population of acid sites of a given sample.

Among the well-documented reviews, Rabo and coworkers [1] reported on the dependence of the acid strength upon a number of parameters. These were thought to influence the
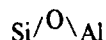
$$Si{\diagup}^{O}{\diagdown}Al$$

bond angle that ultimately determines the lability of the proton attached to the Si–O–Al bridge. Among the parameters that could possibly influence the

$$Si{\diagup}^{O}{\diagdown}T \quad (III)$$
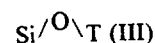
angle (where T is the trivalent element at the origin of the acidity genesis) we can single out the nature of T resulting in both ionic radius and electronegativity variations.

Indeed the substitution of silicon by Al, Ga, Fe and B gave rise to well differentiated acidities within the same structure [2]. Drastic variations of the acid strength were also observed

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upon varying the bond angles as a result of structure variations [3].

Variation of the nature of the nearest neighbours may also affect this bond angle. In the case of zeolites all nearest neighbours are SiO_4 tetrahedra, however the next nearest neighbours may be SiO_4 and/or AlO_4 depending on the overall Si/Al ratio. It was already anticipated [4] and recognized that indeed the acid strength of Y type zeolites was strongly dependent, within a given sample characterized by a given framework Si/Al ratio, on the number of AlO_4 tetrahedra as next nearest neighbours [5,6]. The distortion of the SiOT bond angle was also evidenced within the same structure as a function of the charge balancing cation [7].

Therefore the acid strength should also vary with the nature and content of the charge balancing cation. Indeed several catalytic studies involving decationated Y zeolites showed that the catalytic activity of the zeolite did not increase linearly with the exchange level, thus indicating a simultaneous variation of the activity per site which could be due either to steric restrictions or more probably to acid strength variation with the exchange level [8–10].

The acid strength requirements of acid catalyzed reactions vary depending on the type of reaction and on the substrates to be converted. Even among a single variety of reaction, for example alkylation of aromatics, the acidity requirements vary drastically on the aromatic substituents and on the nature of the alkylating agent.

It is therefore of interest to probe quantitatively and qualitatively the acidity of potential acid catalysts. HZSM-5 zeolites are, among such solids, those which offer the widest potential in acid catalysis due to an outstanding thermal stability and resistance to coking, not to mention their shape selectivity and their ability to catalyse acidic as well as redox reactions when appropriate elements are included in T sites.

The major catalytic properties of zeolites, including catalytic conversion of crude oil and various hydrocarbons, are related to their acidic

properties. Various methods were used or designed to monitor the acidity of various zeolitic catalysts. Among these methods, IR spectroscopy associated with the adsorption of various bases, most frequently pyridine and/or ammonia [11–14] provided information on the nature of acid sites and also on their strength provided a carefully temperature programmed desorption was carried out. Thermogravimetric measurement also gave a very useful information concerning the quantitative aspects of the acidity irrespective of the nature of the acid sites. NMR spectroscopy was also used to monitor the acidity of solids including zeolites, either upon analysis of the ^1H NMR spectra at various hydration states or via the adsorption of probe molecules. Lastly microcalorimetric adsorption of appropriate probe bases appeared to be a very powerful method in that it gave a direct measurement of the neutralization energy together with the energy spectrum of the acid sites within the solid. Various zeolites were investigated in this context to trace the determinant factors that govern the acidity strength within a zeolite family or within a larger group. Quite extensive and well documented reviews with all aspects of the subject are available [15].

In this work we concentrated on the investigation of the variation of the acidity of ZSM-5 zeolites as a function of the degree of decationization in order to obtain a dynamic information on the number of acid sites and on their strength.

2. Experimental

The starting NaZSM-5 was obtained according to Argauer and Landolt method [16]. After calcination at 550°C in air, thorough exchange with 1 N NH_4NO_3 solution provided the NH_4 form (95% exchange level). The samples with variable exchange levels were obtained by back exchange of the NH_4 form with appropriate aliquots of 1 N NaCl solution. Samples with 15, 30, 45, 60 and 75% exchange levels were thus obtained.

Prior to any calorimetric measurements, the samples were first evacuated at 400°C and 1.33 mPa overnight. Differential heats of adsorption of NH_3 were measured at 120°C.

The heats of adsorption of the probe molecules were measured in a heat-flow microcalorimeter of the Tian–Calvet type, C80 from Setaram, connected to the adsorption unit.

The equilibrium pressure relative to each adsorbed amount was measured by means of a differential pressure gauge (Datametrics). Successive doses were sent into the sample until a final equilibrium pressure of 133 Pa was obtained. The primary and secondary adsorption isotherms were collected at the temperature of the calorimeter in order to calculate, by subtraction, the irreversible chemisorbed amount (V_{irr}). Secondary isotherms were collected after the saturated sample was pumped out 3 hours at 1.33 mPa at the temperature of the experiment. Such pumping presumably should remove all the physically adsorbed gas. V_{irr} was adopted as a measure of the number of strong acidic sites.

3. Results and discussion

Fig. 1 shows the variation of the irreversibly adsorbed NH_3 volume as a function of the exchange level α. The observed variation is
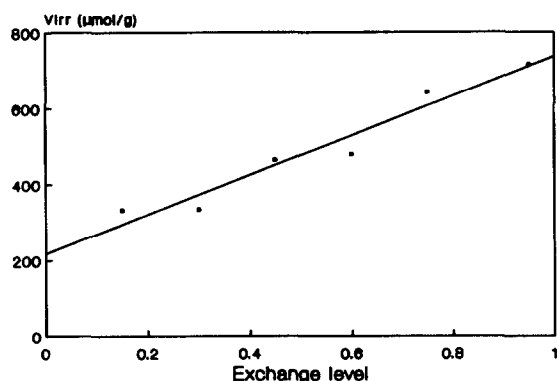

Fig. 1. Variation of the irreversibly adsorbed NH_3 volume as a function of the exchange level α.

almost linear as would be expected from an irreversible adsorption of NH_3 on Brønsted sites generated by the decomposition of the parent NH_4^+ ions upon calcination of the exchanged zeolite.

Remarkably a positive intercept is observed showing that the pure sodium form adsorbs irreversibly a significant amount of NH_3. This is presumably due to the behaviour of part of the Na^+ ions as strong Lewis centers. Such a behaviour is not unexpected as earlier work showed that even in Y type zeolites, alkali ions strongly chemisorb pyridine with, the smaller the ionic radius the stronger the bond [17,18].

In a recent paper, Karge et al. [19] have shown that indeed a purely sodium Y zeolite adsorbs ammonia irreversibly with a heat of adsorption of ~ 80 kJ/mol. It is expected that the behaviour of Na^+ ions in NaZSM-5 zeolites would be similar to those in Y type zeolites. It is even conceivable that their Lewis acidity would be stronger than that of Na^+ ion Y zeolites in as much as the latter exhibit a stronger Lewis acidity than those of an X type zeolite.

Under a pressure of 27 Pa and at a temperature of 393 K the amount of adsorbed NH_3 is almost independent of the exchange level and is within 1 NH_3 per potential acid site be it a Brønsted or a Na^+ site.

Differences however appear when heats of adsorption are considered. Indeed as shown in Fig. 2, exhibiting the variation of the differential heats of adsorption of variously exchanged samples as a function of NH_3 coverage, several features may be singled out:

The initial heat of adsorption increases as α increased thus indicating an increased acid strength of the strongest sites of these samples. In addition differences in the curve shapes also appear.

In particular, the histogram corresponding to the highest α includes two semi-plateaus suggesting two identifiable energetically homogeneous populations. In between the plateaus a steep decrease of the differential heat is observed and the last portion of the histogram is
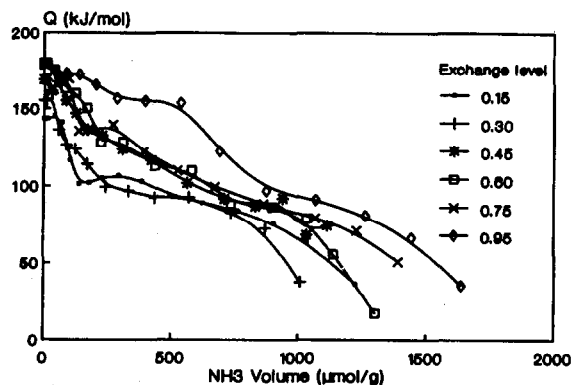
Fig. 2. Differential heats of adsorption of NH_3 for NaZSM-5 zeolites exchanged to 15 (●), 30 (+), 45 (∗), 60 (□), 75 (×) and 95% (◇).

characterized by a rather smooth decline of the differential heat.

Samples with intermediate α values exhibit a continuous decrease of the differential heat as the coverage increased with heats always well below those recorded for the extensively exchanged sample. The lowest two exchange levels are associated with samples whose differential heats decrease steeply at the lowest coverages and further smooth decline as the coverage increased is observed.

It is noteworthy that all samples exhibited an important homogeneous population that chemisorbs NH_3 with the same differential heat of ~ 100 kJ/mol which are labeled as weak sites.These results may be most conveniently presented as bloc population diagram to better envision the strength spectrum as a function of α: two populations are defined within each sample: the one that is characterized by adsorption heats over 120 kJ/mol and the other by heats within the 100 kJ/mol range. The variation of these populations with α is represented in Fig. 3a.

Clearly the major part of the acid sites at the low values of α are rather weak sites. Interestingly, while the population of the weak sites remained almost constant as α increased, the population of the strongest sites increased progressively with α up to the point where the

strongest sites become the majority for extensively exchanged samples.

This drastic change is even more spectacular if we consider the population of sites whose heat of adsorption is over 150 kJ/mol illustrating the effect of removing the very last sodium ions on the acid strength not only of newly created sites but also on preexisting sites. These features are clearly illustrated in Fig. 3b.

It could be seen that as the exchange proceeds new sites characterized by differential heats over 120 kJ/mol are generated. In fact most of the new sites are medium energy sites that correspond to differential heats within the 120–150 kJ/mol range and a sizeable minority of strong sites with differential heats over 150 kJ/mol.

However extensively exchanged samples experienced a sharp increase of both medium and strong sites populations. In fact this population increase is well beyond the increment of sites generated upon increasing α from 75 to 95%. In addition there appears to be an even distribution of strong to medium to weak sites with an almost 1:1:1 ratio.

This distribution is far in excess assuming all newly generated sites are of the strong type. Thus it must be assumed that the change of strength distribution within a Brønsted site population is far more important than the simple addition of the ones generated by the removal of sodium ions.
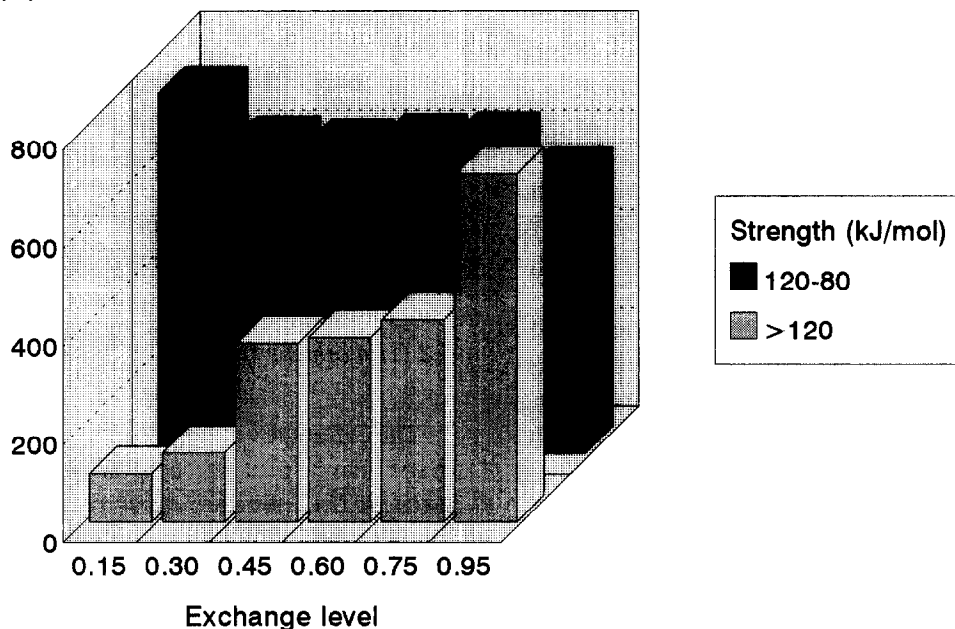
Very similar results were reported by Karge et al. in the case of Y type zeolites [19]. They showed indeed that the number of sites providing higher differential heats of NH_3 adsorption than that recorded for Na^+ remained very low as the exchange level α increased up to $\sim 75\%$, then dramatically increased.

To account for this behaviour quite similar to the variation of the rate of acid catalyzed reactions with α [8–10], several hypotheses were offered. These hypotheses include a premature dehydroxylation of the least exchanged samples and alternatively a higher thermal stability of the corresponding NH_4^+ i.e. incomplete deam-

minations. However both hypotheses were found to be insufficient to account for the observed results.

Interestingly the dQ/dn variation with α paralleled that of the intensity of the OH groups associated with the L.F. band at 3550 cm^{-1}

(a) Number of sites (μmol/g)

Strength (kJ/mol)
■ 120-80
▨ >120

(b) Number of sites (μmol/g)
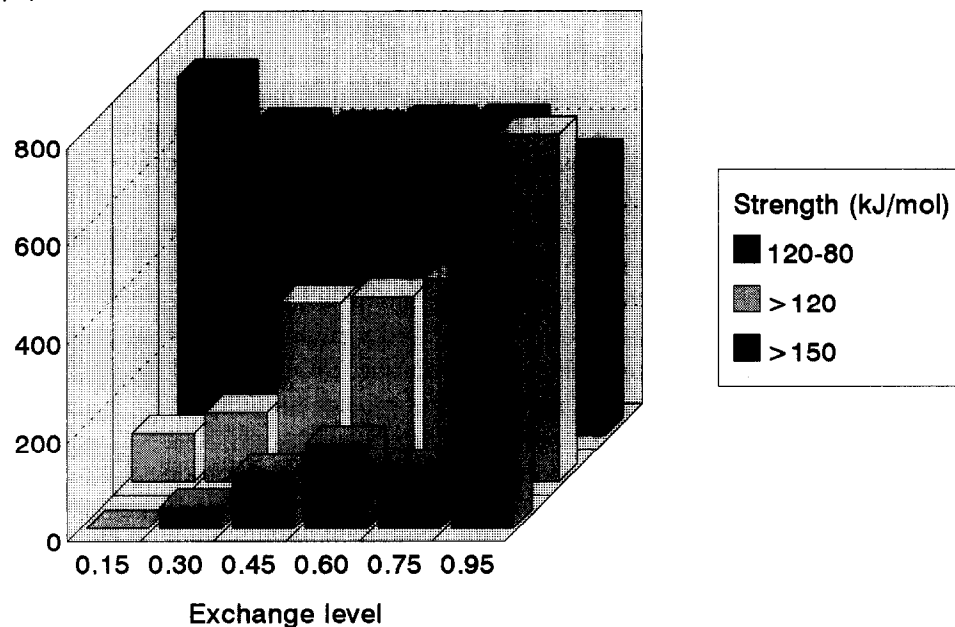
Strength (kJ/mol)
■ 120-80
▨ >120
■ >150

Fig. 3. Populations of sites and strength spectra as a function of the exchange level α.

which are known to be the least acidic [20]. Thus neither the location nor the stability of the OH groups could account for this peculiar variation of the differential heats with α.

In our case, also, it could not be argued that premature dehydroxylation of the least exchanged samples or a particular siting of the OH groups may account for these results, as only one type of acidic OH groups is present and these are thermally more stable than in Y type zeolites. Incomplete deammination may not be invoked as it has been checked that under the pretreatment conditions no νNH or δNH are present in the IR spectra at whatever exchange level.

In addition, the number of adsorbed NH_3 molecules per site is constant and therefore independent on the exchange level, thus leaving little chances that at low α values OH groups could have been prematurely removed during the activation process.

Therefore one is left with two possible hypotheses to tentatively interpret the peculiar results.

3.1. Hypothesis (i)

The protons may be of an equal strength irrespective of the residual sodium ion content and therefore may give rise to identical heats of neutralisation. However when Na^+ are present, adsorption of NH_3 may induce an energy consuming Na^+ migration to locations quite different from the initial location of these ions in the activated samples. In other words the change from OH to NH_4^+ cations may induce a quite different cation distribution and end up with a different free energy of the new system thus significantly depressing the differential as well as the integral heats of adsorption. The effect would be the more pronounced the more residual Na^+ are to be redistributed.

Such a hypothesis is not devoid of experimental background, such as is the case of faujasite type zeolites. Indeed it was shown from

earlier studies that the location of Na^+ within the crystallographic sites varied with the hydration state of the zeolite which is in fact a far milder change than the change from a decationated to an ammonium form. In addition, NH_3 binds to Na^+ ions, thus possibly modifying the locations of these ions. This concept was supported in many cases irrespective of the nature of cations and adsorbates [21–23].

However, this hypothesis, although it may account for the variation of evolved heat may not be reconciled with the very similar variation of acid catalyzed reaction rates with α, which were recorded over the equilibrium catalysts.

3.2. Hypothesis (ii)

The alternative hypothesis assumes a dramatic increase of the acid strength as the very last few Na^+ ions are removed as it is accepted that these effectively poison the Brønsted sites. Although this idea has been widespread for many decades, little explanation was given to account for the drastic effect of few Na^+ ions over a much more important proton population. It may be envisaged that the presence of a limited number of Na^+ ions imposes larger $_{Si}\diagup^{O}\diagdown_{Al}$ bond angles at the neighbouring tetrahedra and therefore affects the bond angle at remote sites. The bond angles most susceptible to modifications are the Si(OH)$\cdots$Al bridges while the Si–O–Si are least affected. Thus it may be conceived that the distortion exerted over the closest Si–O–Al bridges by the Na^+ results in a compensation, so as to fit the lattice stability requirements, that will particularly affect the SiOHAl bond angles thus decreasing the proton mobility over a large number of bridges.

Indeed it was observed that while T–O–T bond angles are larger when the bridge oxygen is coordinating a Na^+ cation than when involved in the formation of a hydroxyl group [7]. Therefore in order to preserve the general order, the departure of T–OH–T bond angle from

normal would be reduced thus modifying the charge on the oxygen and therefore the mobility of the attached hydrogen.

Hypothesis (ii) better matches the catalytic results and may seem to be more satisfactory, yet the effect on the residual cations redistribution on the evolved heat might not be negligible.

In conclusion we have established that the acid strength of ZSM-5 zeolites is alike that of faujasites strongly dependent on the residual alkali content and that a rather reduced number of residual alkali ions strongly decreases the acid strength of the proton population thus producing a remote effect probably transmitted via lattice remote adjustments to local perturbations.

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