Thermochimica Acta, 126 (1988) 325–337
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

A MICROCALORIMETRIC STUDY OF NH_3-SORPTION ONTO DIFFERENTLY MODIFIED AND PRETREATED ZSM-5 SURFACES

MOEIN B. SAYED
Chemistry Department, Faculty of Science, Al-Azhar University, Cairo (Egypt)

(Received 13 July 1987)

ABSTRACT

A comparative study of NH_3-sorption onto several ZSM-5 samples differently modified by acid-dealumination, boron incorporation in the zeolite (by synthesis), as for lattice aluminum and boron impregnation as H_3BO_3, has been carried out at 423 K for differently pretreated (1.33 mPa/673 K/12 h and 1.33 mPa/1073 K/12 h) surfaces. Various volumetric, calorimetric and thermokinetic parameters have been found to correlate well, revealing that (i) acid treatment, whilst it eliminates a portion of the zeolite aluminum of potential acidity, creates new surface Brønsted sites of moderate acidity, (ii) boron replacement for a portion of the zeolite aluminum, however, does not alter the number of exchangeable acid sites, decreases markedly the overall zeolite acidity and enhances heterogeneous distribution of surface acidity, and (iii) boron impregnation, though it neutralizes proportionally the zeolite Brønsted acidity for samples pretreated at 673 K, appears to neutralize the zeolite Lewis acidity as well for samples pretreated at 1073 K, which results in a drastic loss of the overall zeolite acidity. The mechanistic implications illustrating the effect of such modifications are described.

INTRODUCTION

Despite the shortage of distinguishing surface Brønsted and Lewis acidities, microcalorimetry has proven powerful in characterizing the overall surface acidity, sites and distribution. As a technique providing complementary data, Takahashi and coworkers [1–11] have successfully applied microcalorimetry to measuring the energy of interaction at the gas/solid interfaces for a variety of silica, alumina, amorphous silica–alumina and crystalline aluminosilicate zeolite surfaces. Because of its strong interaction, pyridine has often been used and favored over other basic adsorbates in probing surface acidity. The less interacting (although more basic) and less bulky NH_3 has alternatively been employed to probe the acidity of zeolites, particularly those exhibiting narrow channels or small pores [12].

Because of its unique structure, which induces distinct features in catalysis, ZSM-5 has received unceasing interest. Microcalorimetry, particularly of NH_3-sorption, has shared with a significant role in determining the zeolite

0040-6031/88/$03.50

acidity [13–15]. Whilst calorimetric measurement at 293 K yields an average for the heat of NH_3 random interaction with a variety of acidic surface sites, those carried out at higher temperatures differentiate and distinguish surface acidity into order of varied strengths [9,15]. It has been recognized that measurement at 423 K yields the most useful information regarding surface acidity [12,16].

Studying the effect of various modification methods on ZSM-5 acidity, and hence catalytic activity, is the goal of the present investigation, which has been pursued exploiting the feature of computer-processing microcalorimetry of NH_3-sorption.

EXPERIMENTAL

Materials

Dried (over Na-wire) and degassed (by freeze–pump–thaw cycles) NH_3 was used as adsorbate. The adsorbent was ZSM-5 of differently modified samples (Table 1). The methods of zeolite modification with boron are described elsewhere for impregnation [17] and incorporation in the zeolite structure [18]. The dealuminated (Deal.HZSM-5, 28% Al loss) and non-dealuminated (HZSM$_0$-5) samples were obtained from their parent TPA,NaZSM-5 by ion-exchange in 0.5 M HCl and 0.5 M NH_4Cl at 353 K, respectively, with NH_4^+ being decomposed for the latter sample at 773 K under a stream of nitrogen.

Methods and equipment

NH_3-sorption onto the modified samples was followed both volumetrically and calorimetrically using a Setarm Tian Calvet microcalorimeter of the twin-conduction type at 423 K. NH_3 pressure both admitted and at equilibrium was measured for every dose using a Data-metric Barocel gauge of maximum 133 Pa pressure range. The zeolite (ca. 100 mg) was protected

TABLE 1

Zeolite elemental analysis (atom per unit cell)

Zeolite	Symbol	Si	Al	B	Na	B+Al	B/Al
Deal.HZSM-5	*	92.26	3.74	Traces	0.74	3.74	0.00
HZSM$_0$-5	○	91.90	4.10	Traces	0.47	4.10	0.00
HZSM$_1$-5	△	91.13	4.00	0.87	0.62	4.87	0.22
HZSM$_2$-5	□	91.24	3.21	1.55	0.97	4.76	0.48
HZSM$_3$-5	⬢	91.71	2.63	1.66	0.67	4.29	0.63
Impreg.HZSM$_0$-5	▼	91.90	4.10	3.21	0.47	7.31	0.78

from possible hydrocarbon contamination, which could be deposited from neighboring stop-cocks and joints lubricated with grease, by a trap of mixed solid CO_2/acetone. The zeolite pretreatment was carried out at two different temperatures 1.33 mPa/673 K/12 h and 1.33 mPa/1073 K/12 h, with a programmed temperature rise of 2 K min^{-1}. NH_3 was admitted onto the pretreated samples in small doses (ca. 0.04 cm^3) at 423 K. The NH_3 thermogram and pressure were monitored for equilibrium at every dose, which was continued to a final pressure of ca. 133 Pa. The data were computer processed and treated so as to attain volumetric, calorimetric and thermokinetic information capable of interpreting modified zeolite acidity.

RESULTS AND DISCUSSION

One of the great advantages of microcalorimetry applied to characterizing surface acidity is the ability of differentiating the acidity into order of interaction strength. This is particularly useful in distinguishing homogeneous and heterogeneous acidity distribution. A combination of volumetric, calorimetric and thermokinetic data provides a better chance of precisely identifying modified surface acidity.

Volumetric isotherm of NH_3-sorption

It has been long established that degassing the zeolite at 673 K results in surfaces dominated by Brønsted acidity. Figure 1 shows volumetric isotherms of NH_3 sorbed at 423 K for samples degassed at 673 K. As shown, the zeolite accepts NH_3 in the order

Deal.HZSM-5 > $HZSM_1$-5 > $HZSM_2$-5 > $HZSM_0$-5 > $HZSM_3$-5

This order, though it does not obey the acidity order associated with aluminum, H^+_{Al} (Table 2) agrees with that associated with aluminum and boron, H^+_{total}, except for Deal.HZSM-5. That sample is dealuminated by ca. 28%. As previously suggested [19], dealumination results in the formation of groups (nests) containing four silanols, with only one silanol being more acidic. Assuming that all aluminum removed by the acid treatment of the parent Na-form sample was of zeolitic nature, a sum of ca. 1.44 nest Brønsted sites adds up to other Al-associated Brønsted sites to yield a total of 4.44 Brønsted sites per zeolite unit cell (Table 2). Hence, it is not surprising to observe a higher NH_3-sorption for that sample than would be expected to be associated with the zeolite aluminum.

Zeolite degassing at 1073 K is expected to result in surfaces dominated by Lewis acidity [12]. The volumetric isotherm (Fig. 2) of NH_3 sorbed at 423 K for samples degassed at 1073 K reveals sorption capacity following a similar order, which also indicates association with Al + B Lewis sites. However, the

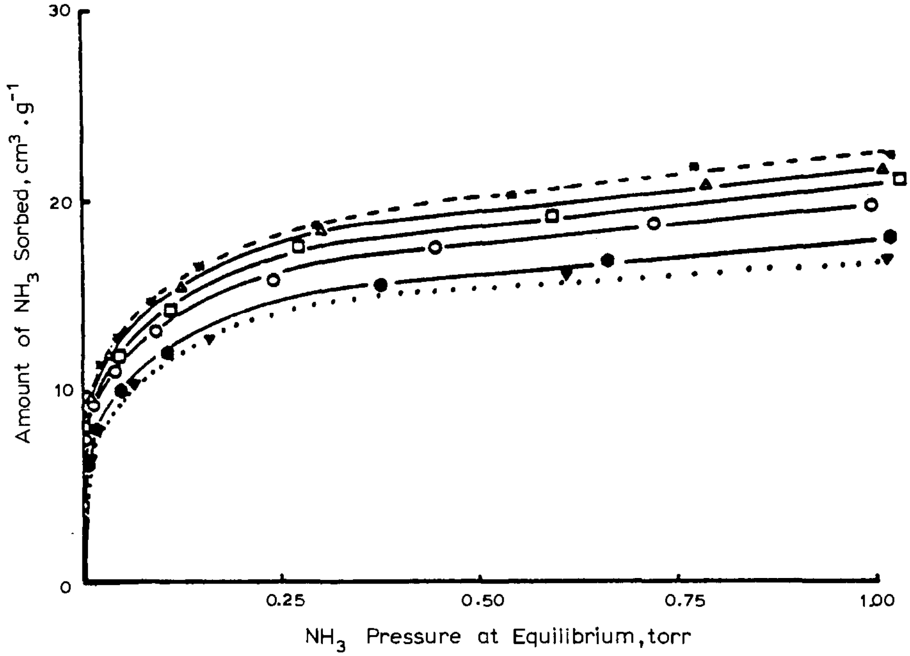


Fig. 1. Volumetric isotherm of NH_3/HZSM-5 for samples degassed at 673 K, sorption temperature, here and elsewhere, is 423 K. For symbol significance, see Table 1.

amount of NH_3 sorbed in this case is clearly less than for samples degassed at 673 K; the ordinate of Fig. 2 is scaled-up to twice that of Fig. 1. This agrees with the hypothesis that a portion of the zeolite Brønsted acidity dehydroxylates, as two Brønsted sites would yield a Lewis site. The excess of

TABLE 2

Data derived from elemental and thermal analyses

Zeolite	Elemental analysis [a]		Thermal analysis	
	H^+_{total}	H^+_{Al}	Brønsted (673 K)	Lewis (1073 K)
Deal.HZSM-5	4.44	3.00	1.60	0.90
$HZSM_0$-5	3.63	3.63	2.00	1.60
$HZSM_1$-5	4.25	3.38	1.40	1.30
$HZSM_2$-5	3.79	2.24	1.10	0.80
$HZSM_3$-5	3.62	1.96	0.90	0.50
Impreg.$HZSM_0$-5	3.63	0.42	1.30	0.40

[a] Data based on the result of subtraction of (Al + B) − Na for H^+_{total} and Al − Na for H^+_{Al}. Deal.HZSM-5 and Impreg.$HZSM_0$-5 are exceptions. H^+_{total} is calculated as in ref. 19, provided the sample is dealuminated by ca. 28%, for Deal.HZSM-5 and as in ref. 17, assuming that original Brønsted sites are replaced by less acidic sites associated with surface boric anhydride, for Impreg.$HZSM_0$-5. H^+_{Al} − B, assuming 3.21 out of 3.63 Brønsted sites of $HZSM_0$-5 are neutralized by boron, should yield H^+_{Al} for Impreg.$HZSM_0$-5.

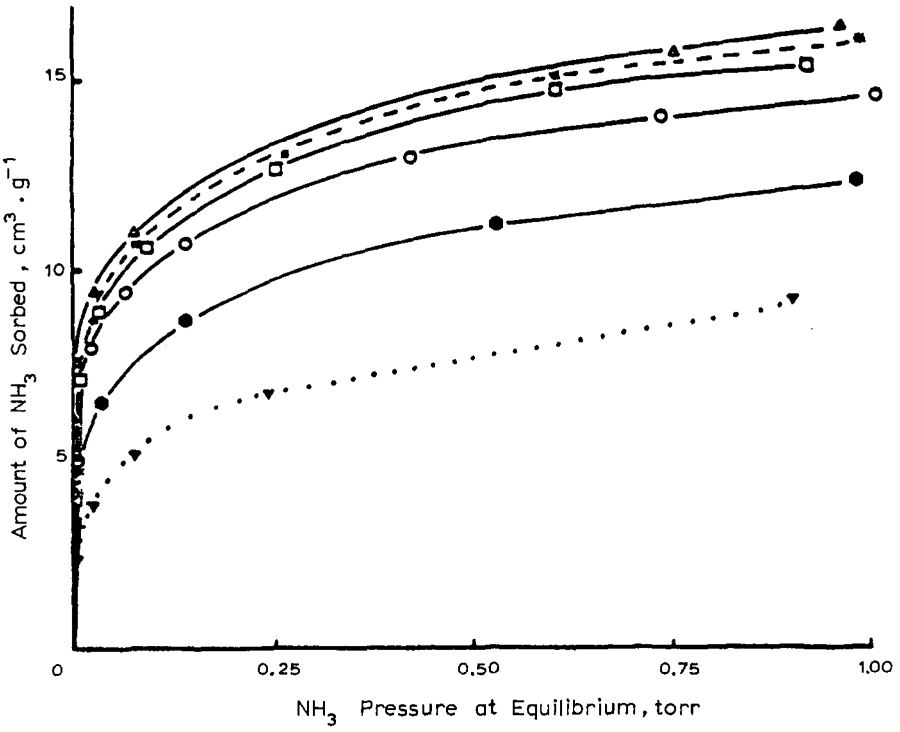


Fig. 2. Volumetric isotherm of NH_3/HZSM-5 for samples degassed at 1073 K.

Brønsted sites (dealuminated nests) obviously dehydroxylates to non-acid sites for Deal.HZSM-5 pretreated at 1073 K. Removal of the origin causing excessive sorption for that sample pretreated at 673 K (above) by pretreatment at 1073 K tends to clear up association of NH_3-sorption with the population of Al + B Lewis sites.

Calorimetric isotherm of NH_3-sorption

At variance with the volumetric isotherm measuring the overall (weak as well as strong) surface acidity, a calorimetric isotherm presumes to identify only the strong sites capable of evolving heat of NH_3 sorbed at 423 K. Figure 3 shows calorimetric isotherms of NH_3 sorbed at 423 K for samples pretreated at 673 K. Except for the dealuminated sample, the order of heat follows the order of Al-associated Brønsted site population, H^+_{Al} (see Table 2)

Deal.HZSM-5 > $HZSM_0$-5 > $HZSM_1$-5 > $HZSM_2$-5 > $HZSM_3$-5

In contrast, this is the opposite order to B-associated Brønsted site population (Table 1), which entirely precludes any contribution of such weak sites to the zeolite's considerable acidity. Dealumination (nest) Brønsted sites, on

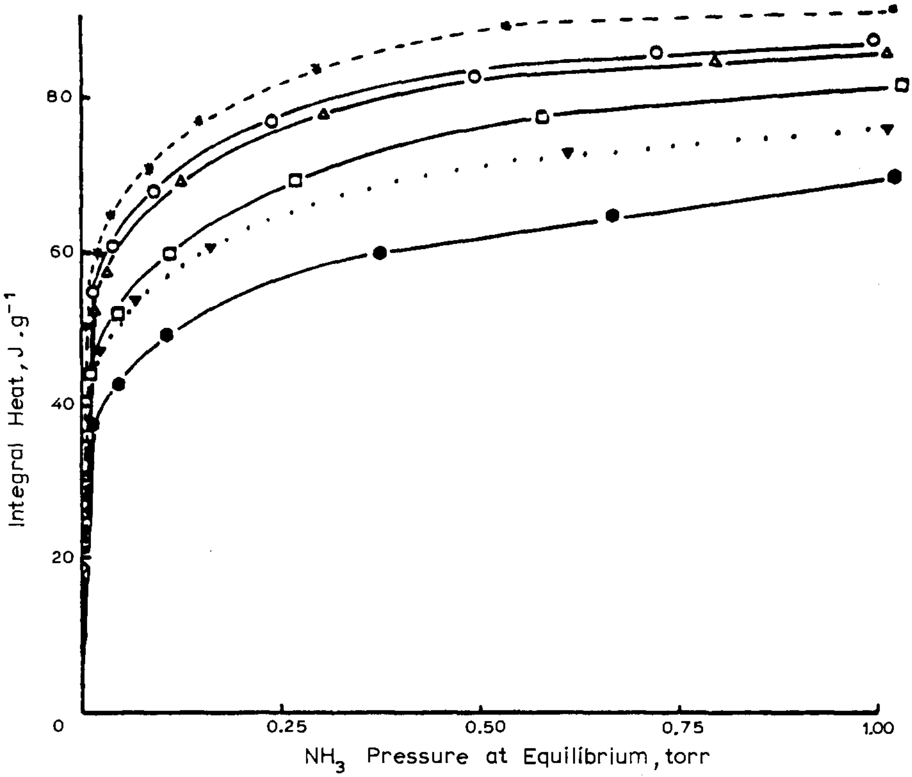


Fig. 3. Calorimetric isotherm of NH_3/HZSM-5 for samples degassed at 673 K.

the other hand, appear to count as strong, thus ranking the relevant sample as first in the order of heat evolved from NH_3-sorption at 423 K.

If this argument is appropriate, removing the origin disturbing the usual sequence correlating the heat of NH_3-sorption to Al-associated acid sites (i.e. removing the nest Brønsted sites) could then reveal ideal association. Indeed, this is shown for samples pretreated at 1073 K (Fig. 4), where the calorimetric isotherm reveals heat varying in order following the population of zeolite aluminum

$HZSM_0$-5 > $HZSM_1$-5 > Deal.HZSM-5 > $HZSM_2$-5 > $HZSM_3$-5

This is typically indicated by H^+_{Al} site population (Table 2).

These findings would reveal that, unlike Al-associated acid sites, B-associated acid sites (whether Brønsted or Lewis), however, sorb NH_3 (volumetric isotherm) and do not evolve heat of adsorption (calorimetric isotherm), which suggests weak acidity. On the other hand, dealumination Brønsted sites exhibit considerable acidity, which should be considered when discussing the role of zeolite acidity for such modified samples.

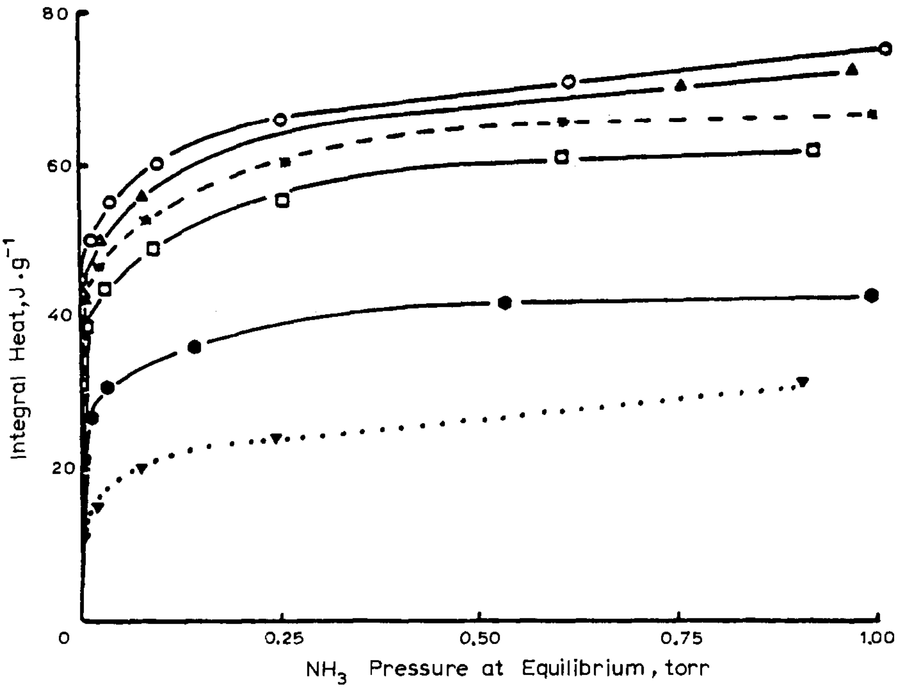


Fig. 4. Calorimetric isotherm of NH_3/HZSM-5 for samples degassed at 1073 K.

Differential heat of NH_3-sorption

As mentioned earlier, microcalorimetric measurements carried out at 423 K are of particular importance in differentiating the surface acidity into order of interaction strength, thus distinguishing homogeneous and heterogeneous acidity distribution. Homogeneous acidity is revealed in an abrupt change of the differential heat with surface coverage, which indicates interaction with two types of surface acidity: strong and weak. When NH_3 neutralizes all the strong sites showing an upper level differential heat plateau, the differential heat drops to a lower level that corresponds with the weak sites. On the other hand, heterogeneous acidity can be viewed as a systematic decrease of differential heat with surface coverage indicating the presence of a variety of surface sites exhibiting gradient strength. Figure 5 shows the differential heat of NH_3-sorption at 423 K for samples degassed at 673 K. As shown, modification of the zeolite surface lowers the acidity strength, which is indicated by lowered differential heats. Weak acid sites obviously replace the original strong sites (as a result of zeolite modification) inducing not only lowered acidity but also surface heterogeneity. Surface heterogeneity is enhanced following the order of increased zeolite modification extent

$HZSM_3$-5 > $HZSM_2$-5 > Deal.HZSM-5 > $HZSM_1$-5 > $HZSM_0$-5

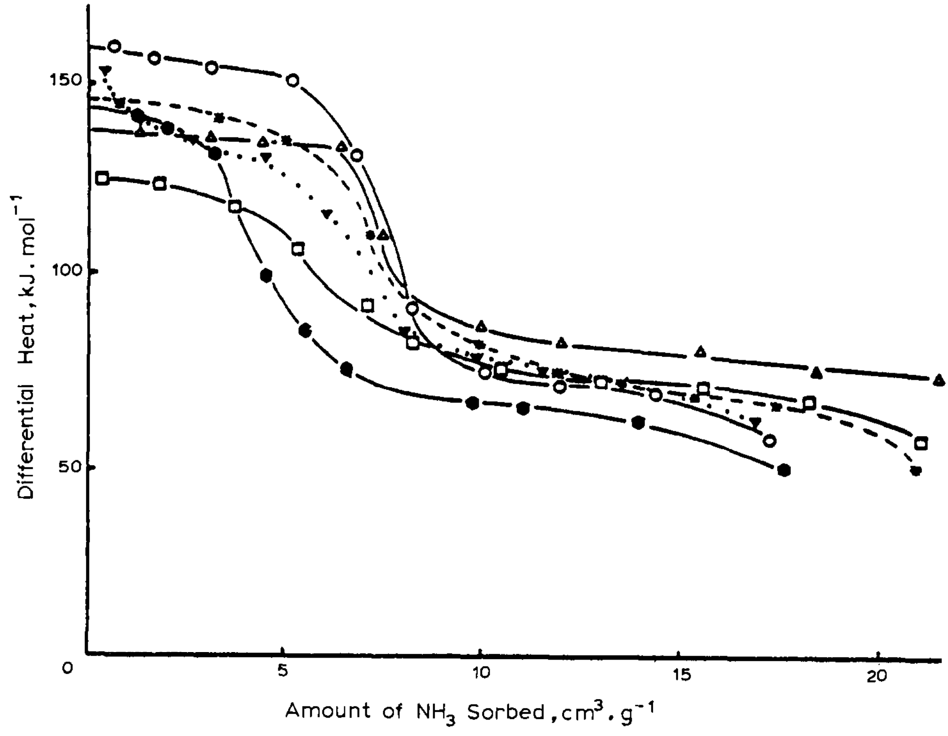


Fig. 5. Differential heat of NH_3/HZSM-5 for samples degassed at 673 K.

As expected for a stronger interaction of NH_3 with Lewis sites, Fig. 6 reveals differential heats of ca. 160 kJ mol^{-1} for all the samples degassed at 1073 K. This is at variance with differential heats measured for samples degassed at 673 K, where they drop with modification to even lower than 130 kJ mol^{-1} (Fig. 5).The effect causing heterogeneous distribution of surface acidity has a minor role for samples degassed at 1073 K (Fig. 6), where almost all the samples show the abrupt change of differential heat with coverage characterizing homogeneously distributed acidic surface sites.

Evaluation of the number of strong surface sites

Because the differential heat of a given process grades interacting sites into order of acidity strength, previous investigators [15,20] have used the differential heat as a method of measuring strong acid sites over differently modified zeolites. On other hand, the acidity spectra of Klyachko et al. [21] have been favored by others [5,6,12] for identifying such sites. In the present investigation, following a method based on thermokinetic features [22,23] which have previously been used by Gatta et al. [24], the number of strong sites is precisely found.

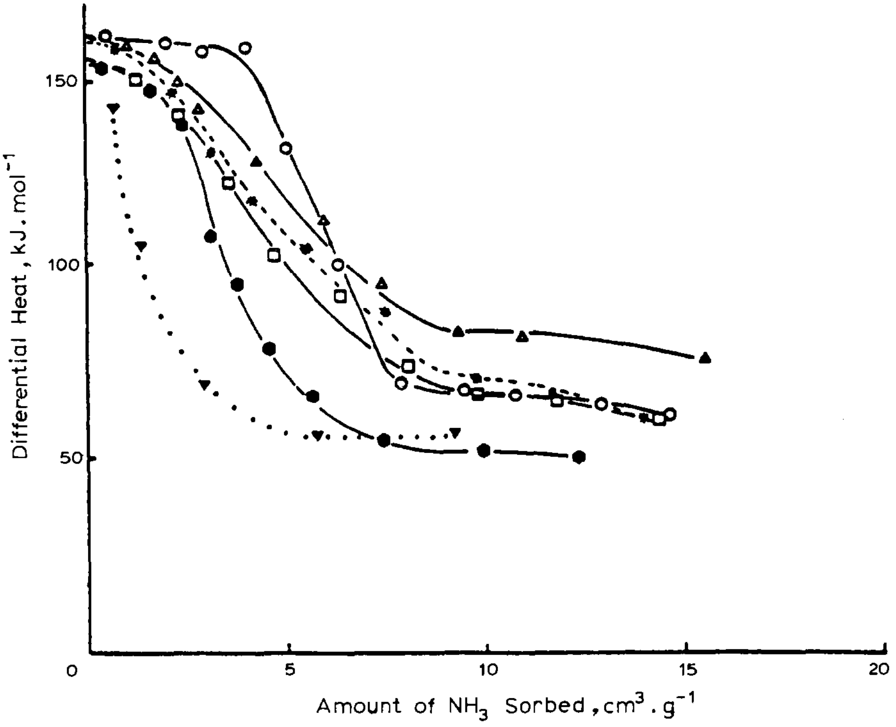


Fig. 6. Differential heat of NH_3/HZSM-5 for samples degassed at 1073 K.

For an irreversible sorption, site activation and sorbate transformation from a weaker site to a stronger site usually involve longer periods than for a quicker reversible process. The thermograms resulting from irreversible processes are therefore often broader than for reversible processes. Figure 7 shows the change in that thermokinetic parameter with surface coverage for samples degassed at 673 K. The data shown in this figure reveal that the sorption starts slowly as a result of site activation/sorbate transformation, continues at a slow rate passing through a maximum, and ends with a faster process. Such a sequence would indicate that the process starts with chemisorption reaching maximum interaction before tending to end with the faster reversible physisorption stage at high surface coverage. The peak maximum is zeolite dependent, and the amount of sorbed NH_3 at this maximum corresponds with the number of strong surface sites, provided one NH_3 mole sorbs on one acid site. The advantage of this method is that, being the maximum interaction defined by a peak maximum, estimating the number of strong surface sites is precise. Table 2 reports the number of strong surface sites for every sample in terms of site per zeolite unit cell. As reported, regarding the population of Brønsted sites (samples degassed at 673 K), the acidity strength follows the same order shown by integral heat

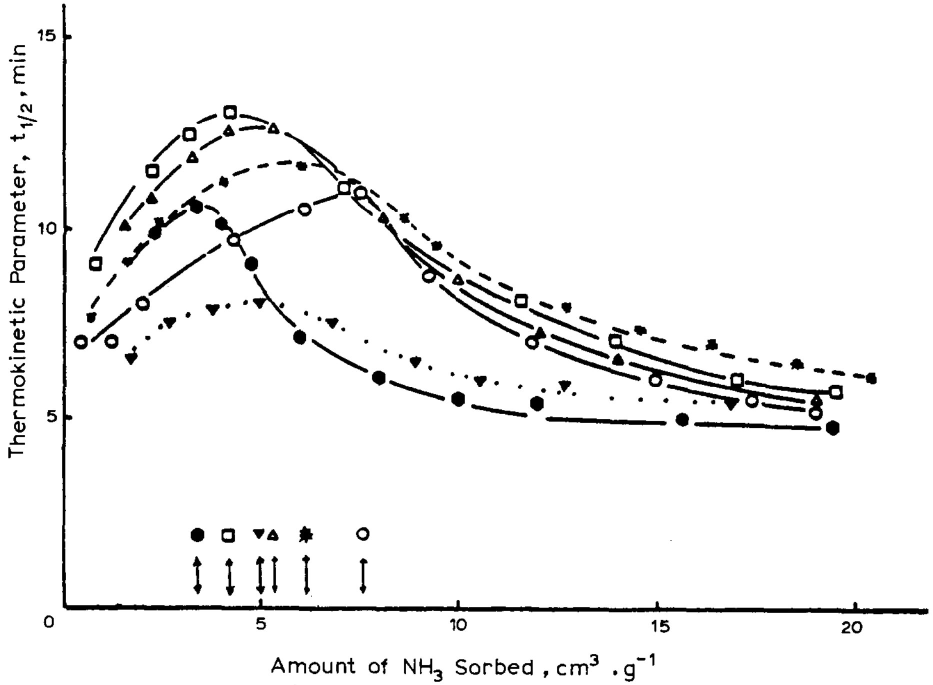


Fig. 7. Dependence of NH_3-interaction strength (in terms of $t_{1/2}$ of the thermogram) on surface coverage of NH_3/HZSM-5 for samples degassed at 673 K.

(not reported)

$HZSM_0$-5 > Deal.HZSM-5 > $HZSM_1$-5 > $HZSM_2$-5 > $HZSM_3$-5

This would indicate that the more acidic sites are those associated with zeolite Al. Dealumination (nest) Brønsted sites appear as less acidic.

Samples degassed at 1073 K (Fig. 8 and Table 2) reveal acidity strength following the order

$HZSM_0$-5 > $HZSM_1$-5 > Deal.HZSM-5 > $HZSM_2$-5 > $HZSM_3$-5

This is a typical order shown by the integral heat of such samples, which indicates entire association with zeolite Al–Lewis sites. It is clear that no contribution of considerable acidity is revealed for B-associated surface sites, whether as Brønsted or Lewis.

Finally, comparing the number of Lewis and Brønsted sites (Table 2) evaluated by thermal analysis suggests that surface dehydroxylation does not solely proceed by mechanism I (Scheme I) proposed by Utterhoeven et al. [25] and Ward [26], since Lewis site population is not half that of Brønsted sites, and there must be other approaches, e.g. mechanism II, which yield two (instead of one) Lewis sites. Moreover, since dehydroxylated surfaces do not restore original Brønsted acidity upon further [12,27] hydration, mecha-

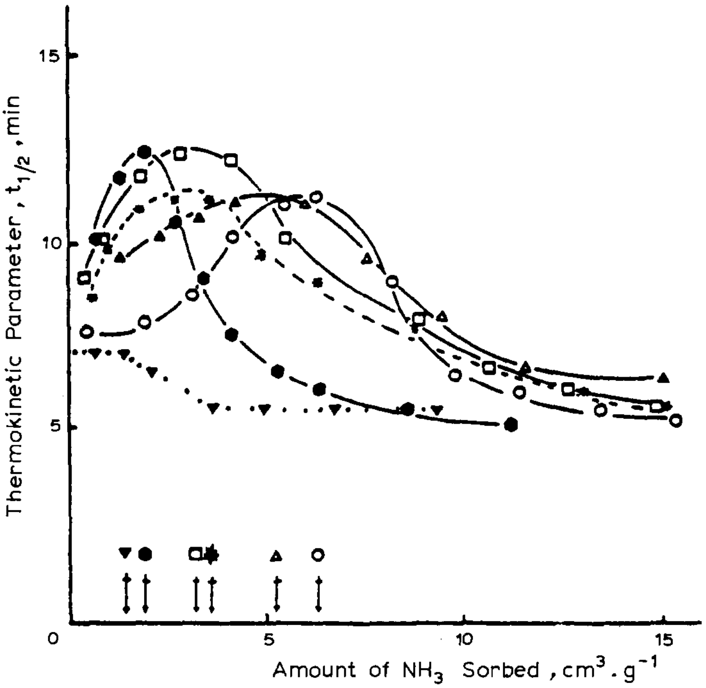
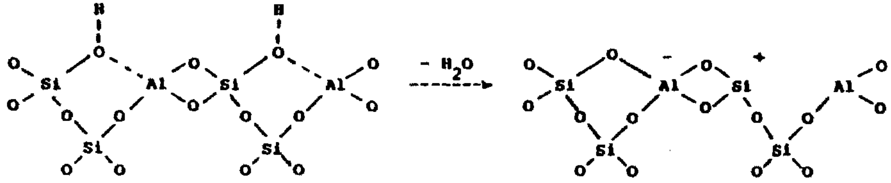


Fig. 8. Dependence of NH_3-interaction strength (in terms of $t_{1/2}$ of the thermogram) on surface coverage of NH_3/HZSM-5 for samples degassed at 1073 K.

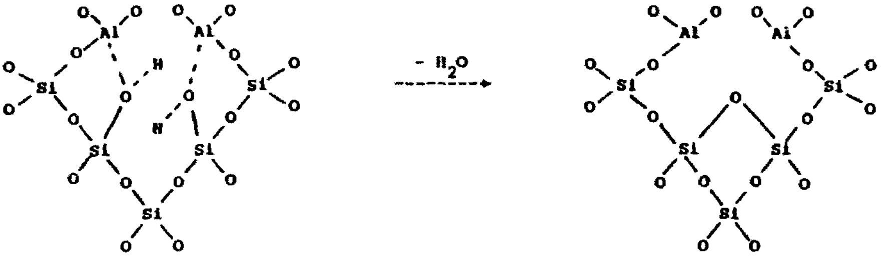
nism III could be possible. The ≡Si–O–O–Si≡ bridge is not easily hydrogenated upon surface hydration. However, surface dehydrogenation may occur with such severe treatment.This can be highly probable if one considers the loss of sorption capacity induced by surface dehydroxylation [28]. Such a loss can be a consequence of ≡Si–O–Si≡ or ≡Si–O–O–Si≡ bridge formation causing a steric barrier.

In order not to confuse structurally incorporated and impregnated boron data, I will discuss them separately. The data of NH_3-sorption onto Impreg.$HZSM_0$-5 are shown in Figs. 1–8, denoted by a solid triangle, ▼. Impregnating $HZSM_0$-5 with 0.6% B as H_3BO_3 (3.21 B per u.c) effects a loss of NH_3-sorption by ca. 15 and 40% and a loss of NH_3-heat by ca. 15 and 60% for samples degassed at 673 and 1073 K, respectively. This would indicate that zeolite degassing at 673 K neutralizes strong Brønsted sites by boron as described elsewhere [29], which reduces sorption and integral heat to the same extent. Zeolite degassing at 1073 K, however, may involve formation of some weak Lewis sites, which might sorb NH_3 but would not release heat. This can be illustrated in Scheme II. Such weak sites can be associated with boron.

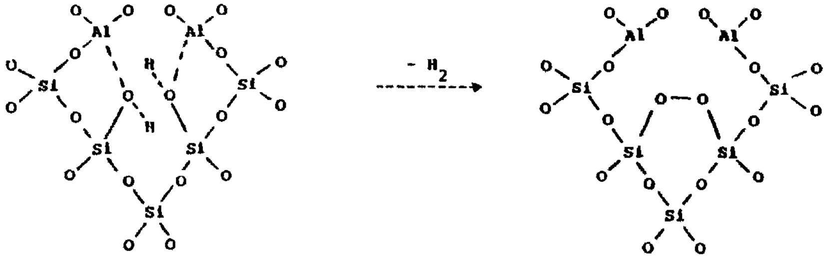
Mechanism I, Dehydroxylation of remotely located Brønsted sites:



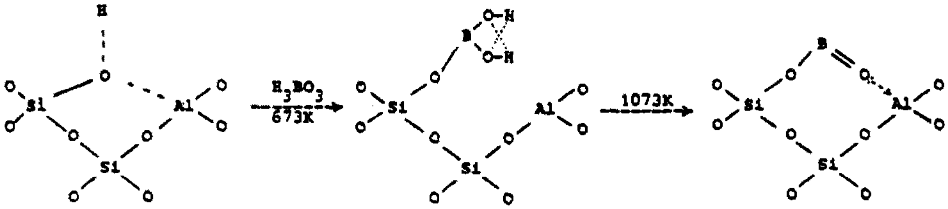
Mechanism II, Dehydroxylation of closely located Brønsted sites:



Mechanism III, Dehydrogenation of closely located Brønsted sites:



Scheme I



Scheme II

ACKNOWLEDGEMENTS

The authors is very grateful to Dr Aline Auroux for fruitful assistance and discussion, and to the Institut de Catalyse, CNRS, France, for generous permission to use the microcalorimeter.

REFERENCES

1 K. Tsutsumi, H.Q. Koh, S. Hagiwara and H. Takahashi, Bull. Chem. Soc. Jpn., 48 (1975) 3576.

2 T. Masuda, H. Taniguchi, K. Tsutsumi and H. Takahashi, Bull. Chem. Soc. Jpn., 51 (1978) 1965.

3 H. Taniguchi, T. Masuda, K. Tsutsumi and H. Takahashi, Bull. Chem. Soc. Jpn., 51 (1978) 1970.

4 H. Taniguchi, T. Masuda, K. Tsutsumi and H. Takahashi, Bull. Chem. Soc. Jpn., 52 (1979) 2195.

5 T. Masuda, H. Taniguchi, K. Tsutsumi and H. Takahashi, Bull. Chem. Soc. Jpn., 52 (1979) 2849.

6 H. Taniguchi, T. Masuda, K. Tsutsumi and H. Takahashi, Bull. Chem. Soc. Jpn., 53 (1980) 362.

7 H. Taniguchi, T. Masuda, K. Tsutsumi and H. Takahashi, Bull. Chem. Soc. Jpn., 53 (1980) 2463.

8 K. Tsutsumi, S. Hagiwara, Y. Mitani and H. Takahashi, Bull. Chem. Soc. Jpn., 55 (1982) 3572.

9 K. Tsutsumi, Y. Mitani and H. Takahashi, Bull. Chem. Soc. Jpn., 56 (1983) 1912.

10 Y. Mitani, K. Tsutsumi and H. Takahashi, Bull. Chem. Soc. Jpn., 56 (1983) 1917.

11 Y. Mitani, K. Tsutsumi and H. Takahashi, Bull. Chem. Soc. Jpn., 56 (1983) 1921.

12 A. Auroux, J.C. Vedrine and P.C. Gravelle, in J. Rouquerot and K.S.W. Sing (Eds.), Adsorption at the Gas/Solid and Liquid/Solid Interfaces, Elsevier, Amsterdam, 1982, p. 305.

13 A. Auroux, V. Bolis, P. Wierzchowski, P.C. Gravelle and J.C. Vedrine, J. Chem. Soc. Faraday Trans. 2, 75 (1979) 2544.

14 A. Auroux, P. Wierzchowski and P.C. Gravelle, Thermochim. Acta, 32 (1979) 165.

15 J.C. Vedrine, A. Auroux and G. Coudurier, in Whyte et al. (Eds.), Catalytic Materials, ACS Symp. Ser. 248, Washington, 1984, p. 253.

16 A. Auroux, P.C. Gravelle, J.C. Vedrine and M. Rekas, in L.V. Rees (Ed.), Proceedings of the Fifth International Conference on Zeolites, Heyden, London, 1980, p. 433.

17 M.B. Sayed and J.C. Vedrine, J. Catal., 101 (1986) 43.

18 M.B. Sayed, A. Auroux and J.C. Vedrine, J. Catal., (1987) in press.

19 M.B. Sayed, R. Kydd and R.P. Cooney, J. Catal., 88 (1984) 137.

20 J.C. Vedrine, A. Auroux, P. Dejaifve, V. Ducarm, H. Hoser and S. Zhou, J. Catal., 73 (1982) 147.

21 A. Klyachko, T.R. Brueva, I.V. Mishin, G.I. Kapustin and A.M. Rubinstein, Acta Phys. Chem., 24 (1978) 183.

22 M.B. Sayed, A. Auroux and J.C. Vedrine, Thermochim. Acta, 93 (1985) 557.

23 M.B. Sayed, A. Auroux and J.C. Vedrine, Appl. Catal., 23 (1986) 49.

24 G.D. Gatta, B. Fubini and E. Giamello, in J. Rouquerol and K.S.W. Sing (Eds.), Adsorption at the Gas/Solid and Liquid/Solid Interfaces, Elsevier, Amsterdam, 1982, p. 331.

25 J.B. Utterhoeven, L.G. Christner and W.K. Hall, J. Phys. Chem., 69 (1965) 2117.

26 J.W. Ward, J. Catal., 37 (1975) 383.

27 J.C. Vedrine, A. Auroux, V. Bolis, P. Dejaifve, C. Naccache, P. Wierzchowski, E.G. Derouane, J.B. Nagy, J.P. Gilson, J.H.C. Van Hooff, J.P. Van Der Berg and J. Wolthuizen, J. Catal., 59 (1979) 248.

28 M.B. Sayed, J. Chem. Soc. Faraday Trans. 1, 83 (1987) 1149; see also G.P. Babu, S.G. Hedge, S.B. Kulkarni and P. Ratnsamy, J. Catal., 81 (1983) 471.

29 M.B. Sayed, J. Chem. Soc. Faraday Trans. 1, 83 (1987) 1751.