Adsorption 11: 415–424, 2005

Heats of Adsorption of Ammonia and Correlation of Activity and Acidity in Heterogeneous Catalysis

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Abstract. Adsorption microcalorimetry was applied to determine heats of adsorption of ammonia on zeolites Y, mordenite, ZSM-5, heteropolyacid $H_3PW_{12}O_{40}$, as well as silica gel and amorphous aluminosilicates. The plots of differential heats against coverage served to construct the acidity spectra and, in this way, to determine the number of acid sites with different acidity strengths. The behavior of these materials in acid-catalyzed reactions, primarily, in the transformations of hydrocarbons is discussed. Evidence is presented that heats of adsorption of ammonia can be used to obtain correlation plots that describe relations between acidic and catalytic properties of zeolite catalysts.

Keywords: differential heat of adsorption, acid site, acid site distribution, zeolite, framework composition, extra-framework aluminum, catalytic activity, correlations

1. Introduction

Calorimetric measurements of heats of adsorption of gases and vapors represent a reliable technique for the investigation of surface chemistry of sorbents and catalysts. Heats of adsorption characterize adsorbate-adsorbent systems and can be used to clarify the main features of intermolecular adsorbate—adsorbent and adsorbate—adsorbate interactions. Measurements of heats of adsorption of bases are currently the only reliable way to qualitatively determine the number and the strength of acid sites.

Calorimetric determination of heats of adsorption of bases produces curves of the type differential heat of adsorption as function of amount adsorbed, from which the distribution of adsorption sites over adsorption energies can be derived. This information indicates the concentration of acid sites with different strengths in catalysts and offers a possibility to search for the relation between acidity and activity of different catalytic systems.

Unfortunately, this sophisticated but laborious method is rarely used in catalysis. Besides, some researchers question the possibility to apply heats of adsorption of bases to unravel the strength of active sites (Parrillo et al., 1995). However, the lack of single correlations between calorimetric and catalytic data does not mean that adsorption calorimetry is not suitable for an investigation of acidity of heterogeneous catalysts. The knowledge of both structure and composition of a catalyst coupled with a proper choice of experimental conditions are needed to obtain satisfactory correlations between acidity and activity.

In this paper account is given of the relation between the distribution of acid sites and catalytic behavior of the zeolite based catalysts. Protonic modifications of zeolites prepared by decationization and dealumination of parental materials are the principal objects of this study.

2. Experimental

2.1. *Differential Heats of Adsorption of Ammonia*

Differential heats of adsorption of ammonia, NH_3, were measured by a home-made Calvet-type microcalorimeter connected to a volumetric adsorption unit. The

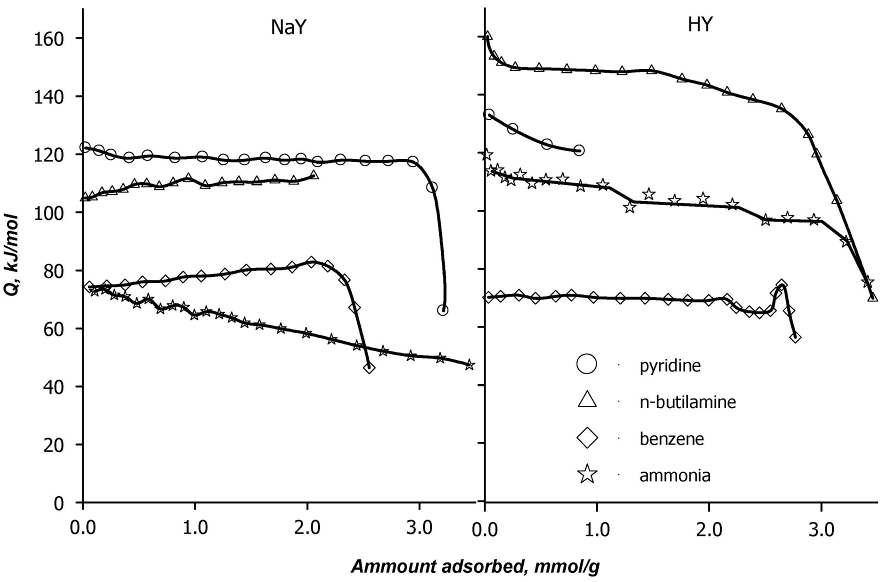

Figure 1. Differential heats of adsorption of *n*-buthylamine, pyridine, benzene and ammonia at 30°C as a function of coverage for sodium (a) and hydrogen (B) forms of *Y* zeolite.

procedure of calorimetric measurements has already been described (Brueva et al., 2001). On analyzing acid properties of the heterogeneous catalysts, pyridine, *n*-buthylamine and NH_3 are the most frequently used probe molecules (Klyachko et al., 1978). In Fig. 1, the differential heats of adsorption of pyridine ($pK = 5.5$), *n*-buthylamine ($pK = 10.6$), benzene and NH_3 ($pK = 9.2$) as a function of micropore filling are shown for the sodium and hydrogen forms of *Y* zeolites. The lack of differences between the energies of interaction between pyridine and the protonic sites and cations makes pyridine an unsuitable base to determine both strength and number of acid sites. Similarly, due to insufficient selectivity of adsorption on acid sites the number of these sites cannot be determined by *n*-buthylamine either.

Since molecular dimensions of NH_3 are smaller than those of pyridine and *n*-buthylamine, ammonia molecules can directly contact a large number of active sites. Calorimetric measurements showed that heats of adsorption of NH_3 on protonic sites are higher than those for the interaction with Na^+ ions. The most dramatic changes of heats of adsorption of NH_3 with micropore filling occurs at low fillings where NH_3 interacts with the strongest sites. Generally, the curve that describes heats of adsorption of NH_3 as a function of micropore filling has a step-wise form, which implies the heterogeneous nature of adsorption sites. Accordingly, NH_3 is the preferable base for the determination of the number and the strength of acid sites using adsorption microcalorimetry.

On measuring heats of adsorption, temperature is varied from 30 to 300°C. We were able to show that at 30°C NH_3 molecules interact with Brönsted acid sites (BAS) of decationated *Y* zeolites with $q = 95$–$110\,\text{kJ/mol}$. Over this range of micropore filling the heat of adsorption displays a number of discrete levels. If the temperature of adsorption on a hydrogen form of *Y* zeolite was increased from 30 to 300°C the heats of adsorption remained unchanged.

For a number of zeolites the effect of temperature on adsorption heats could be investigated. The following observations were made. At temperature as low as 30°C NH_3 molecules redistribute themselves from weaker to stronger sites. The rate of redistribution decreases remarkably on going from large-pore to small-pore zeolites and depends on the strength of adsorption sites. In some experiments as many as 48 hours were needed to establish heat equilibrium. As the strength of acid sites increases, the residence time of a molecule bound to a site increases, and the molecule moves more slowly to a stronger site. Consequently, we were not able to record changes in heats of adsorption with temperature on a large-pore *Y* zeolite. Contrarily, increasing temperature affected strongly the heats of adsorption of NH_3 on mordenite and ZSM-5 type zeolites (Fig. 2). Moreover, as the measurement temperature was increased from 30

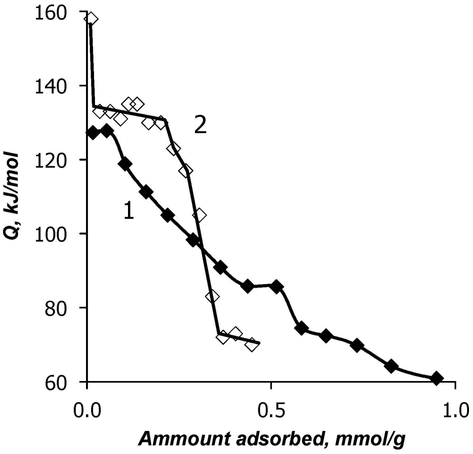

Figure 2. Differential heats of adsorption of ammonia at 30 (1) and 300°C (2) as a function of coverage for ZSM-5 zeolite with a Si/Al ratio of 30.

to 200°C a sizable enhancement in heats of adsorption was observed but no change in heats was recorded with further increase in temperature. The time needed to establish heat equilibrium decreases with temperature. In addition, the dissociative chemisorption of NH_3 on Lewis-acid sites that occurs at 300°C should be taken into account. Temperatures above 100°C are therefore preferred if applying adsorption of NH_3 to study acidity of zeolites and other acid catalysts. Most experimental results discussed below were obtained at 300°C.

2.2. *Adsorbents*

The sample holders used in our experiments contain a large amount of adsorbent (1–1.2 g.) to ensure a better accuracy of adsorption measurements. Prior to every run the adsorbent samples were pressed into pellets without binder. The pellets were crushed to produce a grain fraction of average size, ca. 1 mm, and this fraction was put into the sample holder. Save for special cases the sample holders were evacuated at 480°C for 100 hr.

Sodium forms of Y-type zeolite (Si/Al = 2.4), mordenite (Si/Al = 5) and ZSM-5 (Si/Al = 20), were used as parental materials. To prepare a series of decationated samples, the zeolites were equilibrated with a 1N solution of NH_4NO_3 at room temperature. Low-sodium zeolites with 83–92% cation-exchange degrees were obtained by treatment of their sodium forms with a 1N NH_4NO_3 solution followed by calcination at 400–700°C for 2 hr and repeated exchange with an 1N NH_4NO_3 solution. Faujasites that were dealuminated to different extents were prepared by treating NaY zeolites with $SiCl_4$ vapor at 220–400°C, and by extracting aluminum with EDTA. Ultrastable Y-type zeolites were prepared by steaming and acid leaching protonated zeolites. High-silica mordenites were produced by direct synthesis or by treatment of H-mordenite with 0.25-6N HCl. Silica gel was prepared by hydrolyzing tetraethoxysilane at ambient temperature whereas amorphous aluminosilicate was made by hydrolyzing tetraethoxysilane in presence of aluminum nitrate.

2.3. *Catalytic Activity*

Catalytic properties of the solids were tested in simple carbonium-ion reactions. The procedures for evaluating the catalytic activity in reactions of cracking n-octane and iso-octane, of disproportionation of ethylbenzene and dehydration of 3-methylbutanol-2 were described earlier (Brueva et al., 2001).

3. Results and Discussion

3.1. *Acidity of Protonated Y-Type Zeolites*

The parental NaY zeolite adsorbs NH_3 with an adsorption heat that amounts to $Q_{\mathrm{NH3}} < 85$ kJ/mol. The main portion of NH_3 is characterized by heats, 75–50 kJ/mol, which indicates interaction of Na^+ cations with NH_3 molecules. Heats with $Q > 90$ kJ/mol appear upon decationization, and all-site adsorbing NH_3 with $q > 90$ kJ/mol can be related to the acid sites. Up to about 60% exchange the sites with $Q = 117$–120 kJ/mol are formed. The concentration of these sites in the samples with low exchange degrees (below 60%) does not exceed the value of 0.5 mmol/g. In zeolites with $\alpha > 60\%$ the strength of acid sites increases, and the fraction of acid sites characterized by Q values higher than 110 kJ/mol accounts for more than 50% of the total acidity. Moreover, the fraction of acid sites with $Q > 120$ kJ/mol is quite significant (Mishin et al., 1993a).

Changes in the framework Si/Al ratio are accompanied by changes in zeolite acidity. Evidence of a strong impact of the framework Si/Al ratio on the acidity of faujasites is supported by calorimetric results obtained for adsorption of NH_3 on $NH_4Y_{2.4}$ at 300°C and on dealumininated zeolites with varying composition (Fig. 3). The initial heats of adsorption on the parental protonic form reach a value of ≤ 112 kJ/mol, whereas the number of sites with $Q > 90$ kJ/mol amounts to

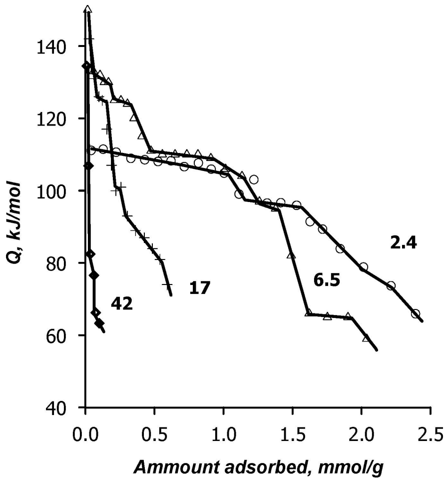

Figure 3. Differential heats of adsorption of ammonia at 300°C as a function of coverage for dealuminatedY zeolites with framework Si/Al ratios of 2.4, 6.5, 17, and 43.

1.8 mmol/g. Following aluminum reduction, the total number of acid sites decreases, so that not more than 0.05 mmol/g with heats higher than 90 kJ/mol was adsorbed by the sample with a Si/Al ratio of 42. The aluminum-deficient *Y* zeolites have, however, stronger acid sites ($Q > 120$ kJ/mol) than their parental forms. An increase in strength of acid sites can be seen up to a limiting value of $N_{\mathrm{Al}} = 25$–30 Al per unit cell, u.c., after which such an increase could not be observed anymore. Consequently, the dependence of the number of strong acid sites ($Q \approx 122$–136 kJ/mol) on aluminum content is described by a curve with a maximum at Si/Al $\approx$ 5–7, which corresponds to 50% dealumination (Fig. 9(a)).

A clear relation between the number of framework aluminum atoms and the position of the maximum on the acidity-composition profile demonstrates the influence of the framework Si/Al ratio on the properties associated with the Brönsted acidity. It is generally accepted that the acidity of hydroxyl groups increases as the framework Si/Al ratio increases. This behavior can be readily explained using a simple model, which implies that the presence of next –nearest aluminum neighbors (*NNN Al*) weakens the strength of the acid sites associated with the AlO4 tetrahedra, so that a minor decrease in the aluminum concentration makes the acid sides more active. The model initially introduced by D. Barthomeuf suggests that *0-NNN* atoms are associated with the especially strong acid sites.

3.2. *Acidity of High-Silica Mordenites*

Figure 4 shows variations in differential heats of adsorption of NH_3 with coverage for mordenites with different framework Si/Al ratios prepared by direct hydrothermal synthesis and by dealumination. The initial Na-form adsorbs NH_3 with heats that amount to 85–75 kJ/mol and show little change with coverage. The sites with $Q = 140$ kJ/mol could be detected in samples of the hydrogen form of small-port mordenites, while those with heats equal to 150 and 160 kJ/mol were found in decationated large-port specimens (Mishin et al., 1993b).

The figure indicates that after dealumination with HCl or reduction of Al density in the process of

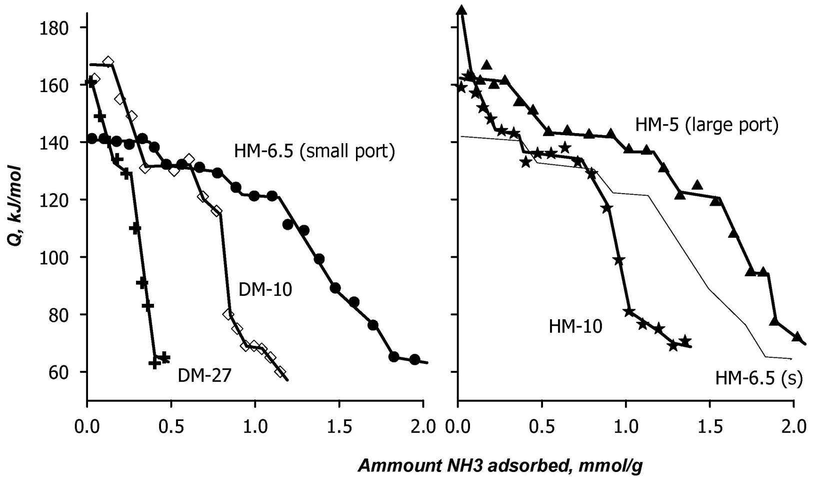

Figure 4. Differential heats of adsorption of ammonia at 300°C as a function of coverage for small-port and large port-mordenites and for dealuminated mordenites with different framework Si/Al ratios.

hydrothermal synthesis the fraction of acid sites with heats that amount to 120–140 kJ/mol decreases, but stronger acid sites with $Q > 150$ kJ/mol appear that seem to be absent in the parental hydrogen zeolites. Dealumination reduces, therefore, the density of acid sites but increases their strength. The increase in the strength of acid sites in dealuminized mordenites was reported by other researchers (e.g., by Auroux, 1997). The increase in acidity strength at low dealumination levels occurs at the expense of weak acid sites. As for faujasites, removal of the second half of framework aluminum does not generate new strong acid sites. The number of very strong sites formed by dealumination makes up less than 20% of the total acidity. Again, a plot of the number of strong acid sites against the aluminum content is represented by a curve with a maximum that corresponds to 50% dealumination. It can be seen from a comparison of the heats of adsorption that high-silica zeolites slightly differ in their content of strongest acid sites with $Q > 150$ kJ/mol. In siliceous samples prepared by direct hydrothermal synthesis (HM_{10}), sites with $Q = 120$–140 kJ/mol predominate, but the number of these sites in dealuminated mordenites (DM_{10}, DM_{27}) appears to be significantly lower.

3.3. *Acidity of ZSM-5 Type Zeolites*

The heats of adsorption of NH_3 at 300°C for ZSM-5 zeolites with Si/Al $= 20$–140 are given in Fig. 5. On all three samples, the initial heats are about 160–180 kJ/mol and fall dramatically with micropore filling, specifically at low concentrations. Over the range of 125–135 kJ/mol, every curve shows a step that implies the presence of a large number of sites with similar energy. Once these sites are covered, the heats decrease rapidly to reach a level of about 60–70 kJ/mol. The figure demonstrates that the pattern of variation of heats with filling is almost indistinguishable for all ZSM-5 type zeolites, and it is independent of the Si/Al ratio.

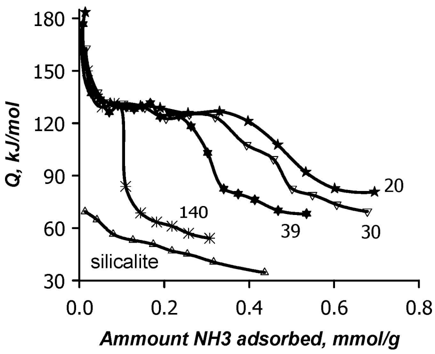

Figure 5. Differential heats of adsorption of ammonia at 300°C as a function of coverage for HZSM-5 type zeolites with different framework Si/Al ratios.

3.4. *Construction of Acidity Spectra and Their use for Comparing Acidity of Different Zeolites*

To compare acidity of different zeolites it is convenient to use acidity spectra of various zeolites, which can be constructed by graphical differentiation of the experimental curves that describe the dependence of heats of adsorption on concentration. Figure 6 shows acidity spectra of HZSM-5 zeolites, hydrogen mordenites with Si/Al $= 5$ and 10 along with the spectra of hydrogen mordenite (HM_{10}) calcined at 650°C. On comparing the spectra it becomes evident that each zeolite is characterized by a specific set of sites. In H-mordenite, three types of acid sites of different strength can be discriminated. As the concentration of framework aluminum decreases, sites with $Q > 150$ kJ/mol appear that cannot be observed in the spectra of H-mordenite with Si/Al $=$ 5. On calcining a conventional HM_5 at 650°C, the sites with $Q = 170$ and 100 kJ/mol attributable to Lewis-acid sites are generated as evidenced by infra-red data (Kapustin et al., 1984). Finally, in the spectrum of HZSM-5 zeolite that has a higher framework Si/Al ratio than dealumininated mordenites only Brönsted sites with $Q > 125$–130 kJ/mol could be found.

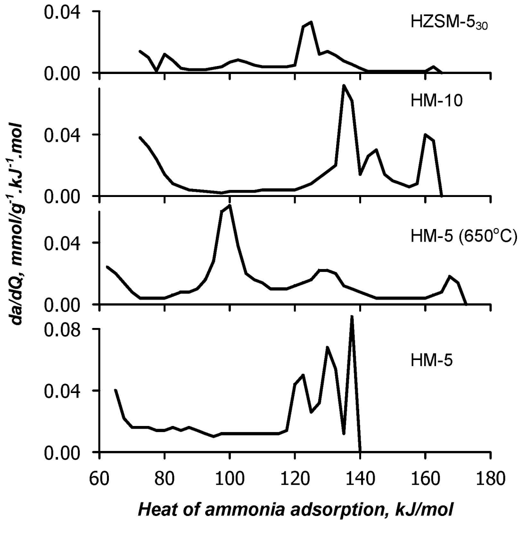

Figure 6. Acidity spectra of zeolites constructed by graphical differentiation of plots of heats of adsorption *vs.* micropore filling.

Table 1. Acidity and catalytic activity of mordenite and pentasil type zeolites in the cracking of *n*-octane.

	Acidity, meq/g			The number of Brösted sites adsorbing NH_3 with heat (kJ/mol)				$K * 10^7$ (mol/g min Pa)	
Zeolites	L + B	L	B	120 ± 5	130 ± 5	140 ± 5	150 ± 5	Exp	Calc
$HNaM_{10}$-46%	0.8		0.8		0.7	0.1		3.8	
$HNaM_{10}$-90%	1.5		1.5	0.62	0.46	0.42		7.8	
$HNaM_{10}$-90% (650°C)	1.35	0.93	0.42		0.42			2.0	
$DM_{12.6}$	0.95	0.35	0.6		0.25	0.35		2.9	2.8
DM_{20}	0.8	0.18	0.62		0.1	0.4	0.12	6.5	6.6
DM_{55}	0.35	0.05	0.3		0.23		0.07	3.6	
HM_{20} (TEA)	0.94		0.94		0.56	0.24	0.14	9	8.8
ZSM-5_{70}	0.48	0.14	0.34		0.1	0.04		2	1.84
ZSM-5_{60}	0.28	0.02	0.26		0.21			0.9	1.25
ZSM-5_{80}	0.3	0.01	0.29		0.18			1.52	1.5

3.5. Search for Acidity—Activity Correlations for Mordenites in n-Octane Cracking

Based on the acidity spectra and on the assignment derived from the combined investigation of mordenites by means of infra-red spectroscopy and microcalorimetric measurements we could distinguish between sites of Brönsted (B)- and Lewis (L)-types. Brönsted acid sites with similar strengths were in turn grouped into four categories according to the positions of maxima in their acidity spectra. Distributions of acid sites in mordenites and ZSM-zeolites along with data on catalytic activity of these samples in the cracking of *n*-octane are summarized in the Table 1.

From these data it can be concluded that *L*-sites are lacking in high-silica mordenites prepared by direct crystallization. On the contrary, they are present in large quantities in dealumininated samples. The number of the sites with $Q > 150$ kJ/mol is fairly low and accounts for not more than 20% of the total number of Brönsted acid sites. However, the sites with a similar strength are about 10 times more active in the cracking of normal hydrocarbons than the less acidic OH groups. This conclusion emerges from comparison of data on acidity of high-silica mordenites and activity in the cracking of iso-octane.

There was no correlation between catalytic activity and the total number of acid sites (Fig. 7(a)). Such a correlation could be expected if all the active sites were of both same nature and strength. The results given in the Table 1 indicate, however, some degree of heterogeneity of acidity for hydrogen mordenite and ZSM-5

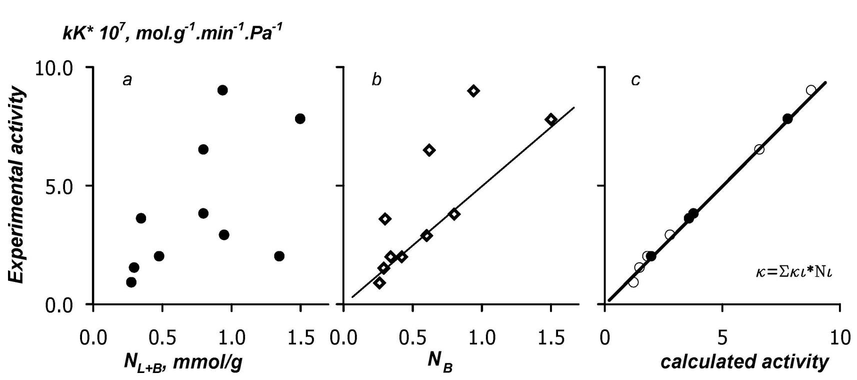

Figure 7. Experimental reaction rate constants for cracking of *n*-octane on high-silica mordenites against the total number of acid sites (a), the number of Brönsted sites (b), and the correlation between observed and calculated rate constants (c).

type zeolites. If the activity was plotted against the total number of acid sites, the activity increased linearly as the Brönsted acidity increased (Fig. 7). The experimental values for some samples were well outside the line suggesting that the sites with varying acid strength have different cracking activity. It appears that each type of sites makes its specific contribution to the overall activity. The contribution from any particular type of acid site is a function of specific activity and the number of sites:

$$k = \sum k_i n_i$$

where k_i is the specific reaction-rate constant for a single site of i-type and n_i, the number of i-sites.

Such treatment termed "regional analysis method" was first introduced by Yoneda (Tanabe, 1970). In more recent publications, this approach has not been developed since the number of particular sites could not be determined. Data on adsorption heats give the required information on the distribution of acid sites by identifying the number of sites with particular acid strengths. This helps to determine the specific activity of each single site for catalysts with a number of sites of varying activity.

Lewis acid sites are not very active in catalysis. Dehydroxylation of mordenite increased the number of Lewis-acid sites but activity of the dehydroxylated sample was greatly reduced. To determine the activity of Brönsted sites of different types, one can write four relations with reaction-rate constants and the numbers of the acid sides of each particular type. Solution of these relations gives the specific rate constants for each particular type of acid site, which characterizes the contribution to activity from acid sides of each type. As the calculation shows, all sites that adsorb NH_3 with a heat equal to 120,130 ± 140 kJ/mol are similarly active in cracking of n- octane ($ki = 0.8 * 10^{-27}$ mol site^{-1}/min^{-1} Pa^{-1}). The sites with $Q = 150 \pm 5$ kJ/mol are several times more active, $ki = 6.0 * 10^{-27}$ mol site^{-1}/min^{-1} Pa^{-1}. Also, according to the same calculation, Lewis acid sites are inactive for cracking of n-octane.

3.6. *Catalytic Activity of High-Silica Mordenites*

Figure 8 demonstrates activity of mordenites in the transformation of various hydrocarbons and 3-methylbutanol-2 as a function of framework composition. As can be seen in the plots, the activity of mordenites increases with increasing degree of dealumination, passes through a maximum and then decreases upon further removal of aluminum. The curve for n-octane follows the course of very strong sites, and the maximum corresponds to the maximum of the strong acidity. The position of the maximum lies near a value of $Al/Al + Si = 0.09$. This value is close to the chemical composition of the frameworks that contain the highest number of "isolated" aluminum atoms. The frameworks with these Si/Al ratios are typical of mordenites with an extent of dealumination near 50%. The coincidence of the position of the curves' maxima relating strong acidity and activity to the framework composition, implies an important catalytic role of acid sites associated with the "isolated" aluminum atoms.

A similar relationship exists between the density of framework aluminum atoms and activity of mordenites in transformation of various reactants. However, for mordenites the position of the maximum on the

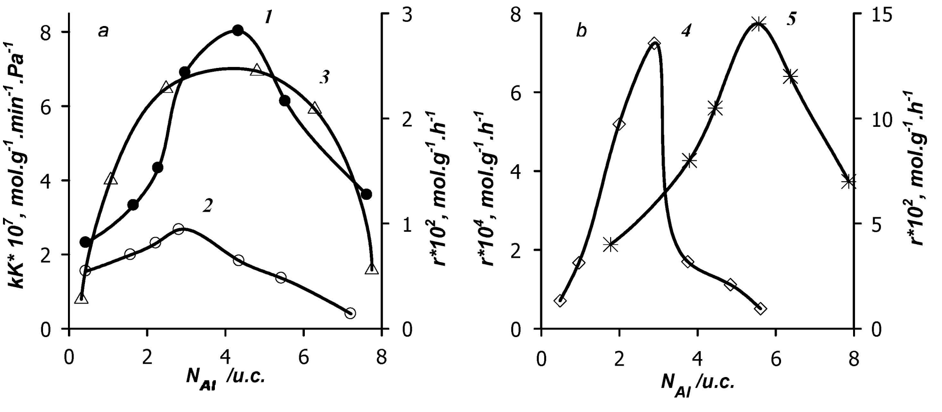

Figure 8. The effect of the framework aluminum content on catalytic activity of mordenites. (A) in cracking of n-octane (1) and iso-octane (2), in isomerization of o-xylene (3); (B) in disproportionation of ethylbenzene (4) and in dehydration of 3-methylbuthanol-2 (5).

activity-composition profile depends on reactivity of the organic compound transformed. Figure 8 shows the effect of the aluminum content on the rate of formation of olefins in the dehydration of 3-methylbutanol-2 at 180°C. In agreement with the change in acidity, progressive dealumination results first in an increase and than in a decrease in catalytic activity passing through the maximum at Si/Al $\approx$ 7. It appears that for transformation of high reactive secondary alcohol, weaker acid sites are needed than for hydrocarbon conversions. Accordingly, the highest activity for dehydration is observed with the sample dealuminated to 15%. On the other hand, as follows from Fig. 8, the highest activity in the disproportionation of ethylbenzene exhibit mordenites with a dealumination degree of 60%, whereas in isomerization of *o*-xylene and in the cracking of *n*-octane the most active are mordenites dealuminated to 50%. Thus, the higher reactivity of the substrate, the less strong sites are necessary for its transformation and the lower is the Si/Al ratio corresponding to the highest activity.

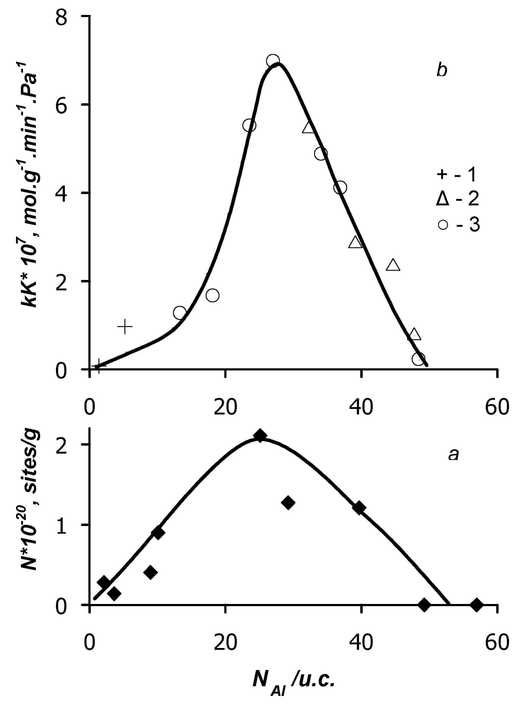

Figure 9. Variation in the number of strong acid sites with $Q_{\mathrm{NH_3}}$ = 122–136 kJ/mol (*a*) and activity in cracking of isooctane as a function of N_{Al} for *Y* zeolites (b): prepared by treating the stabilized *Y* zeolites with HCl (1), prepared by thermal dealumination at 600–700°C (2) and produced by treatment of sodium faujasites with $SiCl_4$ (3).

3.7. Catalytic Activity of High-Silica Faujasites

The approach to analyze the reactivity of Brönsted acid sites can be applied if the framework and bulk compositions of zeolites are identical. Real samples frequently contain, however, extra-framework aluminum species which make the search for correlations between activity and acidity difficult. Some results on activity of faujasites in the cracking of iso-octane are shown in Fig. 9 for the samples dealuminated by different methods. The variation of the strong acidity (Fig. 9(a)) and the change of activity (Fig. 9(b)) with progressing dealumination show a similar trend. The crucial role of the aluminum removal on acidity is clearly demonstrated for zeolite treated with $SiCl_4$. The cracking activity doubles, if the aluminum content in zeolites produced by direct synthesis decreases from 60 to 50 Al/u.c. For comparison, after extraction of 10 more Al atoms from *Y* zeolites with $SiCl_4$, the value of *kK* increases by nearly one order of magnitude. Activities reach a maximum if about 25 Al/u.c. remain in the framework. This shows that the activity of faujasites increases 8–10 times as the N_{Al} values decrease from 50–60 for the parental hydrogen forms to about 20–25 Al per u.c. for the sample with a dealumination degree of 50%. Figure 9 also contains the data for *Y* zeolites prepared by calcination of ammonium forms at $T > 500$°C that results in the expulsion of tetrahedral aluminum from the framework and in the formation of exra-framework aluminum compounds. Thermal dealumination is also accompanied by partial contraction of the framework. Calculation of the activity, based on the bulk catalyst composition, gives reaction-rate constants much lower than those of $SiCl_4$-treated zeolites. After allowing for the presence of catalytically inert amorphous material, activities for the sample prepared by thermal dealumination could be estimated, and they are comparable with those of the $SiCl_4$-treated counterparts.

The importance of this approach can be illustrated by the data obtained on acidity and activity of faujasites dealuminated with EDTA. A plot of apparent reaction-rate constants as a function of the bulk aluminum reveals but a slight increase in activity for the EDTA-treated samples (Fig. 10). By contrast, the response of activity to aluminum removal is much more pronounced for the $SiCl_4$-extracted zeolites. Since the content of the framework aluminum decreases only below 50% for the EDTA-treated zeolites and then remains unaltered, calculation of activity based on the lattice composition yield a curve with a sharper maximum. An even more pronounced increase in activity

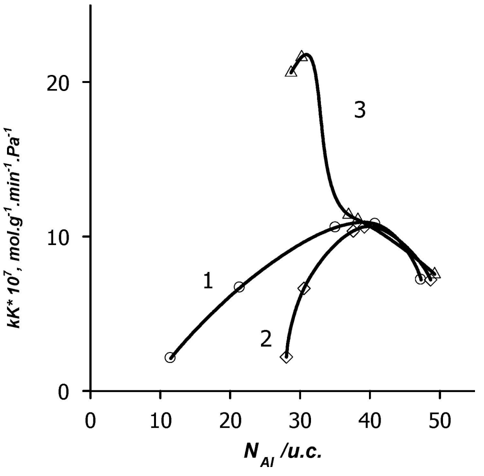

Figure 10. Dependence of the catalytic activity of *Y* type zeolites dealuminated by EDTA in the cracking of iso-octane on the number of Al atoms: (1) in the catalyst, (2) in the framework, (3) in the framework with correction for the presence of amorphous material.

can be obtained by relating the *kK* values to the fraction of crystalline material rather than to the bulk catalyst.

3.8. *Acidity of Heteropolyacids, Silicagels, and Amorphous Aluminisilicates*

The heats of adsorption of NH_3 on the bulk heteroplyacid (HPA) $H_3PW_{12}O_{40}$, silica gels, and amorphous aluminosilicates are given in Fig. 11 with the results for protonic forms of zeolites reported in the above sections shown for comparison. For the bulk HPA the initial heat of 165 kJ/mol decreases slowly in the low-coverage regime to 140 kJ/mol. HPA contains a small number of sites (0.03 mmol g^{-1}) characterized by heats $>$120–140 kJ/mol. In the case of adsorption on zeolites such high values are associated with dissociative interaction with L sites. The heats of the same magnitude are produced by adsorption of ammonia on the strongest B-sites present in mordenite. The total number of strong acid sites derived from the measurements of heats of adsorption is internally consistent with theoretical population of protons in $H_3PW_{12}O_{40}$ (1.04 mmol g^{-1}). The calorimetric measurements failed to find weaker acid sites. At moderate concentrations the heats of adsorption of NH_3 fall rapidly from140 to 60 kJ/mol.

Guisnet et al., (2000) also reported that protonic sites evaluated from the thermodesorption of pyridine are comparable in $H_3PW_{12}O_{40}$ and in protonic mordenite in terms of their strengths. Much lower activity of the protonic sites in mordenite was attributed to the particular geometry of the pore system of this zeolite.

The same figure is complemented with the calorimetric data for pure silica gel and amorphous aluminosilicate. On silica gel, the initial heats of adsorption of NH_3 do not exceed the level of 70 kJ/mol, which indicates the absence of strong acid sites on the surface of SiO_2. Over broad ranges of concentration (from 0.1 to 1.7 mmol g^{-1}) Q_{NH_3} decreases slowly to reach values of

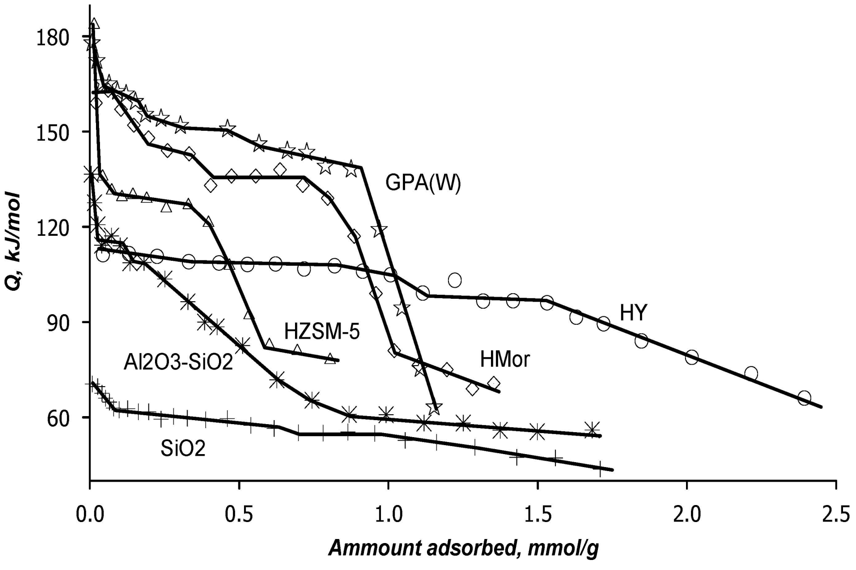

Figure 11. Differential heats of adsorption of NH_3 at 30 and 300°C as a function of coverage for: silica gel (30); amorphous aluminisilicate (30); HZSM-5 zeolite with Si/Al = 25; H-mordenite with Si/Al = 5, HY with Si/Al = 2.4, and bulk heteropolyacid.

60 to 45 kJ/mol. This suggests the homogenous nature of acid sites on silica gel.

On introducing 15% Al_2O_3, the initial heat increases to 130 kJ/mol. On aluminosilicate, the differential heats for concentrations of NH_3 below 0.3 mmol g^{-1} NH_3 are higher than 100 kJ/mol. On comparing acid properties of amorphous aluminosilicate and HY zeolite it becomes evident that both samples contain the same acid sites with Q that varies from 80 to 110 kJ/mol. It appears that unique properties of zeolites are related primarily to the regular array of internal pores where the catalytic transformations occur.

4. Conclusion

The purpose of this work was to prove the power of adsorption calorimetry in the context of acidity of heterogeneous catalysts. The heats of adsorption can be converted into acidity spectra, which are characteristic of acid zeolites with different framework structure and composition. If combined with spectroscopic and structural information, the knowledge of interaction energy between the adsorbed molecules and acid sites contributes to an understanding of catalytic significance of particular sites.

The evidence presented in this work shows that the heats of adsorption of ammonia on zeolites with different chemical composition are sensitive to the modification procedure and the extent of such a modification. An increase in the heats of adsorption was observed on introducing alumina into silica gel and on reducing the framework-aluminum content by direct synthesis or dealumination. This tends to support the view that adsorption calorimetry serves to reliably identify acid sires of varying reactivity.

An approach to the search "acidity-catalytic activity" correlations, described above is based on straightforward concept tacitly implying that the heat of adsorption of the base is directly related to the energy needed for the protonation of hydrocarbon molecules leading to carbocation formation. Quantum-chemical calculations conducted in the last two decades, have shown, however, that the mechanisms of interactions of the adsorbed hydrocarbons with active sites on the walls of zeolites and character of the intermediates resulted from these interactions, depends on many other factors. Among these participation of oxygen framework atoms of in the stabilization of intermediates, the size of cavities and the channels influencing local concentration of reactants and a degree of filling of intracrystaline volume (van Santen and Kramer, 1995). The account of these factors will help to better characterize a role of acidity in activation C—C and C—H bonds in the course of various catalytic transformations.

It appears, however, that a prerequisite to successful correlations lies in the proper choice of the way to evaluate catalytic activity that would reflect the performance of active sites. Reaction-rate constants or initial reaction rates rather than conversion degrees need to be taken as a measure of catalytic activity. In addition, the procedures chosen for calorimetric measurements are expected to be accurate enough to respond to subtle differences in surface chemistry. From results of our work, the appearance of a small number of active sites brings about an increase in the heats of adsorption of ammonia in the order of 5–10 kJ/mol. Such an increment can only be recorded by careful measurements of low heat effects over a wide range of micropore filling.

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