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Distribution of acid-site strengths in hydrogen zeolites and relationship between acidity and catalytic activity

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Abstract

Adsorption microcalorimetry was applied to determine heats of adsorption of NH_3 over hydrogen forms of zeolites with different framework topologies. Differential heats of adsorption of ammonia indicate the presence of acid sites with different energies that characterize the pattern of distribution of acid-site strengths in zeolites. The calorimetric values suggest that in hydrogen faujasites the number of the strong sites with $q > 110$ kJ/mol is negligibly low, whereas in hydrogen mordenites such sites predominate among the acid centers. Dealumination of faujasites results in the appearance of the very strong acid sites with $q > 120$ kJ/mol, and in dealuminized mordenites the sites with $q > 150$ kJ/mol are formed. The plots of the number of very strong sites as a function of Al content are described by the curves with the maximum both for Y zeolites and mordenites. The maximum typically corresponds to composition dealuminized to 50%. The behavior of zeolites in the cracking of octanes, isomerization of *o*-xylene, aromatization of ethylene, disproportionation of ethylbenzene and dehydration of 3-methylbutanol-2 is discussed. These results clearly show that catalytic activity of zeolites in the conversions of hydrocarbons is related to protonic acid sites. The most active acid sites appear to associate with the "isolated" AlO_4 tetrahedra.

Keywords: Calorimetry; NH_3; Zeolites; Acidity spectra; Framework composition; Catalytic activity

1. Introduction

The problem of identification of the active sites in acid catalyzed reactions is closely related to the development of reliable methods suitable to calculate the number and the strength of acid sites. Based on the plots of differential heats of adsorption of ammonia versus coverage, acidity spectra of zeolites can be constructed that indicate distribution of acid sites with different energies and in this way characterize the pattern of distribution of acid-site strengths in zeolites [1]. Unfortunately, this laborious technique is not frequently used to characterize the zeolite materials. In this report, acidity spectra are discussed that were derived from calorimetric measurements of heats of adsorption of ammonia on hydrogen forms of Y zeolites and mordenites with varying degrees of decationization and different Si/Al framework ratios. The measurements of catalytic activity in the cracking of octanes, aromatization of ethylene, disproportionation of ethylbenzene and dehydration of 3-methylbutanol-2 supplement the data on reactivity of acid sites.

2. Experimental

Commercial Na forms of Y zeolite (Si/Al = 2.4) and mordenite (Si/Al = 5) were used as parent materials. To prepare a series of NH_4 zeolites with 25–96% exchange degrees, the samples were equilibrated with a 1N solution of NH_4NO_3 at room temperature. Faujasites, dealuminized to different extents, were

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obtained by treating NaY zeolite with Si/Al = 2.4 with $SiCl_4$ vapor at 220–400°C [2]. Dealuminized mordenites were prepared by refluxing Na or NH_4 forms in the solutions with varying concentration of hydrochloric acid [3].

Differential heats of adsorption of ammonia were measured at 30 and 300°C with a Calvet-type microcalorimeter connected to the adsorption unit. All samples were evacuated at 400°C and at 1×10^{-5} Torr for 40 h and then exposed to NH_3. The procedure of adsorption calorimetric measurements was described earlier [4].

The number of the framework Al atoms in a unit cell (N_{Al}) was calculated from the lattice parameters according to previously reported equations [5,6].

Catalytic properties of zeolites were tested in the cracking of octanes, the disproportionation of ethylbenzene and the dehydration of 3-methylbuthanol-2. Cracking was carried out in a micropulse unit at 400°C. The apparent rate constant (*kK*), calculated according to the Basset and Habgood equation, was taken as a measure of activity. The disproportionation of ethylbenzene and the dehydration of 3-methylbutanol-2 were performed in stainless steel tubular fixed bed reactors at 150–200°C. The mean conversions below a 15% level were used to calculate the rates of these reactions.

3. Results and discussion

3.1. The effect of decationization on distribution of acid sites in decationized zeolites

Fig. 1 shows the plots of differential heats of adsorption of ammonia versus coverage for hydrogen faujasite and mordenite. It can be seen that the plots are described by stepwise curves. This shape is accounted for by the presence of the sites with different strength in the framework. By differentiating these curves, the acidity spectra can be derived, which show more clearly a change in both the number and strength of acid sites caused by modification of zeolites.

Figs. 2 and 3 show the acidity spectra of sodium and hydrogen forms of Y zeolite and mordenite. Earlier we have shown that all sites adsorbing NH_3

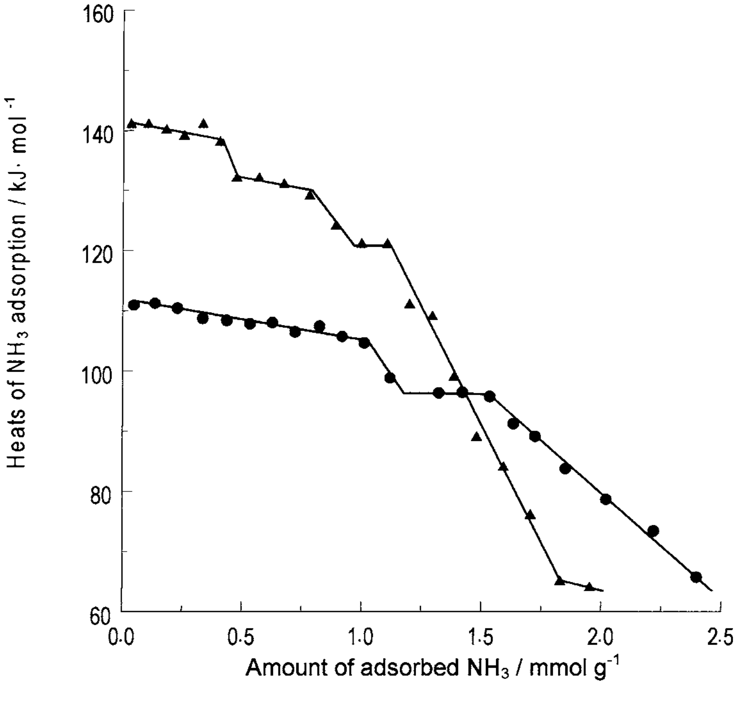

Fig. 1. Heats of adsorption of NH_3 at 300°C as a function of the coverage for $HY_{2.4}$ (lower curve) and $DM_{6.3}$ (upper curve).

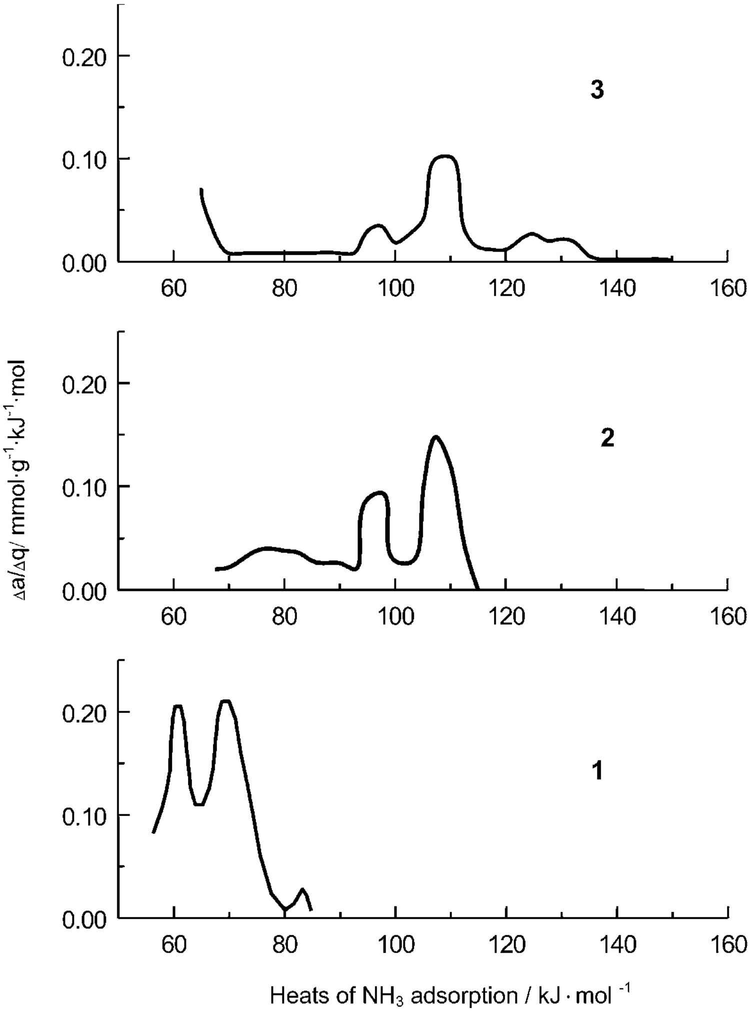

Fig. 2. Acidity spectra for Y zeolites: $NaY_{2.4}$ (1); $HY_{2.4}$ (2); $DY_{6.5}$ (3).

with $q > 90$ kJ/mol can be related to the acid sites [7]. The parent NaY zeolite adsorbs NH_3 with heats lower than 85 kJ/mol. The main portion of ammonia is characterized by heats 75–50 kJ/mol, indicating interaction of Na^+ cations with NH_3 molecules. Heats with $q = 100$–115 kJ/mol appear upon decationization.

Heats of adsorption of ammonia on sodium mordenites vary ranging from 85 to 75 kJ/mol. At the earlier stages of exchange, a small number of acid sites are formed. Accordingly, initial heats of adsorption increase to 145–140 kJ/mol. As the exchange level increases both the number of acid sites and the values of initial heats increase steadily. In the small-port mordenite the sites with $q = 140$ kJ/mol are detected, while the large-port variety shows the presence of acid sites with $q = 150$ and 160 kJ/mol.

3.2. Acidity and catalytic activity of decationized zeolites

Table 1 shows the effect of decationization on the catalytic activity of NH_4Y and NH_4M zeolites in the cracking of *n*-octane and in the disproportionation of ethylbenzene. The rapid increase of the catalytic activity at high exchange degrees is evident.

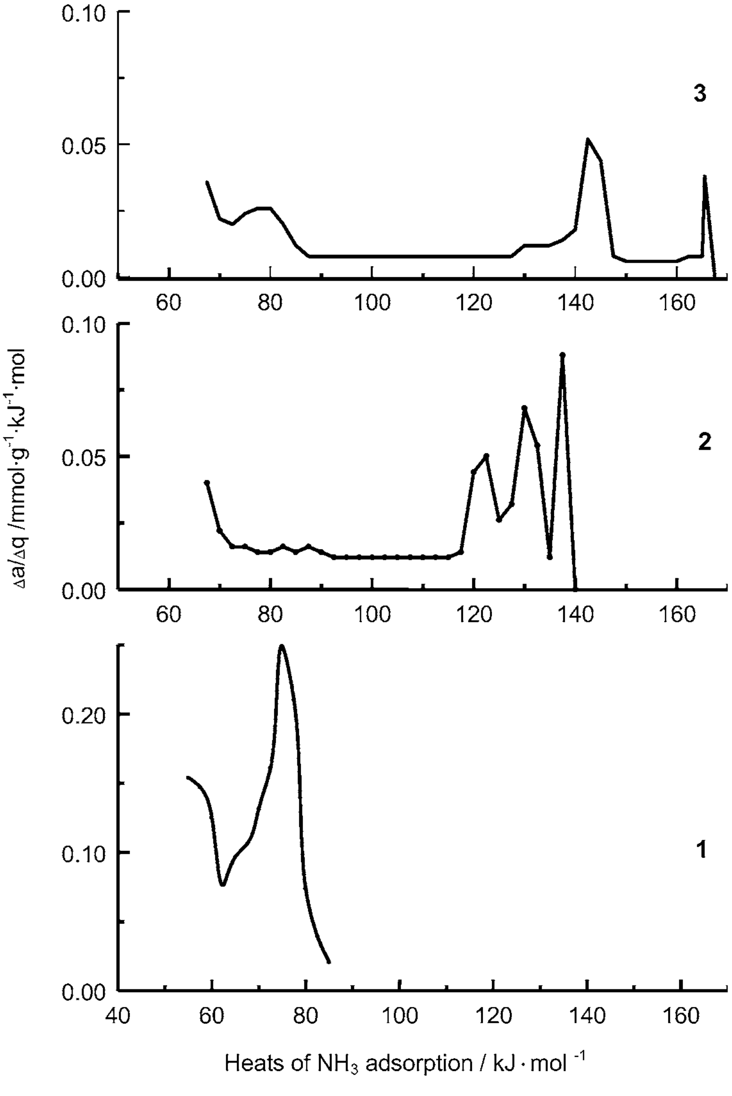

Fig. 3. Acidity spectra for mordenites: NaM_5 (1); HM_5 (2); HM_{10} (3).

This pattern of behavior is especially pronounced for hydrogen faujasites. Low activity appears as the first half of Na^+ ions is removed, but then it increases by nearly an order of magnitude beyond the 50% level. The rapid increase in activity is associated with the appearance of strong acid sites with $q = 110$ kJ/mol in Y zeolites and with $q = 140$–145 kJ/mol in mordenites. This behavior strongly implies the heterogeneity of acid sites. It would be reasonable to assume that the increasing exchange level affects both the number and the strength of acid sites.

The heterogeneity of acid sites can be explained by the screening action of a sodium cation on several AlO_4 tetrahedra. In zeolites each cation is surrounded by several oxygen atoms, and the positive charge can be shared by neighboring AlO_4 tetrahedra. At earlier stages of decationization weakly bound cations are preferably removed. Even when a 50% decationization level is achieved, the number of remaining cations is still enough to neutralize the largest portion of AlO_4 tetrahedra and to weaken OH acidity. At higher degrees of decationization, nearly four to five AlO_4

Table 1
Cracking of *n*-octane and disproportionation of ethylbenzene over ammonium exchanged faujasites and mordenites

Sample (Si/Al, %)	$kK \times 10^8$ (mol/g min Pa) (400°C)	$r \times 10^4$ (mol/g h) (200°C)
NH_4Y, 30	0.03	0.1
NH_4Y, 56	0.07	0.23
NH_4Y, 75	0.47	1.69
NH_4Y, 83	1.66	2.1
NH_4Y, 90	4.3	3.67
NH_4M, 46	38	0.076
NH_4M, 60	50	0.135
NH_4M, 80	70	2.32
NH_4M, 89	78	2.52
NH_4M, 96	110	4.68

tetrahedra in faujasite become free from the neutralizing effect of a neighboring cation after removing one Na^+ ion from an S_{II} site. A very rapid increase in the number of strong acid sites can be expected accordingly.

Comparing catalytic performances of faujasites and mordenites, one can see that mordenites are more active in the cracking of *n*-octane, although 1 g of Y zeolite with a 90% decationization level has twice as much acid sites with $q > 90$ kJ/mol as the mordenite exchanged to the same degree. The reason lies probably in the fact that the sites with $q > 110$ kJ/mol make up ~50% of the mordenite acidity, while in H-faujasite they account for 10% of the acid sites.

According to data presented in Table 1 mordenites and faujasites show similar activities in the disproportionation of ethylbenzene to benzene and diethylbenzenes. It appears that involvement of bulky reactants makes the reaction rates more susceptible to diffusion limitations within the mordenite channels.

3.3. Acid-site strength distribution in dealuminized zeolites

Table 2
Distribution of acid sites in dealuminized faujasites

Sample (Si/Al)	Number of sites (mmol/g) with q (kJ/mol)			
	>90	90–100	100–115	115–130
$NH_4Y_{2.4}$	3	1.2	1.8	
$DY_{6.5}$	1.5	0.3	0.85	0.35
DY_{17}	0.3	0.15		0.15
DY_{42}	0.05			0.05

Changes in the framework Si/Al ratio are accompanied by changes in zeolite acidity. Fig. 2 compares the acidity spectra of the $NH_4Y_{2.4}$ sample and of high-silica faujasite with Si/Al = 6.5 derived from the differential heats of adsorption. Both the acidity spectra and acid-site strength distribution (Table 2) indicate that the initial heats of adsorption on the parent hydrogen form reach a value of ≈112 kJ/mol, whereas the number of sites with $q > 90$ kJ/mol amounts to 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 43. The aluminum deficient Y zeolites have, however, stronger ($q > 120$ kJ/mol) acid sites than the parent zeolites. Increase in the strength of acid sites can be seen up to a limiting value of N_{Al} = 25–30 Al per u.c., after which an increase in acidity strength could not be observed. Consequently, the dependence of the number of strong acid sites ($q \approx 122$–136 kJ/mol) on the aluminum content is described by the curve with a maximum at Si/Al = 5–7, corresponding to 50% dealumination [8].

This behavior resembles that of aluminum deficient mordenites (Fig. 3, Table 3). Dealumination results in the appearance of sites with $q > 150$ kJ/mol, which are absent in the non-dealuminized samples. A decline in the heats of adsorption occurs at lower coverages. Thus, dealumination reduces the density of acid sites but increases their strength. The number of very strong sites formed by dealumination makes up less than 20% of the total acidity. Again, the plot of the number of strong acid sites against the aluminum content is represented by the curve with a maximum corresponding to 50% dealumination.

Table 3
Distribution of acid sites in dealuminized mordenites

Sample (Si/Al)	Number of sites (mmol/g) with q (kJ/mol)				
	>90	90–115	115–145	145–165	>165
NH_4M_5	1.55	0.24	1.31		
$DM_{6.3}$	1.05	0.25	0.49	0.11	0.20
DM_{10}	0.8	0.12	0.4	0.12	0.16
DM_{27}	0.32		0.22	0.1	

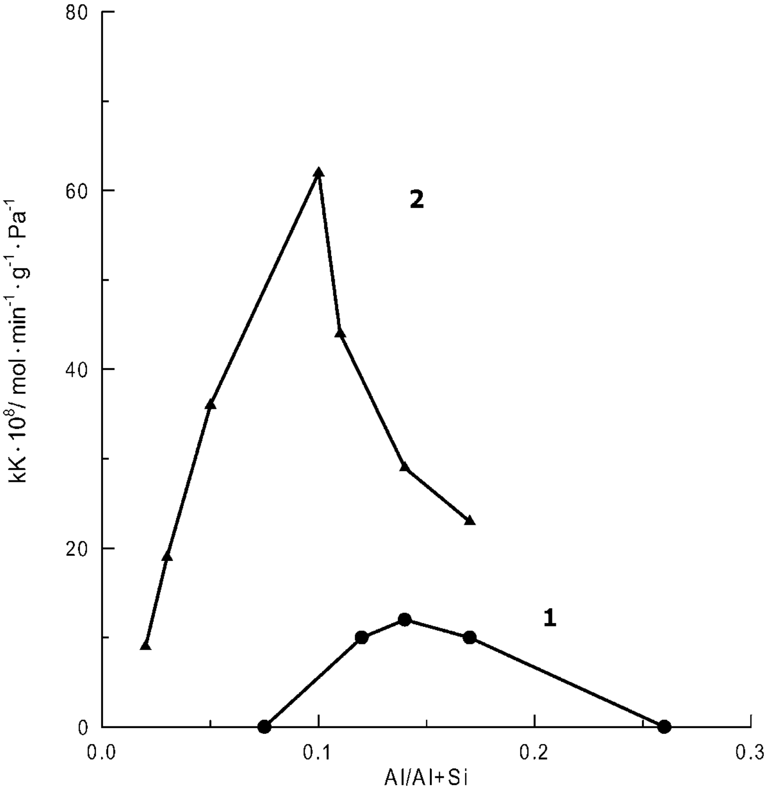

Fig. 4. Catalytic activity of high-silica faujasites (1) and mordenites (2) in the cracking of *n*-octane.

3.4. *The effect of the framework composition on catalytic activity of zeolites*

Fig. 4 shows the relationship between the activity in the cracking of *n*-octane and the Al/(Al + Si) ratio in faujasites and mordenites. As can be seen in the plot, the activity of mordenites and faujasites increases with rising degree of dealumination, passes through a maximum and then decreases upon further dealumination. Both curves follow the course of very strong sites and the maximum in the curves corresponds to the maximum of the strong acidity. The position of the maximum corresponds the values of $\mathrm{Al}/(\mathrm{Al}+\mathrm{Si}) = 0.15$ for faujasites and 0.09 for mordenites. These values are close to the chemical composition of the frameworks containing the highest number of "isolated" aluminum atoms. The frameworks with these Si/Al ratios are typical for faujasites and mordenites with the extent of dealumination near 50%. The coincidence of the position of maximum on the curves relating strong acidity and activity to the framework composition, implies an important catalytic role of acid sites associated with the "isolated" aluminum atoms.

Fig. 5 demonstrates data on activity of dealuminized faujasites in the cracking of *iso*-octane and the disproportionation of ethylbenzene. In these reactions the plots of activity against aluminum content are described by the curves with maxima. Activities reach a maximum when about 25 Al per u.c. remains in the framework. This shows that the activity of faujasites increases 8–10 times as the N_{Al} values decrease from 50 to 60 for the parent hydrogen forms to 20–25 Al per u.c. for the sample with a dealumination degree of 50%.

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 activity–composition profile depends on reactivity of the organic compound transformed. Fig. 6 shows the effect of the aluminum content on the rate of formation

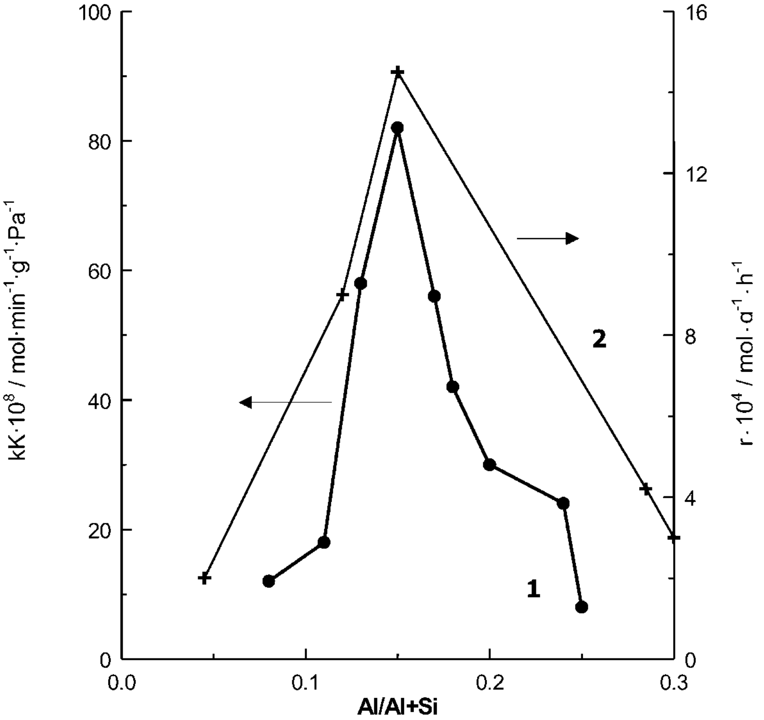

Fig. 5. Catalytic activity of high-silica faujasites in the cracking of *iso*-octane (1) and in the disproportionation of ethylbenzene (2).

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 = 7. It is accepted that the catalytic dehydration of this alcohol follows the mechanism of α-elimination to produce 2-methylbutene-1. The reaction involves a step in which one OH-group and eliminated hydrogen atom of the alcohol are adsorbed on an acid and basic sites of the catalyst. In mordenites Brönsted sites act as acid centers, while oxygen lattice atoms, play the role of basic sites.

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 dealuminized to 15%. On the other hand, the highest activity in the disproportionation of ethylbenzene exhibited mordenites with the dealumination degree of 60% (Fig. 6). 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.

As follows from the data outlined above, the activity of mordenites increases only three to four times as an appropriate portion of aluminum is extracted. A stronger response of faujasites to dealumination can be explained by the fact that initial samples of hydrogen mordenites contain “isolated” aluminum atoms, whereas for faujasites at least a 10% extent of dealumination is needed to form “isolated”AlO_4 tetrahedra.

The reason for the enhanced catalytic activity of dealuminized zeolites has been a subject of discussion with indirect arguments in favor of either an increase in acid-site strength [1] or an easier accessibility of active sites [9]. Analysis of adsorption isotherms of benzene indicates that acid treatment of mordenite increases the volume of micropores [10]. However, treatment faujasites with $SiCl_4$ leaves the pore structure of dealuminized products intact but generates the acid sites with an increased acid strength [8]. Similar pattern of dependence of catalytic activity on dealumination extent observed for faujasites and

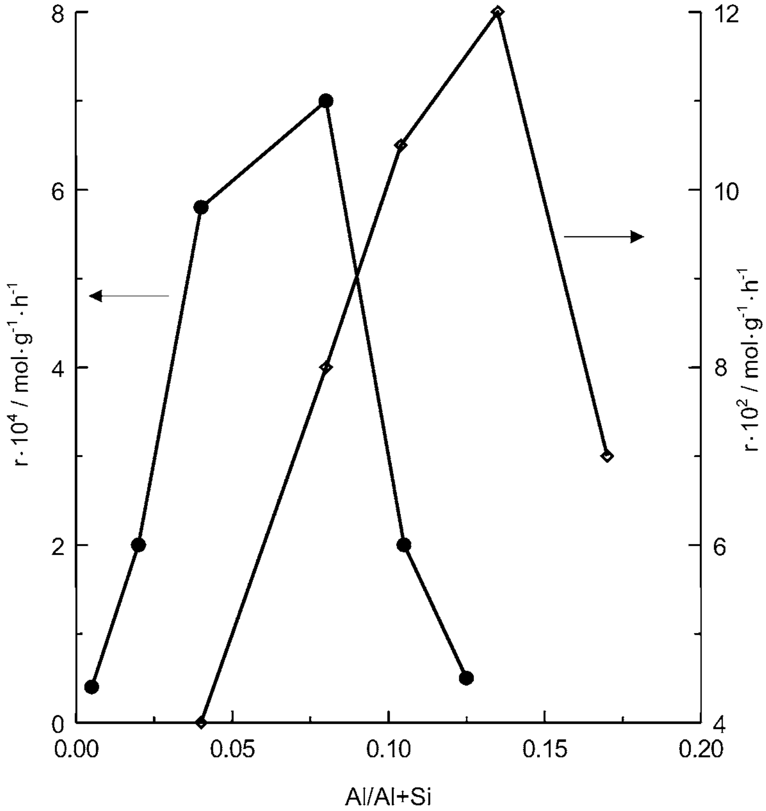

Fig. 6. Catalytic activity of high-silica mordenites in the disproportionation of ethylbenzene (left curve) and in the dehydration of 3-methylbutanol-2 (right curve).

mordenites suggests the primary role of acidity in catalytic properties of aluminum deficient zeolites.

4. Conclusions

1. Dealumination of faujasites generates very strong sites with $q > 120$ kJ/mol and extraction of Al from mordenites creates acid sites with $q > 150$ kJ/mol. The sites with such acid strengths can not be detected in the initial hydrogen zeolites. The plots of the number of very strong sites as a function of Al content are described by the curves with the maximum both for Y zeolites and mordenites. The maximum typically corresponds to compositions dealuminized to 50%.
2. The plots of the catalytic activity versus the number of Al atoms in the unit cell of Y zeolites are represented by the curves with the maximum corresponding to the 50% dealumination level. The position of the maximum for mordenites depends on the reactivity of the feed molecules. The higher the reactivity the lower level of dealumination is needed for the reaction to attain the maximum rate.
3. These results clearly show that catalytic activity of zeolites in the conversions of hydrocarbons is related to protonic acid sites. The most active acid sites appears to associate with the "isolated" AlO_4 tetrahedra.

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