Comparison of the Acidity/Site Energy Distribution in Catalytically Important Zeolites

The most commonly used zeolites in various catalytic reactions are HY, rare-earth-exchanged X- and Y-type zeolites, H-mordenite (HM), L-type zeolites, and the pentasil high silica (ZSM-5, ZSM-8 and ZSM-11) zeolites. These zeolites differ (1) very widely in their Si/Al ratios and also in their channel structures and diameters. The structural Al (i.e., tetrahedral Al) is responsible for the presence of high-strength acid sites in the zeolites (2, 3). Because of their different Al contents and structures, zeolites differ widely in their acidity and consequently in their catalytic properties. In the present investigation the acidity (strong acid sites) and acid strength distributions of catalytically important zeolites HY, CeNaY, CeNaX, HKL, HM, H-ZSM-5, H-ZSM-8, and H-ZSM-11 have been compared by measuring step-wise thermal desorption of pyridine from the zeolites using the GC adsorption/desorption technique (4).

The chemical compositions of the HY, CeNaY, CeNaX, HKL, HM, H-ZSM-5, H-ZSM-8, and H-ZSM-11 zeolites are given in Table 1.

Samples of the zeolites CeNaY (Ce^{3+} exchange: 72%) and CeNaX (Ce^{3+} exchange: 90%) were provided by Professor J. Weitkamp (University of Stuttgart, FRG). The zeolite HY was obtained by deammoniating NH$_4$Y (Si/Al = 2.4, Na/Al = 0.08) packed in a stainless-steel tube (6 mm o.d., zeolite bed 4 mm diameter and 10 mm long) in a flow of nitrogen (10 cm^3 min^{-1}) at 623 K for 4 h.

The HKL zeolite was prepared by exchanging KL (Laposil 2000 series, obtained from Laporte, UK) with 0.1 M HCl. The zeolite HM (Zeolon 900H), in the form of 20- to 50-mesh aggregates, was obtained from Norton Co. (U.S.A.). The H-ZSM-5 zeolite was obtained by deammoniating NH$_4$-ZSM-5 (Si/Al = 31.1, Na/Al = 0.01) at 773 K in a flow of nitrogen (10 cm^3 min^{-1}) passing through the zeolite bed (4 × 4 mm) for 4 h. The H-ZSM-11 zeolite was obtained by calcining the NH$_4$ · TBA-ZSM-11 in air at 773 K for 12 h. The preparation and characterization of the NH$_4$-ZSM-5 (5), NH$_4$ · TBA-ZSM-11 (6), and H-ZSM-8 (7) zeolites have been described earlier.

Before measuring their acidity distribution, the zeolites CeNaY, CeNaX, NH$_4$Y, HKL, and HM were calcined in situ at 623 K for 4 h in a flow of nitrogen (10 cm^3 min^{-1}) passing through the zeolite bed. The in situ calcination of the pentasil zeolites was done at 673 K in a flow of nitrogen (10 cm^3 min^{-1}) for 1 h. In the calcination of all the zeolites, the temperature was raised at a rate of 10 K min^{-1}.

The acid strength distribution on the zeolites was measured by studying the stepwise thermal desorption (STD) of pyridine and also by determining the chemisorption of pyridine at different temperatures, using GC techniques (4, 8). The procedures for the measurement of chemisorption and STD of pyridine and also for evaluating the chemisorption data from STD have been given earlier (4, 7–9).

Comparisons of the acidity distribution [viz., the temperature dependence of the chemisorption of pyridine and the site energy (or acid strength) distribution, obtained by the STD of pyridine] on the low and high silica zeolites are shown in Figs. 1 and 2. The strong acid sites (measured in

TABLE 1

Data on the Strong Acid Sites of the Zeolites

Zeolite	Si/Al ratio	C_{Al} (mmol g^{-1})	C_{Na} (mmol g^{-1})	Chemisorption (at 623 K) q_i (mmol g^{-1})		No. of strong acid sites per Al*,[a] $\left[\dfrac{q_{i(Py\ at\ 623K)}}{(C_{Al}-C_{Na})^b}\right]$
				Pyridine	2,6-DMPy	
HY	2.4	3.59	0.290	0.78	0.80	0.24
CeNaY	2.4	3.13	0.880	0.44	0.47	0.20
CeNaX	1.3	4.37	0.440	0.51	0.53	0.13
HKL	3.0	3.63	0.190	0.22	0.20	0.06
HM	6.6	1.97	0.060	0.77	0.63	0.40
H-ZSM-5	31.1	0.51	0.005	0.25	—	0.50
H-ZSM-8	29.4	0.53	0.020	0.31	—	0.61
H-ZSM-11	35.3	0.45	0.000	0.07	—	0.16

[a] Al* indicates active Al (i.e., the Al not blocked by Na$^+$ cations).

[b] C_{Al} and C_{Na} are concentrations of Al and Na, respectively, in the zeolites.

terms of the amount of pyriding chemisorbed at 623 K) on the zeolites are compared in Table 1. The data on the chemisorption of 2,6-dimethylpyridine (2,6-DMPy) in the zeolites at 623 K as well as those on the concentrations of structural Al$^-$ and of Na cations in the zeolites are also included in Table 1.

Pyridine is chemisorbed on both the protonic and the Lewis acid sites, whereas, 2,6-DMPy is expected to be chemisorbed preferentially on protonic acid sites (10, 11). A comparison of the chemisorption data for pyridine and 2,6-DMPy at 623 K (Table 1) indicates that the HY, CeNaY, and CeNaX zeolites contain only protonic acid sites (a somewhat higher chemisorption for 2,6-DMPy is expected mostly due to its higher basicity), whereas the HKL and HM zeolites contain both the protonic and the Lewis acid sites.

Chemisorption of 2,6-DMPy in the pentasil zeolites could not be measured because of its slow diffusion in the zeolites. However, earlier studies on H-ZSM-5 (9) and H-ZSM-8 (7) zeolites have indicated that the chemisorption of pyridine on these zeolites essentially measures the protonic acid sites, as the Lewis acid sites are not easily accessible to pyridine.

The decrease in the chemisorption of pyridine with increase in the temperature for all the zeolites (Figs. 1a and 2a) reveals that the pyridine chemisorption sites (which are expected to be mostly the acid sites) on all the zeolites are not of equal strengths, thus indicating the presence of site energy (or acid strength) distribution on the zeolites. The site energy distribution on the zeolites is clearly shown in Figs. 1b and 2b. The columns in these figures show the distribution of the sites involved in the chemisorption/desorption of pyridine. Each column of the site energy distribution represents the number of sites measured in terms of pyridine desorbed in the corresponding temperature step. The strength of these sites is expressed in terms of the desorption temperature of pyridine, T_d, which lies in the range in which chemisorbed pyridine is desorbed.

A comparison of the chemisorption vs temperature curves and the site energy distributions for the zeolites shows that the zeolites differ from each other markedly in their acidity and acidity distribution.

The acidity of the zeolites is attributed to the presence of tetrahedral Al in their structures (2, 3). The total (or maximum) number of acid sites expected to be present in a
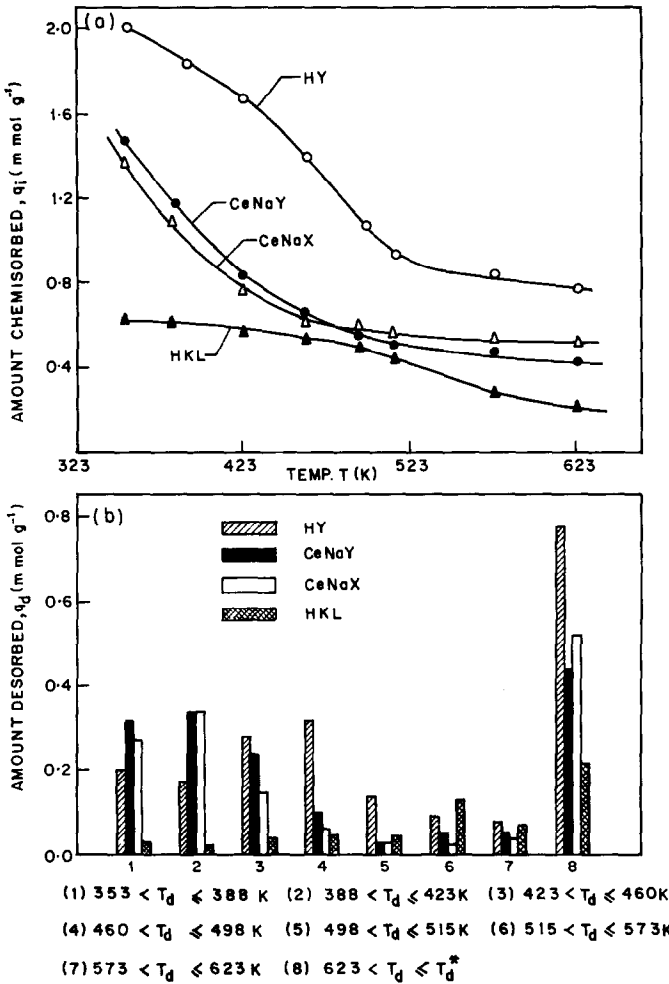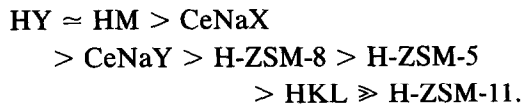
FIG. 1. Acidity/site energy distribution on the low silica zeolites.

zeolite is, therefore, equivalent to the number of structural Al. However, in partially cation-exchanged zeolites (i.e., those containing Na$^+$ or other alkali cations), the maximum number of acid sites is expected to be equal (for H$^+$-exchanged zeolites) or proportional (for Ce^{+3}-exchanged zeolites) to the number of active Al (Al*) [concentration of Al* = concentration of Al (C_{Al}) − concentration of Na$^+$ (C_{Na})]. Because of their different Al contents (Table 1), the zeolites are expected to differ from each other widely in their total numbers of acid sites. These zeolites could be arranged in the order of their total acidity, as follows:

CeNaX > HKL > HY > CeNaY > HM
> H-ZSM-8 > H-ZSM-5 > H-ZSM-11.
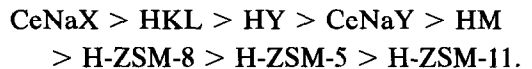
The above order is, however, changed when the zeolites are arranged in the order of their strong acid sites (i.e., those acid sites which can chemisorb pyridine at 623 K), as follows:

HY ≃ HM > CeNaX
> CeNaY > H-ZSM-8 > H-ZSM-5
> HKL ≫ H-ZSM-11.

The order is changed further when the zeolites are arranged in the order of their num-
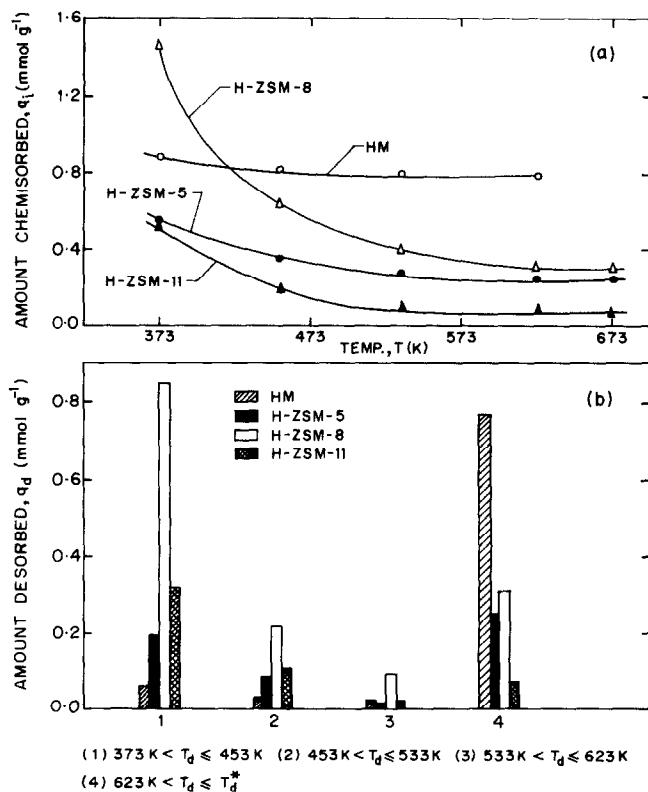
FIG. 2. Acidity/site energy distribution on the high silica zeolites.

ber of strong acid sites per active Al [i.e., $q_{i(\text{pyridine at }623\,\text{K})}/(C_{Al} - C_{Na})$], as follows:

H-ZSM-8 > H-ZSM-5 > HM > HY
> CeNaY > H-ZSM-11 > CeNaX > HKL.

A graphic presentation of the dependence of strong acid sites per active Al of the zeolites on their Si/Al ratio is given in Fig. 3. The data show a general trend of increase in the number of strong acid sites per active Al with an increase in the Si/Al ratio of the zeolites. For H-ZSM-5 zeolite, the strong acid sites (6) or the active sites (12) per active Al were found to increase with an increase in the Si/Al ratio up to 31.1 and to level off thereafter. These observations reveal that the acid strength or activity of acid sites is decreased when the framework Al^- are close enough to interact among themselves.

From the comparison of the acidity data on the pentasil zeolites, which have similar Si/Al ratios (Table 1), the following order in the strong acid sites and also in the number of strong acid sites per active Al of the zeolites is observed:

H-ZSM-8 > H-ZSM-5 ≫ H-ZSM-11.

This is consistent with the observations made earlier on the acidity of H-ZSM-5 and H-ZSM-11 zeolites, measured by TPD of ammonia (13) and by microcalometric measurement of heats of adsorption of ammonia (14, 15).

The acid strength distributions on the zeolites and the observed differences in strong acid sites, acidity distributions, and numbers of strong acid sites per active Al of the zeolites are most probably attributable to the presence of their structural Al^- in
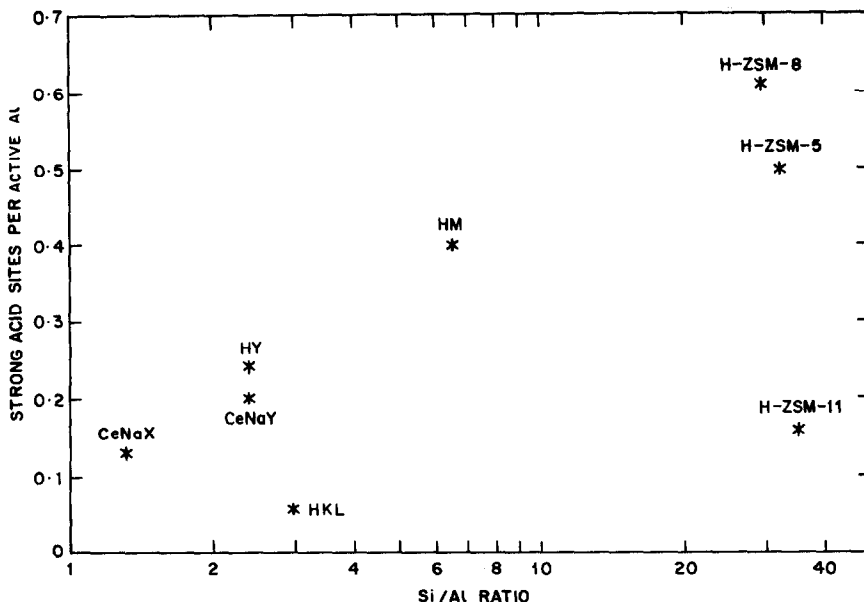
FIG. 3. Dependence of strong acid sites per active Al of the zeolites on their Si/Al ratio.

different environments/configurations (or topology), depending on their Si/Al ratios, cations (such as H^+, Ce^{3+}, Na^+, etc., and their degrees of exchange), and channel structures. The interactions of the structural Al^- within themselves and/or with the cations (or also with the adsorbed species) are expected to modify the acidity/acidity distribution of the zeolite. However, in the case of dilute siliceous zeolites (i.e., very high silica zeolites), the quality of Brønsted Al sites is expected to be the same (3) because of a wide separation in the framework Al^- from each other.

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