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NOTES

Characterization of Dealuminated Hydrogen Mordenites by Thermometric Titration

The acidity of zeolites has been frequently characterized by using *n*-butylamine adsorption but serious doubt has been raised as to whether equilibrium is established between the acid sites inside the zeolite pore and the adsorbed *n*-butylamine molecules, particularly in the case of smaller pore zeolites like mordenite (*1–3*). If this is so, the Benesi method using colored indicators and calorimetric titration using *n*-butylamine as base for the characterization of acid sites of mordenite are not satisfactory. Recently Bezman (*4*) found that calorimetric titration was not satisfactory for the characterization of the acidity of hydrogen mordenite and concluded that *n*-butylamine molecules block the entrance to the pores of HM. Our previous results (*5*) supported this conclusion but preliminary results with a dealuminated hydrogen mordenite (deal-HM) showed that the method seemed to be satisfactory in this particular case.

The aim of the present work has been to measure the acidity of dealuminated hydrogen mordenites having SiO_2/Al_2O_3 ratio 9–26 with a view to assessing the validity of the *n*-butylamine titration method for these catalysts.

The starting materials were NaM and HM obtained from Norton Company with the following unit cell compositions NaM: $Na_{5.14}H_{1.24}Al_{6.38}Si_{41.62}O_{96}$ and HM: $Na_{0.31}H_{5.58}Al_{5.89}Si_{42.11}O_{96}$.

The dealuminated mordenites listed in Table 1 were prepared by treating the specified starting material with HCl at its boiling temperature. The zeolite samples were preheated overnight at 423 K in air, evacuated while increasing the temperature slowly to 773 K after which oxygen was admitted overnight, evacuated for 2 hr at 773 K, and finally cooled to room temperature.

The calorimetric assembly consisted of a reaction vessel with a quartz thermometer (Hewlett–Packard 2804A), a magnetic stirrer and a microburette and was insulated with a thick cork. It was maintained in a thermostat at 303 ± 0.001 K.

An accurately known amount of activated zeolite (1–2 g) was placed in the calorimetric reaction vessel and covered with 25 cm^3 of benzene which had been distilled and dried over sodium wire. The transfer of the zeolite to the reaction vessel and the immersion in benzene was effected in a dry bag under ntirogen. The contents of the calorimeter were allowed to equilibrate with the thermostat at 303 K for about 1 hr before the titration. The titration was carried out by stepwise addition of aliquots (~0.02 meq/g) of standardized (0.852 *M*) *n*-butylamine solution in dried benzene. The temperature was recorded every 15 or 30 sec. The temperature rise due to the addition of an aliquot of *n*-butylamine solution was calculated (*6*). The addition of *n*-butylamine was repeated until no temperature rise due to heat of adsorption could be observed. No temperature change was observed when a blank titration was carried out in the absence of zeolite.

The initial and final heat capacity of the calorimeter system was measured from the temperature rise due to the passage of a dc electric current through a heater immersed in the calorimetric reaction vessel.

The calorimetric titration of a solid cata-

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TABLE 1

Preparation and Characterization of Dealuminated Mordenite

Sample	SiO_2/Al_2O_3 ratio	Starting material	Conc. of HCl (mol dm^{-3})	Duration of HCl treatment (hr)	Cell composition
HM	(9.39)	NaM	1.5	4	$Na_{0.31}H_{5.04}Al_{5.35}Si_{42.65}O_{96}$
HM	(14.81)	NaM	1.5	5	$Na_{0.06}H_{3.48}Al_{3.54}Si_{44.46}O_{96}$
HM	(17.91)	HM	10	2	$Na_{0.04}H_{2.92}Al_{2.96}Si_{45.04}O_{96}$
HM	(25.72)	HM	10	6	$Na_{0.07}H_{2.03}Al_{2.10}Si_{45.90}O_{96}$

lyst against a standard reagent provides an evaluation of the heat of adsorption from a knowledge of the heat capacity of the calorimeter system and the temperature rise resulting from the addition of reagent to the calorimeter. The heat evolved represents an average heat of adsorption for the amount of reagent added. The titration results are thus obtained as average differential heats of adsorption for successive additions of reagent. It should be mentioned that the titers determined from the calorimetric titration include a certain amount of weakly, possibly physically, adsorbed base and furthermore that the determined heat of adsorption is subject to resolution errors related to titrant aliquot size and the sensitivity of the temperature measurement device (*4*).

The results of the calorimetric titration using nonaqueous *n*-butylamine are shown in Fig. 1. It shows that the dealuminated HMs with SiO_2/Al_2O_3 ratios 9.39, 14.81, 17.91, and 25.72 require *n*-butylamine titers 0.42, 0.71, 0.63, and 0.59 meq/g, respectively. Not only the acidity but also the distribution of acid strength may also be derived from the shapes of the titration plots (*3*). Such acid strength distribution is shown in Fig. 1 and Table 2.

The total number of acid sites was calculated from the chemical analysis of the zeolite assuming that all hydrogen atoms associated with $[AlO_4]^-$ act as Brønsted acid sites. During activation of the zeolite sample some of the Brønsted sites are converted into Lewis acid sites depending on the temperature of activation according to the dehydroxylation reaction. An infrared study (*7*) showed that under the experimental conditions prevailing in these experiments the ratios of Brønsted-/Lewis-acid sites are 3.92, 2.58, 2.04, and 1.73 for the samples having SiO_2/Al_2O_3 ratios 9.39, 14.81, 17.91, and 25.72, respectively. The calculated and the calorimetrically determined number of acid sites together with literature values are tabulated in Table 3. It shows that except in the case of the least dealuminated sample (SiO_2/Al_2O_3 = 9.39) the results are in good agreement with the calculated acid sites and the literature values.

TABLE 2

Acidity Distribution of Dealuminated HM Determined by Calorimetry

Sample	Acidity[a] (meq/g)					
	A_1	A_2	A_3	A_4	A_5	Total
1			0.03	0.02	0.37	0.42
2		0.03	0.005	0.075	0.60	0.71
3		0.04	0.03	0.14	0.42	0.63
4	0.03	0.005	—	0.075	0.48	0.59

[a] Acidity groups are defined by heat of adsorption (kJ mol^{-1}) included between limits as follows: A_1: $118 \leq -\Delta Q$; A_2: $110 \leq -\Delta Q < 118$; A_3: $90 \leq -\Delta Q < 110$; A_4: $40 \leq -\Delta Q < 90$; A_5: $-\Delta Q < 40$.

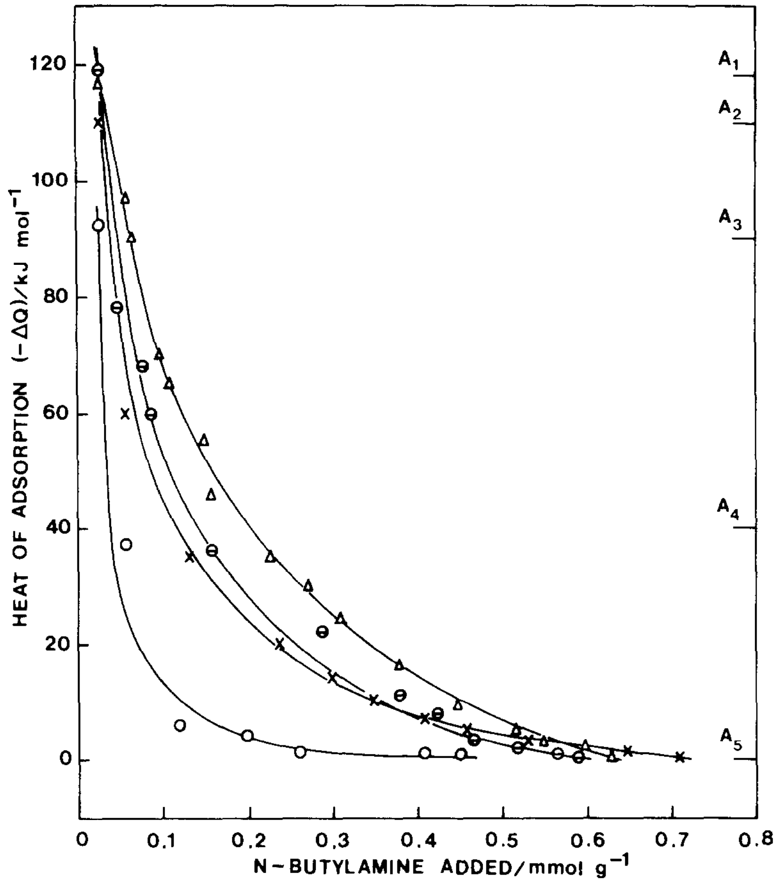

FIG. 1. Calorimetric titrations with *n*-butylamine solution. ○ (9.39), × (14.81), △ (17.91), and ⊖ (25.72). Numbers in brackets indicate SiO_2/Al_2O_3 ratios of mordenites.

The nonaqueous *n*-butylamine calorimetric titration for the characterization of surface acidity is very straightforward but it was found to be unsatisfactory (*5*) for the determination of acid sites of Norton hydrogen mordenite. Mordenites consist of tubular channels having a free diameter of 0.66 nm interconnected by smaller pockets with a free diameter of 0.28 nm (*8*). It is possible for *n*-butylamine molecules with a critical diameter (σ) of 0.44 nm to enter the mordenite pores and interact with acid sites but due to the fact that *n*-butylamine is a relatively strong base ($pK_b = 3.2$) its molecules possibly react with acid sites at the entrance or very close to the entrance of the channels, blocking the mouth of the channel and preventing other *n*-butylamine molecules entering the channel and interacting with other sites inside the pore (*5*). This difficulty may be partly overcome by increasing the adsorption temperature (*9*).

In the case of dealuminated H mordenites, depending on the degree of dealumination, some of the neighboring channels of the lattice of mordenite are connected as a result of the removal of aluminum, in which case larger pores are formed by breakdown of the side walls of the niches (small channels) (*10*). The formation of these new larger pores due to dealumination allows the *n*-butylamine molecules ac-

TABLE 3

Acidity of Mordenites

SiO_2/Al_2O_3 ratio	Pretreatment	Acidity (meq/g)			
		Calculated	Calor.Titrn.	Literature	Reference
7.08	Unknown			1.55[a]	(*11*)
8.65	Unknown			1.69[b]	(*12*)
9.39	773 K *in vacuo*	1.46	0.42		this work
14.75	Unknown			0.76[a]	(*11*)
14.81	773 K *in vacuo*	0.95	0.71		this work
17.91	773 K *in vacuo*	0.76	0.61	0.52[c]	this work
23.50	Unknown			0.96[b]	(*12*)
25.72	773 K *in vacuo*	0.49	0.59		this work
38.30	Unknown			0.37[b]	(*12*)
38.94	Unknown			0.25[a]	(*11*)

[a] Catalysts containing 0.5% Pd; acidity measured by NH_3 adsorption at 700 K at 8 mm NH_3 pressure.

[b] Acidity measured by NH_3 adsorption at the arbitrary conditions of 523 K and 11.2 Torr.

[c] Acidity measured by using colored indicators, calorimetric result of this sample quoted from previous paper (*5*).

cess to acid sites inside the pores. The results of adsorption of decalin on HM, which was found to increase with increase of the SiO_2/Al_2O_3 ratio (*11*), support this fact.

The uptake of *n*-butylamine by mordenite samples depends on the accessibility of amine molecules to the mordenite pore and the total number of acid sites. Dealumination causes an increase in the pore size of mordenite as well as a decrease in the total number of acid sites. It is not certain how much dealumination is critical for the access of *n*-butylamine molecules. It has been mentioned that except for the least deal-HM the results are in good agreement with the calculated acid sites and literature values. It is possible that in the case of HM and only slightly dealuminated HMs *n*-butylamine molecules cannot penetrate mordenite pores so as to react with all the acid sites and block the entrance to the zeolite pore (*4, 5*). For other samples (SiO_2/Al_2O_3 ratio ≥ 15) the pore sizes are possibly sufficiently large to allow *n*-butylamine molecules to penetrate. Therefore, the calorimetric titration using *n*-butylamine appears satisfactory for deal-HM having high SiO_2/Al_2O_3 ratios.

Previous authors have found that dealumination causes a decrease in total acidity (*11, 12*) almost linearly with the aluminium content of the mordenite with a simultaneous increase in the strength of remaining acid sites (*13*). The acid strength distribution (Fig. 1 and Table 2) shows that the number of strong acid sites (groups A_{1-4}: $\Delta Q \geq 40$ kJ mol^{-1}) increases with increase of the SiO_2/Al_2O_3 ratio through a maximum at 18. This is in good agreement with Kiovsky *et al.* (*13*) who found that the number of strong acid sites increases with increase of the SiO_2/Al_2O_3 ratio up to 16.

In conclusion the simple nonaqueous *n*-butylamine titration appears to be suitable for determining the acidity of dealuminated HMs having high SiO_2/Al_2O_3 ratios.

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