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Characterization of Acidic Zeolites by Thermometric Titration

In thermometric titrations of acidic, decationized zeolites with *n*-butylamine, pore volume limitations restricted the titer of activated NH_4–Y to approximately 80% of its ion exchange capacity, whereas neutralization of both Brönsted and Lewis sites caused activated, ultrastable Y to exhibit a titer of 160% of its precursor's ion exchange capacity. Because of pore mouth blockage by strongly adsorbed base, activated large-port mordenite exhibited only a very small titer. In titrations with the weak, sterically hindered base, 2,6-dimethylpyridine, activated ultrastable Y exhibited approximately twice the titer of activated NH_4–Y.

Because of its simplicity, the nonaqueous titration using organic bases in conjunction with color indicators that nominally respond to either proton-donating or carbonium ion-forming ability has frequently been used to characterize zeolite acidity (*1*). The commonly used indicators are as large or larger than the pores of most zeolites, thus the interpretation of titration results is difficult and artifacts are likely. Two recent papers, in fact, specifically address the influence of base and indicator size on titrimetric determinations of zeolite acidity (*2, 3*).

In a thermometric titration, the enthalpy of the titration reaction itself serves as the indicator, thus the technique would seem to be of great potential value not only in general studies of zeolite acidity but particularly in assessments of indicator errors. However, the method has seldom been applied to the study of solid acids and apparently never to the characterization of zeolites (*4, 5*). It is the intent of this note to present some initial results of thermometric titrations of several types of catalytically active acidic zeolites, and to show that even in the absence of chemical indicators, anomalous results associated with pore blockage and steric effects can be encountered.

EXPERIMENTAL PROCEDURES

Zeolite samples were activated in dry air for 1 to 2 h at 500°C prior to use and included H–M(500), large-port H–Mordenite derived from H–Zeolon (Norton Company); Y-62(500), "H–Y" derived from NH_4–Y (Linde LZ-Y62); and Y-82(500), "H–Y" derived from low-sodium, ammonium-exchanged, stabilized Y (Linde LZ-Y82). Relevant data concerning the chemical compositions and pore volumes of the materials are given in Table 1.

The bases that were used as titrants were high-purity materials from various commercial suppliers and were used without additional purification. The benzene used to prepare zeolite slurries and titrant solutions was dried over 5A molecular sieve.

The titrations were conducted in a Dewar jar that was equipped with a magnetic stirrer, a thermocouple connected to a recorder, and a calibration heater consisting of a wire-wound resistor immersed in a glass tube of silicone fluid. The titration procedure consisted of rapidly weighing a 7.0-g portion of zeolite into the jar, adding 80 ml dry benzene, sealing the jar with a Teflon-coated stopper, and stirring until thermal equilibrium was achieved. Aliquots of titrant were then added from a microburet at 15- to 25-min intervals until heat evolution ceased; dissipation of a known amount of electrical energy in the heater

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TABLE 1

Zeolites Characterized by Thermometric Titration

Sample	Chemical composition			
	Na_2O/Al_2O_3	SiO_2/Al_2O_3	Maximum Brönsted acidity[b] (mmole/g)	Pore volume[a]
Y-62(500)	0.18	4.9	4.8	0.32
Y-82(500)	0.02	6.2	1.6	0.25
H-M(500)	<0.01	12	2.4	0.15

[a] Determined by measurement of oxygen adsorption at −183°C and 100 Torr.

[b] Ion exchange capacity not satisfied by alkali metal cation.

permitted determination of the heat capacity of the system. As per the work of Bakshi and Gavalas (*5*), titration data were converted to plots of quasi-differential heat of base adsorption versus cumulative base dosage, from which sample titers were defined as the base dosages beyond which no enthalpy changes occurred. While this is both a convenient and reasonable definition, it should be noted that such titers include a certain amount of weakly, possibly physically, adsorbed base and furthermore are subject to resolution errors related to titrant aliquot size and the sensitivity of the temperature measurement device.

RESULTS AND DISCUSSION

The results of titrations with *n*-butylamine, a small, strong base ($pK_B = 3.4$), are depicted in Fig. 1 from which it is apparent that both Y zeolites show significant titers. Of particular interest is that the Y-62(500) has a titer of only 80% of its maximum Brönsted acidity, i.e., available ion exchange capacity, while the Y-82(500) possesses a titer of 160% of its possible Brönsted acidity. Assuming that titrant is adsorbed as a liquid exhibiting normal density (10 meq/ml), available pore volume should limit the titers of Y-62(500) and Y-82(500) to 3.2 and 2.5 meq/g, respectively. These limits are found in both cases; the "excess" base consumption of the Y-82(500) (that beyond the computed possible protonic acidity) most reasonably being attributed to interaction of the base with Lewis sites.

In contrast to the Y-type zeolites, the mordenite, which possessed a potential Brönsted acidity of 2.1 meq/g and a pore volume of 0.15 ml/g, exhibited only a very small titer. This behavior is essentially identical to that reported for titrations using color indicators (*2*), thus it is reasonable to attribute the effect to a pore-closure phenomenon such as strong adsorption of either base or indicator (if used) at the entrances to the effectively one-dimensional channel system.

In an attempt to elucidate the types of interactions that were occurring during the

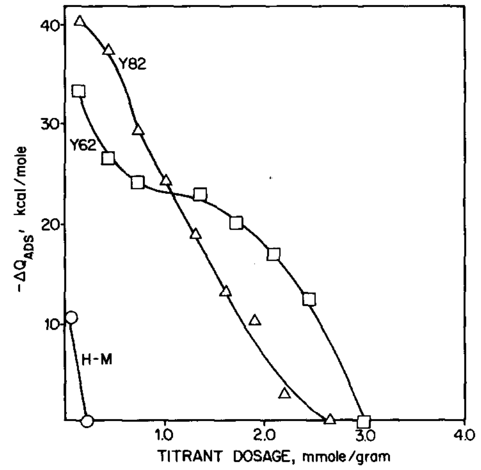

FIG. 1. Thermometric titrations with *n*-butylamine.

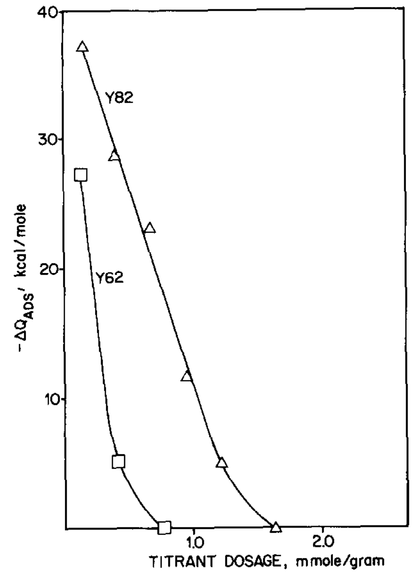

FIG. 2. Thermometric titrations with 2,6-dimethylpyridine.

titrations, portions of both Y-type zeolites were titrated with 2,6-dimethylpyridine, a sterically hindered base that has been suggested for the selective determination of Brönsted acidity (*6*). The results of typical experiments are given in Fig. 2; of particular note is that the Y-62(500) exhibited only a very small titer despite infrared spectral evidence that such a material should possess significant Brönsted acidity (*7*). In contrast, the Y-82(500) interacted strongly with the base and displayed a titer equivalent to its calculated maximum protonic acidity. A satisfactory rationale for these differences in response cannot yet be given; but it should be noted that in addition to possessing a sterically hindered nitrogen, 2,6-diethylpyridine is also a fairly weak base ($pK_B = 7.3$).

From the data that have been presented, it is evident that the thermometric titration is a useful technique for examining the acidic character of at least certain types of zeolites, and is of particular value in resolving problems such as the effects of bulky indicator molecules on such measurements. Specifically, it was shown that pore closure due to strong adsorption of base can hinder the titration of tubular pore zeolites such as mordenite, and that even during the titration of Y-type zeolites the choice of titrant must be made carefully.

While only total acid concentration results have been discussed, the shapes of the titration plots imply that the technique may prove useful in characterizing strength distributions as well. Measurements of this type are critically dependent on rapid equilibration of the base with the various-strength acid sites; in view of evidence that such equilibration may not be facile (*8*, *9*), caution must be exercised in establishing thermometric titration procedures for such determinations.

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