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A Comparison of CaO, Beta, and a Dealuminated Y by Ammonia TPD and by Temperature Programmed 2-Propylamine Cracking

It is normally assumed that acid–base interactions dominate the adsorption of ammonia on solid acidic materials, and that the strength of the interaction is related to acid strength. Zeolite beta, for example, has a high-temperature desorption peak at near 390°C (*1*), while for dealuminated faujasite the high-temperature peak occurs at about 330°C (*2*). The implication is that beta has stronger acid sites. However, other interactions of an electrostatic nature can also be important, especially in the case of oxides. We have compared the ammonia TPD characteristics of three samples of conventional solid acid zeolites, including one sample of dealuminated Y faujasite and two samples of beta, with a sample of a conventional solid base, calcium oxide, used as received from Baker Chemical. We have chosen calcium oxide as a comparison material in an attempt to gauge the potential strength of these other interactions relative to the acid–base interaction. The results show that in the case of ammonia adsorption on calcium oxide these other interactions may be as strong as the conventionally assumed acid–base interaction.

The dealuminated Y zeolite was prepared by exchanging NaY to 3.6% Na_2O, steam calcining at 640°C for 4 h, and washing with a pH 3.0 ammonium sulfate solution. Most of the sodium and all but about five nonframework aluminum atoms per unit cell are removed under these conditions. The beta zeolites were calcined to remove organic template and ammonium-sulfate-exchanged to remove sodium. The properties of all four materials are given in Table 1. A summary of the TPD desorption curves shown in Fig. 1 are given in Table 2. The ammonia desorption curve shows two peaks for CaO, both in the high-temperature or strong acid region. In these experiments the ammonia was monitored with a TCD. In the case of the CaO, a second experiment with a mass spectrometer as a detector gave positive identification of ammonia as well as water as the material desorbing in the high-temperature region associated normally with strong acidity; see Fig. 2. The ammonia TPD experiments involved outgassing 0.1 gm of sample for 2 h at 550°C, ammonia flow over the sample at 100°C for 4 h, a helium flush for 2 h, and temperature programming up to 550°C at 20°C/min.

By the conventional interpretation of the TPD results the calcium oxide would be classified as a stronger acid than either the Y or the beta samples. Although the CaO desorbs a relatively small amount of ammonia per gram of material, the CaO is also a relatively low-surface-area material. The site density given by the amount of ammonia desorbed per surface area is comparable to the zeolites. These results do not necessarily imply that calcium oxide is a strong acid just because it interacts strongly with a weak base. In addition to being a base, ammonia is a polarizable molecule with a pair of electrons capable of bonding with many types of materials, including calcium oxide and other materials classifiable as acids only in the broadest sense.

In a catalytic sense, solid acids are somewhat more narrowly defined as materials capable of catalyzing certain reactions such as cracking, isomerization, alkylation, etc. A TPD method more directly related to cracking activity has recently been reported (*3*). 2-Propylamine is adsorbed on the material

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TABLE 1

Properties of Calcium Oxide and of Three Zeolites Including Decationated and Dealuminated Y and Zeolite Beta Prepared at Two Si/Al Ratios, 10 and 15

	CaO	DEALY	Beta (10)	Beta (15)
Chemical (wt%)				
Water		17.4	19.9	18.1
CaO		—	0.04	0.04
Na_2O		0.11	0.17	0.09
Al_2O_3		17.45	7.54	5.36
SiO_2		82.32	92.20	94.38
Surface area (m^2/gm)	73	813	632	651
Si/Al (chem.)	—	4.01	10.4	15.0
μmoles Al/gm	0	3422	1478	1051
unit cell	—	24.54	—	—
No. Al/unit cell (XRD)		33.2		
Si/Al (XRD)		4.81		
μmoles Al/gm (XRD)		2882		

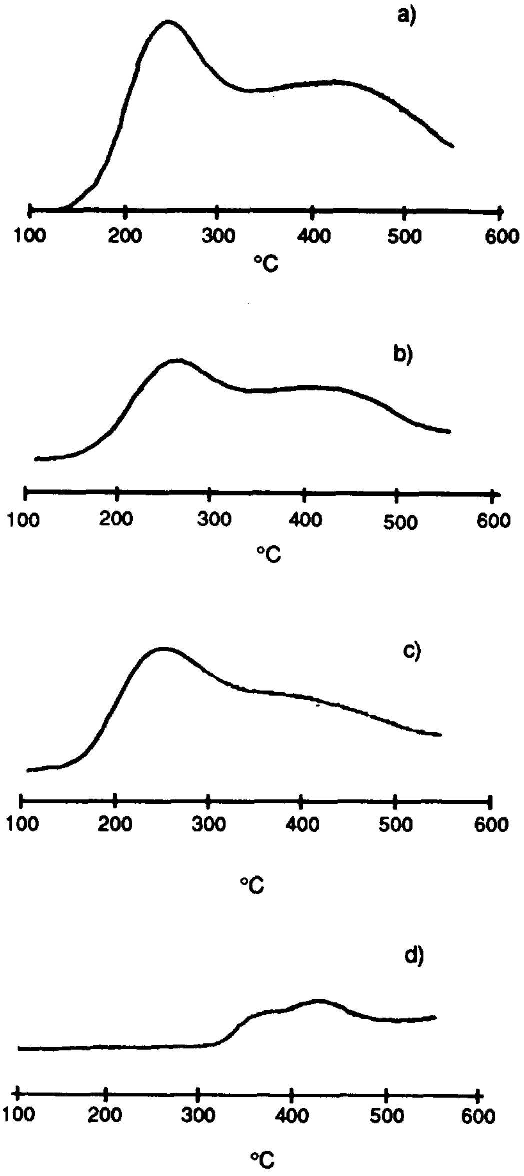

FIG. 1. Temperature programmed ammonia desorption curves (20°C/min.) of (a) decationated dealuminated Y zeolite, (b) beta zeolite, Si/Al = ~10, (c) beta zeolite, Si/Al ~ 15, and (d) calcium oxide, 73 m^2/gm surface area.

to be tested and excess material is desorbed. As the temperature is increased either the amine will desorb intact, or, if the amine is adsorbed on sites capable of catalyzing cracking reactions, the amine will crack to form propene and ammonia as products. This method was used to characterize the materials in Table 1 using the following experimental procedure. Twenty mg of sample was outgassed in helium for 1 h at 550°C and cooled to 100°C. The sample was treated with a total of 5 ml of 2-propylamine picked up using a gas impinger and carried in flowing helium at 100°C. The sample was flushed for 4 h with helium, and temperature programmed at 10°C/min to 550°C. The mass spectrometer detector was used to monitor *m/e* of 44 (2-propylamine), 41 (propylene), and 17 (ammonia).

The results of these experiments are shown in Fig. 3 and reported in Table 2. In the case of calcium oxide there is no reaction, the expected result for a nonacidic material. Calcium oxide is not an acid capable of catalyzing cracking, although it does desorb 2-propylamine at an unusually high temperature, consistent with the ammonia TPD experiments.

For the zeolites studied the amount of ammonia desorbed under the high-temperature TPD peak agrees approximately with the number of catalytically active cracking sites measured by the temperature-programmed cracking of 2-propylamine. Previous results using this method have shown that for high-ratio ZSM-5 every

TABLE 2

Ammonium TPD and Temperature-Programmed 2-Propylamine Cracking Results for Calcium Oxide and for Three Zeolites Including Decationated and Dealuminated Y, Beta, and NaHY

	CaO	DEALY	Beta (10)	Beta (15)
	Experimental			
Ammonia TPD				
Ammonia desorption (μmoles/gm)				
Total desorption	44	2770	1600	1730
High temp. desorption	44	1800	650	650
μmole HT NH3 desorp./m^2 SA	0.6	2.1	1.0	1.0
TP Isopropylamine				
Propene (cracked product)	0	1600	970	620
	Calculated			
μmoles Al/gm (Chem.)	—	—	1462	1044
μmoles Al/gm (XRD)	—	2882	—	—

Note. In the case of CaO the total desorption is the total desorption of ammonia detected by the mass spectrometer.

framework aluminum is associated with a cracking site (*4*), but for faujasite only some of the framework aluminums are associated with cracking (*5*). The results reported here suggest that beta behaves more like faujasite in that not every framework aluminum acts as a cracking center.

Although a discussion of this observation is beyond the scope of this paper, one may suggest that site isolation plays a role. Beta prepared at a low Si/Al ratio of between 10 and 20 is reported to contain paired sites as well as isolated sites (*6*). It is well known that faujasite, even at relatively low Si/Al ratios, may also contain both paired sites and isolated sites. A paired site consists of two tetrahedral framework aluminum atoms connected by a tetrahedral silicon, and an isolated site is an aluminum atom with no second nearest neighbor aluminum atoms. The current work suggests that paired sites behave like dibasic acids where only one site of the pair is active for cracking. In the case of beta about two-thirds of the sites are active, and according to this model the implication is that there are about twice as many aluminums associated with paired sites as there are isolated aluminum sites. In the case of the dealuminated Y sample the same considerations suggest that at a 2.454-nm unit cell size there are only about five or six isolated sites out of a total of 32 to 33 aluminum atoms per unit cell.

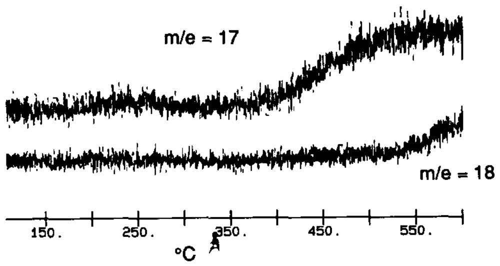

FIG. 2. Temperature-programmed ammonia desorption curve (20°C/min) of calcium oxide using a mass spectrometer as a detector. The results show desorption of both ammonia (*m*/*e* = 17) and, at a higher temperature, water (*m*/*e* = 18).

While ammonia TPD experiments may give interesting information concerning the strength of the interaction between ammonia and a solid acidic or nonacidic surface, the interaction is not a one to one measure of acid strength in the catalytic sense, nor does it measure the number of catalytically active sites. The results suggest that acidity in the broad physical organic chemistry sense may not sufficiently determine catalytic properties. A more narrowly defined

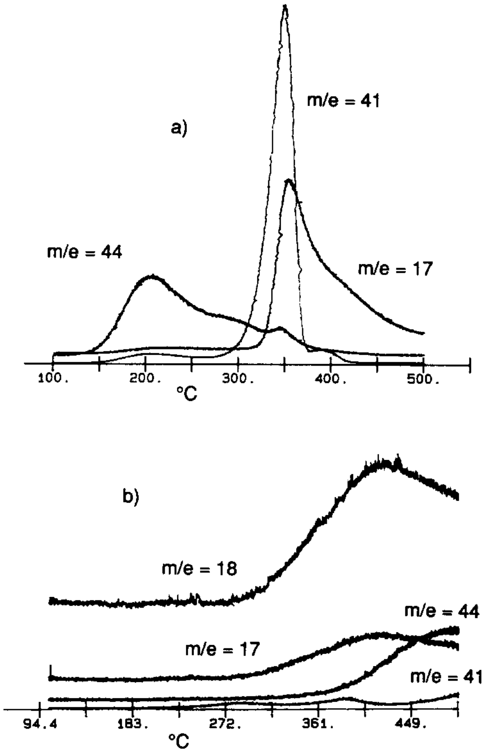

FIG. 3. Temperature-programmed desorption of 2-propylamine from (a) decationated dealuminated Y zeolite with cracking, *m/e* = 41 and desorption, *m/e* = 44, and (b) from calcium oxide showing only a high-temperature desorption peak, *m/e* = 44.

acidity, determined, for example, by the method involving temperature-programmed 2-propylamine desorption and cracking, appears to be a more appropriate measure of the number of catalytic acid sites on a solid acid catalyst.

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