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Measuring Acidity by Temperature-Programmed Desorption

Several studies have been made on the temperature-programmed desorption of amines from solid catalysts (*1–4*) that are characterized by the presence of at least two peaks. We report a method that employs the second, higher-temperature peak as an index of catalyst acidity. t-Butylamine was the chosen adsorbent based mainly on reasons of experimental convenience, despite possible drawbacks due to steric hindrance. *n*-Butylamine also gives a similar spectrum (*4*), but the second peak is not as sharp and requires a temperature of over ~500°C to estimate quantitatively.

In this procedure 30–40 mg of catalyst is preheated at 500°C for 1 h. After cooling to room temperature in flowing He the catalyst is exposed to a mixture of He and t-butylamine vapor for 2 min at a flow rate of 65 cm^3/min, by means of a saturator and a switching valve system. Excess amine is then eluted from the catalyst by continuing the stream of He alone for an additional 15 min. The He flow is adjusted to 10 cm^3/min, and the catalyst is heated 10°C per minute to 500°C. Desorption is measured by a thermal conductivity cell. Figure 1 shows a typical temperature-programmed desorption profile where the high-temperature β peak occurs, on the tail of a broad α peak. Variations of the relative amount of α to β occur with changes of the amine pressure. Table 1 shows that α varies according to the relative amine pressure while the β value remains constant, indicating that α is associated with physical adsorption and β, with chemisorption. Further work has shown that for a number of catalysts α peak also depends on the surface area.

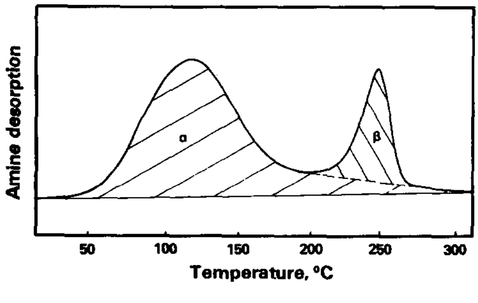

FIG. 1. Temperature-programmed desorption of *tert.*-butylamine from silica–alumina.

Qualitative mass-spectrometric analyses of the compounds that compose β showed unidentified species of low mass number besides those associated with the cracking pattern of t-butylamine. Similar analyses of the second peak of *n*-butylamine desorption from silica–alumina have been reported, and they show the presence of butene and propene (*1*, *4*). Therefore, the origin of the β peak is not always simple desorption of the uncracked parent amine.

Acid values obtained by our method have been compared with those obtained by other techniques. Tables 2 and 3 contain the results from tests of several commercial cracking catalysts that contain REY zeolite. Table 2 compares our acidity values with those obtained from an *n*-butylamine titration method using a color indicator (*5*, *6*), whereas Table 3 compares our values with the relative intensities of the NH_4^+ (1450 cm^{-1}) infrared band, after NH_3

TABLE 1

Amine Desorption as a Function of Relative Pressure P/P_0 of Original Pulse

P/P_0	α peak	β peak
0.100	19.5	4.5
0.012	16.5	4.5
0.006	10.5	4.5

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TABLE 2

Comparative Acidity Measuremtnes: β vs *n*-Butylamine Titration

Catalyst	Acidity (equivalent mmole/g)	
	n-Butylamine titration $pK_a \leq +2.8$	TBA β desorption
A (138)	0.455	0.091
B (115)	0.288	0.080
C (133)	0.249	0.081
D (89)	0.223	0.075
E (138)	0.193	0.060
F (82)	0.155	0.054
G (131)	0.144	0.059

Note. Numbers in parentheses give surface area in square meters per gram.

absorption (*7*). In both cases, the acidity trends are relatively the same; however, in Table 2, where the acidity is measured in the same units, there is a significant difference in the absolute values given by the two methods. The uncertainty of measuring β in terms of equivalent moles of t-butylamine, because of varying products of decomposition, cannot explain discrepancies of this magnitude.

TABLE 3

Comparative Acidity Measurements: β vs Infrared NH_4^+

Catalyst	Relative adsorbance NH_4^+ (1450 cm^{-1})	TBA β desorption (mmole/g)
H (135)	0.250	0.061
I (135)	0.230	0.051
J (84)	0.170	0.048
K (84)	0.140	0.044
L (86)	0.135	0.036
M (86)	0.130	0.037

Note. Numbers in parentheses give surface area in square meters per gram.

TABLE 4

Comparative Acidity Measurements: β vs NH_3 Adsorption

	Acidity (mmole/g)	
	NH_3 adsorption	β desorption butane equivalent
Silica/alumina (287) (ASTM N10074)	0.273	0.0236 0.0242
Alumina (160) (ASTM N10131)	0.163	0.0150 0.0151
Kaolin (11.2) (ASTM N16384)	0.00612	0.00097 0.00106

Lately, we have tried a proposed ASTM D-32 method for measuring catalyst acidities. This technique involves a volumetric adsorption of NH_3 at 175°C and is similar to the procedure reported by Webb (*8*). The results for three different materials are shown in Table 4, and these results are compared with their corresponding β values, in equivalent moles of *n*-butane for ease of calibration. The two methods show excellent agreement in trend but, again, there is a difference in the absolute values. We believe this is a measure of the difference between strong and weak acid–base interactions. The total of α and β measured by desorption would approximate the values found by both butylamine titration and ammonia absorption (i.e., 0.1–0.3 mmole/g) for most acidic catalysts of 100–200 $m^2 g^{-1}$ surface area. However, the values for β (0.01–0.08 mmole g^{-1}) are similar to those found by lutidine and pyridine chemisorption on both alumina and silica–alumina as measured chromatographically (*9*). This suggests that β represents a strong interaction between the catalyst and amine which is further indicated by the dissociation accompanying the peak and its independence of the amine pressure in the original treatment.

In conclusion, the relatively simple brief technique described in this note yields a direct index to strong catalyst acidity. The fundamental significance of this acidity and its effect on catalyst performance must be evaluated for individual catalyst systems.

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