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Study of Surface Acidity of Oxide Catalysts by Photoacoustic Spectroscopy[1]

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Photoacoustic spectroscopy has been employed to estimate quantitatively the acid sites on oxide catalysts. The technique involves the measurement of the ratio of intensities of absorption bands due to conjugate bases and acids of indicators adsorbed on the catalyst surface as a function of the amount of added *n*-butylamine. Basic sites in sodium-impregnated alumina samples have been examined by adsorbing phenolphthalein on these surfaces.

INTRODUCTION

Surface acidity which plays an important role in the performance of oxide catalysts is generally determined by titration with amines. The method involves the use of different indicators, the titer value for each indicator being taken as proportional to the number of acid sites having the acidity function H_0 less than or equal to the pK_{HB^+} of the indicator (*1*). The different methods employed for acidity determination vary in the mode of determination of the end-point or in the set of indicators employed (*2–4*). Thus, in the method of Benesi (*2*), Hammett indicators are employed in visual titrations. Electronic spectra of some adsorbed Hammett indicators have also been employed by some workers (*5–7*). We considered it valuable to investigate if photoacoustic spectroscopy (PAS) could be effectively employed to determine surface acidities of catalysts in view of the high surface sensitivity of this technique (*8–10*). Studies of PAS of monolayers of dyes on oxide surfaces carried out in this laboratory have indeed enabled us to monitor surface areas of oxides. The advantage with PAS is that we can directly investigate the species on the surface by making use of its characteristic electronic absorption bands.

In photoacoustic spectroscopy (PAS) monochromatized light, chopped at a frequency ω, is made to impinge on a sample in an air-tight cell. The light energy absorbed by the sample through an optical transition is given out in the form of heat (nonradiative transition) at the same frequency and causes pressure fluctuations in the cell. The pressure fluctuations give rise to an acoustic signal at the frequency ω. By using an acoustic transducer such as a microphone, photoacoustic spectra are obtained by recording the microphone output as a function of the wavelength (after normalizing for the power spectrum of the illuminating source). The advantage of PAS is that the technique can be gainfully employed to obtain optical absorption spectra of gels, powders, slurries, and so on, even if they are opaque. Saturation effects in PAS begin to appear when the thermal diffusion length is greater than the optical absorption length, or is less than the sample thickness (*8*). In obtaining spectra from monolayers, therefore, no saturation effects are expected and the PAS intensity can therefore be taken as a measure of the concentration of the absorbing species (*9, 10*). Similarly, when the surface is covered with a nonabsorbing layer such as a liquid, the PAS sig-

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nal intensity may be reduced, but flattening of absorption maxima due to saturation effects is not expected. In the present study, we have obtained quantitative spectra of indicators adsorbed on slurries of oxide catalysts in the solvent; the ratio of the intensities of absorption bands due to the conjugate bases and acids directly reflects the proportion of the number of acid sites on the sample.

In this paper we report PAS studies of the acidity distributions in alumina, silica, silica modified with H_2SO_4 (so as to contain 1 mmole/g), and a Linde molecular sieve (13×), as well as several alumina-silica compositions employing *n*-butylamine with appropriate indicators. We also report our results on the interaction of phenolphthalein with alumina surfaces containing varying amounts of sodium.

EXPERIMENTAL

Materials. A commercial alumina sample and a Linde molecular sieve (13×) available in the form of extruded pellets were powdered and activated at 450–500°C. A powdered sample of BDH silica gel was calcined at 500°C to give activated silica. By evaporating a slurry of the activated silica with H_2SO_4 solution followed by calcination at 500°C, modified silica containing 1 mmole/g of H_2SO_4 was prepared. A series of silica-alumina samples was prepared by coprecipitating silica and alumina gels from a solution of potassium silicate and aluminum nitrate (BDH, AR grade) with ammonia solution followed by drying and calcining at 500°C. Alumina catalysts impregnated with Na_2O were prepared by slurrying samples of activated alumina with varying amounts of NaOH solution, evaporating to dryness and calcining at 450–500°C.

Titration procedure. About 0.2 g samples of each catalyst were transferred to a set of weighed stoppered bottles in a dry glove box and weighed again. To each of these bottles 2 ml of dry benzene was added followed by 0.5 ml of the indicator solutions in benzene. A solution of *n*-butylamine in benzene was added in varying amounts to the samples and equilibrated for 30 min to 1 hr with intermittent shaking. The solid slurry was transferred to the cell of a photoacoustic spectrometer fabricated in this laboratory (*10*) and the spectra were recorded with a chopping speed of 70 Hz. The following indicators were employed for the study:

	Color changes at H_0 of
Bromothymol blue	-1.5 and $+6.8$
Bromocresol green	-3.7 and $+4.6$
Thymol blue	$+1.7$ and $+8.9$

RESULTS AND DISCUSSION

Typical photoacoustic spectra obtained with H_2SO_4/SiO_2 as well as two of the silica-alumina samples employing the three indicators are shown in Figs. 1 and 2. In the case of H_2SO_4/SiO_2 (Fig. 1), only one band maximum at 550 nm is observed before the addition of *n*-butylamine with thymol blue and bromothymol blue whereas in the case of bromocresol green two band maxima at 550 and 420 nm are observed. With bromocresol green, silica-alumina (1%) shows only the band at 420 nm whereas silica-alumina (10%) shows only the 550 nm band (Fig. 2). The 550 nm band corresponds to the acid form for the first titration range (lower pK_{HB^+}) of all the three indicators. With addition of small amounts of *n*-butylamine, we observed the development of a band at 420 nm in the case of thymol blue and bromothymol blue. In the second titration region of the indicators, we observe a band maximum at 600 nm corresponding to the base form while the band at 420 nm now corresponds to the acid form.

Since the Hammett acidity function, H_0, may be expressed in the form (*11*),

$$H_0 = pK_{HB^+} - \log(C_{HB^+}/C_B)$$

where HB^+ and B are the conjugate acid and base forms, respectively, of the indicator, from the ratio of the intensities of the

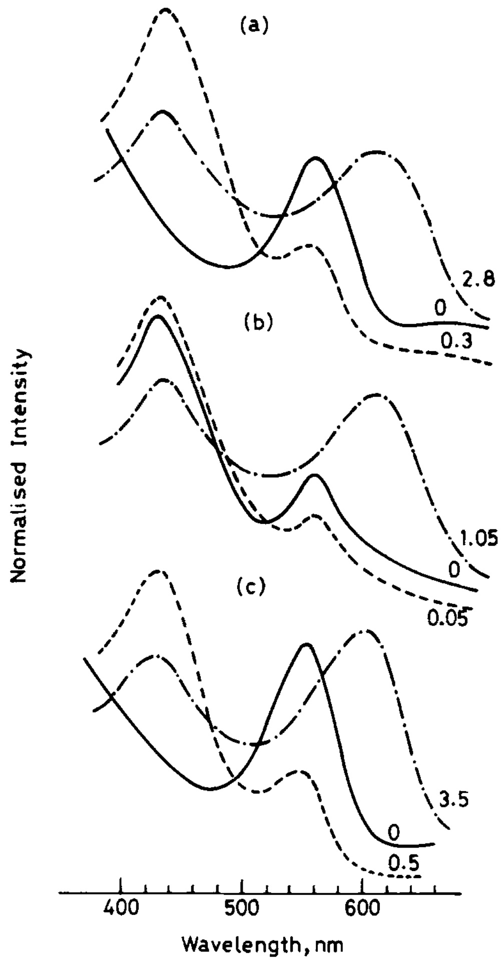

FIG. 1. Photoacoustic spectra of (a) bromothymol blue, (b) bromocresol green, and (c) thymol blue adsorbed on H_2SP_4/SiO_2 with different amounts of *n*-butylamine in mmole/g of the solid (indicated against the curves).

two forms we can directly obtain the H_0 value corresponding to every stage of the titration. Guided by the visual color changes, namely, red to yellow and then from yellow to bluish green (corresponding to the two color change regions of the titration) it is easy to decide on the amounts of *n*-butylamine to be added to give H_0 values on either side of the pK_{HB^+} of a particular indicator.

The acidity distributions of silica, alumina, Linde molecular sieve (13×), and silica modified with H_2SO_4 are shown in Fig. 3. It is gratifying that even for the weakly acidic silica and alumine samples, the distributions correspond well with those reported in the literature (*4*). We consider that PAS provides a reliable and straightforward method for obtaining the acid strength distribution. The method is not only more quantitative than the generally employed visual titration procedures but is also not time consuming.

We considered it worthwhile to carry out a systematic study of the acidity distribution in a series of silica-alumina catalysts by PAS and the results are shown in Fig. 4. We see that with the increasing proportion of alumina, the strength as well as the number of acid sites increase as expected. In going from 0.1 to 1% in alumina content, the H_0 range is extended from about +2.5 to −2.0, toward higher acidity. With silica-alumina (3.5%) the highest acid strength corre-

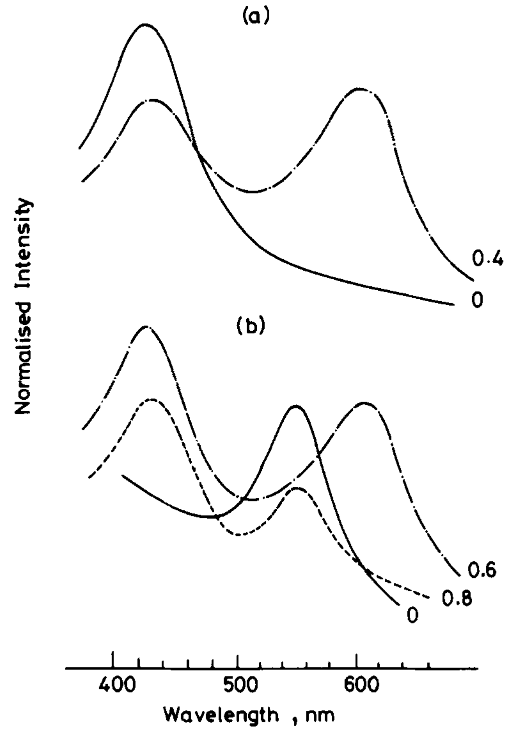

FIG. 2. Photoacoustic spectra of bromocresol green adsorbed on (a) silica-alumina (1%) and (b) silica-alumina (10%) with different amounts of *n*-butylamine in mmole/g of the solid (indicated against the curves).

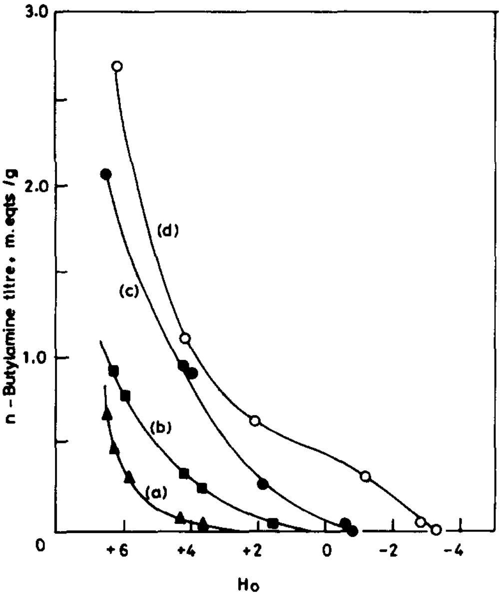

FIG. 3. Plot of the n-butylamine titer against the Hammett acidity function, H_0, for (a) silica, (b) alumina, (c) 13× molecular sieve, and (d) H_2SO_4/SiO_2.

sponds to H_0 of -5.5. Earlier workers have shown that while in the polymerization of propylene there is a linear dependence of the catalytic activity with acidity (*12*), such a linear relation is not observed for the cracking of 2-propylbenzene (*13*). Drushel and Sommers (*4*) have suggested that the indicator used (pK_a of $+3.2$) to measure the acid strength in the case of the cracking experiments probably measured acid sites which are weaker than those necessary for the cracking reaction. They further suggest the use of an indicator with pK_{HB^+} of $+1$ for cracking activity correlations. In this context, the acidity distributions shown in Fig. 4 clearly indicate the exact H_0 ranges over which the catalyst would be effective for a particular type of reaction. A qualitative comparison of our results with the cracking activities of similar catalysts reported by Tamele (*13*) shows a linear correlation around H_0 of 2.8. The silica-alumina (0.1%) catalyst shows some cracking activity but an indicator with pK_{HB^+} of $+1$ (as recommended in Ref. 4) would have shown no acidity at all.

In order to extend our studies to the distribution of basic sites we have carried out a preliminary investigation of phenolphthalein on alumina and sodium-impregnated alumina catalysts. The photoacoustic spectra of phenolphthalein adsorbed on various sodium-impregnated alumina catalysts (from ether solution) are shown in Fig. 5. In addition to the band at 540 nm which is responsible for the characteristic red color, we observe another band at 450 nm. Drushel and Sommers (*4*) have observed similar bands with other indicators and have attributed these bands to a red-shifted band in the uv region due to the interaction with strong Lewis acids. We notice, however, that the position of this band is rather insensitive to sodium impregnation and appears only when the 540 nm band is also found. Thus phenolphthalein does not give any absorption band when adsorbed on catalysts containing Brønsted acid sites as expected, or catalysts with strongly Lewis acid sites such as Cr^{6+} and Mo^{6+}. It there-

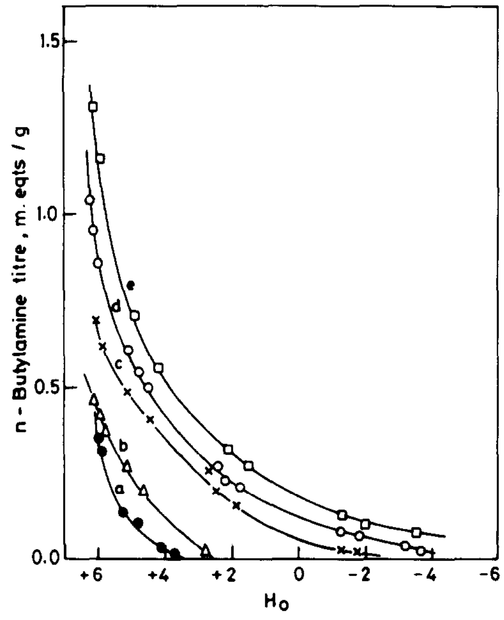

FIG. 4. Plot of the n-butylamine titer against the Hammett acidity function, H_0, for (a) silica and (b) through (e) silica-alumina samples with the alumina contents: (b) 0.1%, (c) 1.0%, (d) 3.5%, and (e) 10.0% by weight.

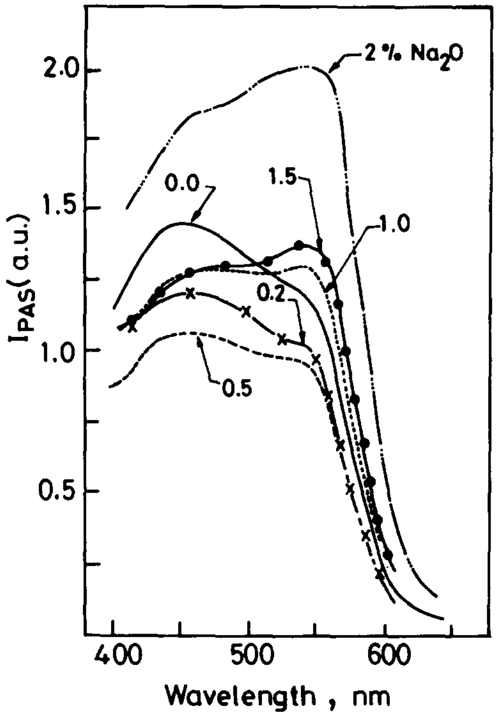

FIG. 5. Variation of the intensity of the 540 nm band in the photoacoustic spectra of adsorbed phenolphthalein with the sodium content of the alumina surface.

fore appears that both these bands are associated with adsorption on basic sites. When the adsorption is on an isolated basic site or a strongly basic site, only the 540 nm band is obtained. When the base is associated with a Lewis acid in a dual acid–base site (*14*, *15*), the band at 450 nm is obtained in addition to the one at 540 nm. The decrease in the intensity of the 450 nm band with increasing sodium impregnation may be attributed to the poisoning of dual acid–base sites associated with strong Lewis acids. At higher concentrations of sodium (when more than a monolayer coverage of Na_2O is likely to be present), the strong basic sites only give rise to the absorption band at 540 nm.

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