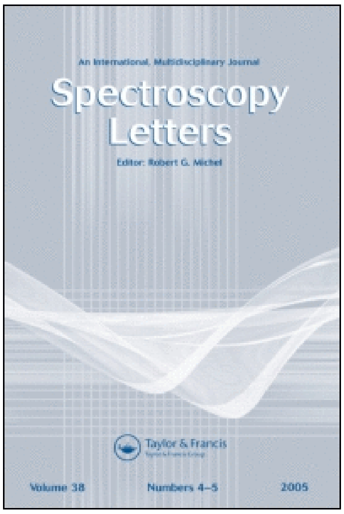

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Investigation of Acidity of Catalyst Surfaces by Photoacoustic Spectroscopy

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To cite this Article Rao, Mohan and Balasubramanian, D.(1980) 'Investigation of Acidity of Catalyst Surfaces by Photoacoustic Spectroscopy', Spectroscopy Letters, 13: 6, 329 — 337

To link to this Article: DOI: 10.1080/00387018008064025

URL: http://dx.doi.org/10.1080/00387018008064025

SPECTROSCOPY LETTERS, 13(6), 329-337 (1980)

INVESTIGATION OF ACIDITY OF CATALYST SURFACES BY PHOTOACOUSTIC SPECTROSCOPY

Key Words: Surface Acidity, Photoacoustic Spectroscopy

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ABSTRACT

Photoacoustic spectroscopy (PAS) has been used to monitor the surface acidity of solid (alumina-silica) catalyst, since PAS has the inherent advantage of measuring absorption bands of solid surfaces conveniently. Three kinds of acidic sites have been detected and their relative abundance estimated.

INTRODUCTION

Among the major features of heterogeneous catalysis, the measurement of surface acidity is very important and is still not easily monitored. Various methods such as the titration of suspensions of solid catalysts with organic amines using adsorbed indicators[1], electronic absorption spectral measurement of adsorbed indicators[2-7], and IR spectral studies of adsorbed organic bases[8] have been adopted to determine the surface acidity, and the acid strength of solid catalysts. Bonardet and others[9] have suggested a NMR method for the determination of acid strengths. Recently, Kuriacose and coworkers[10] have shown that reflectance spectroscopy can be used instead of absorption spectroscopy for this problem.

A major obstacle in using electronic spectroscopy in these systems is the heterogeneous phase and the associated scattering problems. In this context, we demonstrate in this paper the use of photoacoustic spectroscopy (PAS) as a convenient tool for surface acidity determinations.

Photoacoustic spectroscopy is a new analytical tool that provides a simple nondestructive method for obtaining information about the electronic absorption spectra of compounds in a variety of phases such as solids, semisolids, gels and liquids. In this technique, the system is excited to higher electronic states by radiation that is modulated at an audiofrequency. Non-radiative decay to the ground state leads to heat generation modulated at the same frequency, which in turn leads to pressure oscillations in the gas that surrounds the sample. These are sensed by a microphone, and processed and plotted as a function of wavelength. The strength of the acoustic signal is proportional to the amount of light absorbed by the sample and thus there is a close correspondence between the PAS spectrum and the conventional optical absorption spectrum[11]. PAS can be used to great advantage in the study of adsorbed and chemisorbed molecular species on solid surfaces. Such studies can be performed provided the substrate one is dealing with is either non-absorbing or highly reflecting in the spectral region of interest.

EXPERIMENTAL

About 50mg of the solid catalyst SiO_2-Al_2O_3(5% silica) were taken in each glass stoppered tube and the exact weight determined. 0.5ml of benzene is added to each of them so that the solid was completely wetted. Required amount of indicator in benzene was added, maintaining the same amount of indicator per milligram of solid. Varying amounts (0 to 12 μl/mg in 1 μl/mg steps) of the titrant (0.04 mM/ml n-butylamine in benzene) were added and the tubes shaken, left for 24 hrs for equilibration, and the supernatant liquid decanted. The samples were dried under vacuum and stored in a vacuum desiccator over P_2O_5 and acidic alumina until spectral measurements were made. The samples were transferred to the photoacoustic cell in a dry box. The catalyst $SiO_2:Al_2O_3$ used was not preheated. Methyl red and n-butylamine were laboratory grade reagents and benzene was spectral grade.

The PAS spectra were recorded on a Princeton Applied Research Model 6001 instrument. All the spectra were corrected for blank absorption and normalized using carbon black as reference. The normalization corrects the observed spectrum for the power variation in the source over the spectral region of interest. The PAS signal magnitude was recorded keeping the demodulator at 0° with respect to the lamp modulation. A high modulation frequency of 300 Hz was used to minimize the effect of sample thickness on the magnitude of the acoustic signal. In the case of highly absorbing samples such as methyl red, most of radiation will be absorbed within a distance μ_β(optical absorption length), small compared to the sample thickness l. If the thermal diffusion length $\mu_s(=(2\alpha/\omega)^{1/2}$ where α is the thermal diffusivity, and ω the modulation frequency) is more than the sample thickness l and optical absorption length μ_β, then the sample is photoacoustically opaque and signal saturation prevents spectral study. Signal saturation can be avoided by increasing the modulation frequency which will decrease μ_s. When $\mu_s < 1$ and $\mu_s < \mu_\beta$. PAS signal will be proportional to β, and will not depend on sample thickness 1 (for further details, see ref. 11).

RESULTS AND DISCUSSION

Methyl red adsorbed on the solid surface absorbs at 515nm and 410nm in the acid and basic forms respectively. As the surface is neutralized, the absorption and hence the PAS signal strength at 515nm decreases while the signal strength at 410nm increases. The sample that shows no band at 515nm is the one that is fully neutralised and the amount of the titrant butylamine added in this case is the volume required to neutralize the surface.

Figure 1 shows the PAS spectra of a few samples neutralized to varying extents. An interesting feature of the figure is the presence of an isosbestic point near 445nm through which most of the curves pass. The two curves that deviate a little from the isosbestic point, in our opinion, do so due to two reasons. The presence of trace amounts of water will alter the acoustic signal generation so that the signal strength will change over the spectral region. Also

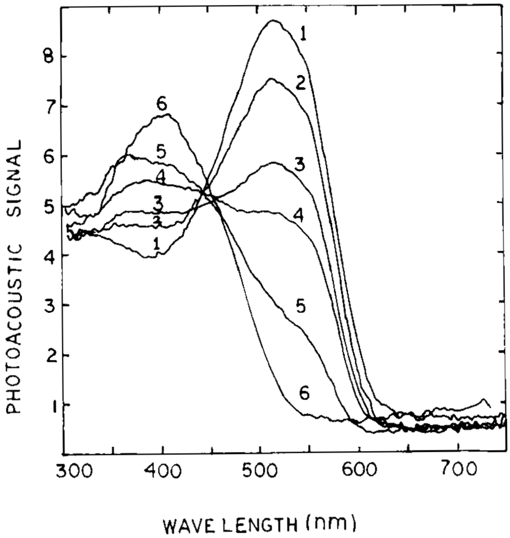

Fig.1. Photoacoustic spectra of methyl red adsorbed onto the catalyst $SiO_2:Al_2O_3$, containing increasing amounts of n-butylamine in μL/mg. Curve (1) 1.0; Curve (2) 2.0; Curve (3) 3.0; Curve (4) 4.0; Curve (5) 9.0; Curve (6) 10.0.

possible differences in the surface concentration of the indicator would lead to deviations. This difference could arise due to the nonuniformity of the particle size of the catalyst. We are currently investigating catalysts with known and uniform particle size in order to trace these deviations. The peak heights at 515nm were measured after normalization at 445nm, where all the PAS spectra should have the same signal strength.

The surface $SiO_2:Al_2O_3$ is known to have at least three different groups of acidic sites, with varying acid strengths[12]. This point is confirmed in our PAS studies when one plots the PAS signal strength at 515nm of the adsorbed dye as a function of the titrant added. Figure 2, which is a derivative plot of ΔS versus V (where ΔS is the difference in peak heights at 515nm between two consecutive volumes $V_1-V_2 = \Delta V$, and V is the average volume $((V_1+V_2)/2)$ of amine added; a derivative plot is made to accentuate the inflexion points) shows two distinct peaks and a shoulder. The relative amounts of the strong, moderately strong and weak acid sites on the surface

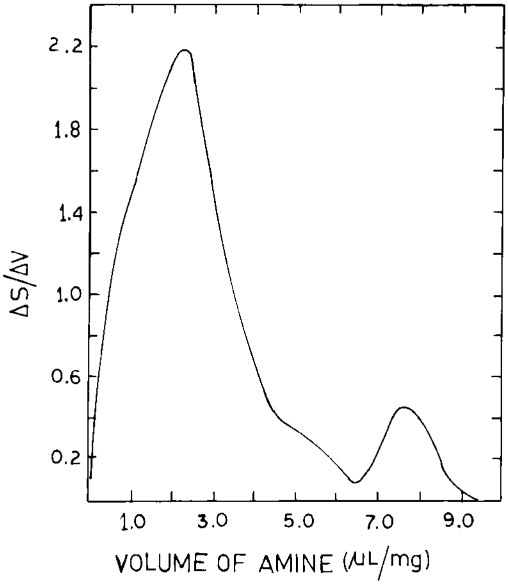

Fig.2. Derivative plot of the titration of catalyst surface with n-butylamine (see text).

investigated are found to be 1.0:1.30:1.09 respectively, on the basis of the relative amounts of the titrant. The peak heights in Figure 2 correspond to the relative distribution of the indicator.

We have shown in this paper that PAS can be used to advantage for surface acidity measurements, and for monitoring the distribution of various acidic sites. Experimental realization of an isosbestic point opens the possibility of more quantitative studies and possibly surface equilibrium constants, aspects that we are currently working on.

ACKNOWLEDGEMENT

Mohan Rao is grateful to the UGC, India for financial assistance.

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Received: March 2, 1980
Accepted: March 17, 1980