CHAPTER II*

INVESTIGATION OF ACIDITY OF CATALYST SURFACES

2.1 ABSTRACT

The surface acidity and the distribution of acidic sites play a major role in deciding the kinetics and the nature of the product formed in several reactions promoted by heterogenous catalysts. A simple method to monitor the surface acidity employing photoacoustic spectroscopy is described. The indicator dye methyl red, which changes its electronic absorption features upon interacting with acidic solids, has been used as a probe of surface acidity of silica-alumina, one of the extensively used catalysts in the petrochemical industry. Photoacoustic spectra of adsorbed indicator dye as a function of the surface neutralization are used to determine the acidity of the catalyst. Acidic sites with three different acid strengths have been detected and their relative abundance estimated.

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2.2.1 Introduction

The catalytic activity at the surface of a solid catalyst is largely due to adsorption, chemisorption or physisorption, which organises at least one of the reactant molecules into a form in which it can very readily undergo reaction. Typically, the catalyst is a solid body with a characteristic structure and a definite boundary surface that might not be completely represented by its bulk stoichiometry or molecular formula. The actual chemical species and the architecture of the accessible surface are of great importance in understanding catalysis and in tailormaking catalysts.

The binary composite of silica and alumina is one of the extensively used catalysts in the petrochemical industry. Neither silica nor alumina alone is effective in promoting catalytic cracking reactions. A catalyst having an appreciable cracking activity is obtained only when prepared from the hydrous oxides, followed by partial dehydration (1, 2). It was considered for long that the silica-alumina catalyst is a combination of the two oxides, alumina and silica. It was not readily obvious which physical or chemical property of the combination of the two oxides should be responsible for its high activity (3). Alkali metal ions and nitrogen-containing organic basic compounds were found effective in deactivating these catalysts to a significant extent. This observation led Mills et al. (4) to conclude that it is the acidic characteristics of the cracking catalysts that are fundamental to their activity.

In the cracking of petroleum, the silica-alumina catalyst performs many other functions besides cracking in the sense of breaking the C-C bond. Thus, at the usual cracking temperatures of around 450-550°C, other concomitant reactions, such as double bond migration in the olefins formed, cyclization
and skeletal isomerisation, hydrogen transfer and polymerization to coke-like polymeric materials, also occur. At temperatures below those of cracking, these catalysts promote various other hydrocarbon reactions, such as the polymerization of olefins, and certain alkylation reactions (3). The reaction that will be catalysed by a particular catalyst under a given set of conditions depends on the strength of the acidic sites participating in the process. For example, dehydration of alcohols can be observed by weak acidic sites, while skeletal isomerisation of alkenes requires stronger acidic sites (5).

The surface of solids may have two kinds of acidic sites, the Lewis and the Bronsted sites. As with molecular Lewis acids, a Lewis acid site on a solid is a site which has an unoccupied orbital with a high affinity for an electron pair. A Bronsted acid site is one which has a tendency to give up a proton. In many cases, the two can be related by the presence of water:

\[ \text{L}^+ + \text{H}_2\text{O} \rightleftharpoons (\text{L:OH}) + \text{H}_r^+ \]

where L\(^+\), the Lewis site, shares an electron pair with OH\(^-\) ion from water molecule and the remaining proton H\(^+_r\) is adsorbed on the surface, but can be easily removed in a chemical reaction. Thus the Lewis acidity converts to Bronsted acidity (6). The origin of acidity in a silica-alumina catalyst is attributed to at least three kinds of structural features: (1) the aluminum cations substituting for silicon cations in a tetrahedral coordination; (ii) aluminum cations in a perturbed tetrahedral arrangement and (iii) silicon in a perturbed tetrahedral arrangement (7). In these perturbed tetrahedral arrangements, at least one among the four oxygen atoms might be displaced, partially exposing the cations to the surface. In the case of silica-alumina catalyst, features of type (i) may be responsible for the Bronsted acidity while type (iii) could provide the
source of Lewis acidity (7). Clearly the heterogenous system is very complex, and sites with whole distribution of electron or proton affinity can be expected, with coordination deficiencies and imperfections of various types causing them, and relocation of ions tending to neutralize them. Both Bronsted and Lewis acidic sites are active in catalytic reactions. However, due to the differences in the mechanisms between a Bronsted acid and a Lewis acid site, it is sometimes found that they catalyze different reactions. For example, with a silica-alumina catalyst, it is shown that only the Bronsted acidic sites will polymerise propylene (8) whereas the decomposition of isobutane correlates with the density of Lewis acid sites (9). In the case of the isomerisation of cis-2-butene on a silica-alumina catalyst, it was shown that both types of sites were active, but with different rates and different detailed mechanisms (10, 11).

From the foregoing it can be seen that the surface acidity and distribution of acidic sites play a major role in deciding the kinetics and the nature of the products formed. There has hence been considerable interest in detecting and quantifying the types and the abundance of acidic sites on a catalyst surface, and several methods to determine these have been suggested.

2.2.2 Measurement of surface acidities

Various methods, such as the titration of suspensions of solid catalysts with organic amines using adsorbed indicators, electronic absorption spectral measurements of adsorbed indicators and IR spectral studies of adsorbed organic bases have been adopted to determine the surface acidity, and the acid strength of solid catalysts. Bonardet et al. have suggested a NMR method for the determination of acid strengths.
G.N. Lewis was the one who first reported the titration of a solid using an indicator dye to determine the end point. He had shown that $\text{AlCl}_3$ suspended in carbon tetrachloride could be titrated with an amine solution using crystal violet as the indicator (q.v. 12). The basic indicator forms a coloured conjugate with the acid sites on the surface; upon addition of the titrating base (which must be a stronger base than the indicator) the indicator base is displaced by the titrating base, and the colour changes or fades. Johnson (12) has developed a method for the determination of the acidity of solid surfaces which involves the titration of the solid suspended in benzene with n-butylamine, using p-dimethylaminobenzene as the indicator. Hammett and Deyrup (13) have developed a measure for describing the acid strength of concentrated acids, known as the Hammett acidity function.

$$H_0 = \text{pK}_{BH^+} - \log \frac{C_{BH^+}}{C_B}$$

where $H_0$ is the Hammett acidity function, $\text{pK}_{BH^+}$ is the ionisation constant of the conjugate acid $BH^+$, and $C_{BH^+}$ and $C_B$ are the concentrations of the conjugate acid, and the unprotonated base respectively. Benesi (14) has used Hammett indicators to measure the acid strengths of solid surfaces. If the solid has acidic sites with acidic strength (on the Hammett scale) less than the $pK_a$ of the indicator, a colour change can be seen. By using several indicators with differing $pK_a$ values, it is possible to estimate the acid strengths of surface sites. For example, if a solid gives yellow colour with benzalacetophenone ($pK_a = -5.6$), and does not show any colour change with anthraquinone ($pK_a = -8.2$), it can be concluded that the solid surface has acidic sites with $H$ values bracketed, or ranging between, -5.6 and -8.2.
A complete description of the surface acidity requires the determination of the acid strength as well as the number of acidic sites or acidity. The estimation of the acid strength is possible by the use of an adsorbed Hammett indicator. Benesi (15) combined his acids strength bracketing technique with titration and could determine the acidity of groups of sites differing in their acidic strength. The solid surface is titrated with a base using various Hammett indicators. The amount of base required to observe the colour change of a particular Hammett indicator is proportional to the number of acidic sites (or acidity) having H less than or equal to the pK of that indicator. Yamanaka and Tanabe (16) have developed a method of determining the basicity of a solid surface at various basic strengths by titrating the solid suspended in benzene with trichloroacetic acid using a series of Hammett indicators. This method makes it possible to determine the basic strength expressed by a Hammett acidity functions and, hence, the acid base strength distribution of a solid surface on a common scale.

Electronic absorption spectra of adsorbed indicators provide a means of determining the acidic or basic nature of the surface (17, 18). This method has been developed by Kobayashi et al. for determining both the acid strength and the total acidity of solids (19, 20). The $\pi-\pi$ band of pyridine is known to redshift a little upon adsorption. Protonated pyridine and hydrogen bonded pyridine show characteristic vibrational structures in their electronic absorption peak at 256 nm, while pyridine coordinated to Lewis acid sites shows a broad band, which is red shifted compared to the protonated one. This method has the advantage of being able to detect small amounts of adsorbed pyridine, due to the large molar absorption coefficient of the transition (21). Similarly, the infrared absorption spectra of adsorbed ammonia (22) and of pyridine (23) have
also been used for determining the acidity of solid surfaces. The spectrum of pyridine coordinated to the surface is markedly different from that of the pyridinium ion. This again permits the differentiation of acidic type on the surface.

Bonardet et al. (24), have used an NMR method for determining the Bronsted acid strengths of solid surfaces. NMR peaks for the solid samples are very wide and prevent any accurate chemical shift measurements. But if the surface proton participates in a heterogeneous equilibrium with an adsorbed proton acceptor molecule, AH, as

\[
\text{S-OH} + \text{AH} \rightleftharpoons \text{S-O}^- + \text{AH}_2^+ 
\]

where S-OH is a surface hydroxyl. The chemical shift will be altered by the acid proton if the rapid exchange occurs between the proton of the surface S-OH and the adsorbed AH. The experimentally observed high resolution NMR spectrum should then contain only a single line with a chemical shift due to the coalescence of the lines \( \delta_{\text{AH}} \), \( \delta_{\text{AH}^+} \), and \( \delta_{\text{OH}} \). The observed chemical shift, \( \delta_{\text{obs}} \), is then given by:

\[
\delta_{\text{obs}} = P_{\text{OH}} \delta'_{\text{OH}} + P_{\text{AH}} \delta'_{\text{AH}} + P_{\text{AH}_2^+} \delta'_{\text{AH}_2^+}
\]

where \( P_i \) is the concentration of hydrogen atoms in the group i. If the chemical shifts of the two nuclear types in the AH and AH\(^+\) species (e.g. \(^1\)H and \(^15\)N) are known, the relative concentrations of AH and AH\(^+\) can be calculated, and the chemical shift of the surface proton (OH) can also be deduced.
2-2.3 The Photoacoustic Method

From the foregoing, it can be seen that the surface acidity - the ability of the surface to convert an adsorbed neutral base to its conjugate acid - can be measured by titrating the solid suspensions in nonaqueous media using appropriate indicators. The use of spectrophotometry to monitor the colour changes associated with the titration should enormously increase the accuracy of measurement. A major obstacle in using electronic spectroscopy in these systems is the heterogeneous phase and the associated scattering problems. In this context, we have explored the idea of using PAS to circumvent these difficulties.

The method is rather simple. An organic dye molecule, which changes its electronic absorption features upon interaction with acidic solids, adsorbed on the surface of the catalyst serves as the reporter of the acidity of the surface. Recording the PA spectrum of this sample as a function of the surface neutralization, achieved by adding varying amounts of a base, provides an accurate titre value for calculating the acidity.

The dye chosen should exhibit distinct changes in its optical absorption features in its acidic and basic forms. Methyl red is a satisfactory choice as such a reporter; since it absorbs at 515 nm in the acidic form and at 410 nm in the basic form. Thus the PA signal strength at 515 nm can be taken as a measure of the acidic form of the indicator, provided the PA signal strength at 515 nm varies linearly with the concentration of the dye on the surface. The base chosen for the neutralization of the surface was n-butylamine in benzene.
2.3 Materials and Methods

The silica-alumina catalyst, \( \text{SiO}_2 - \text{Al}_2\text{O}_3 \) (5% silica), prepared by calcining the mixtures of hydrous oxides was provided by Prof. Kuriacose of the department of Chemistry, Indian Institute of Technology, Madras, and the sample was used without any pre-heating. Methyl red and butyl amine were laboratory grade reagents and benzene was spectral grade. About 50 mg of the solid catalyst was taken in each of several preweighed glass stoppered graduated tubes, the exact weights determined, and 0.5 ml of benzene was added to each of the tubes to wet the sample. Varying amounts of dye solution (12 mg of methyl red dissolved in 30 ml of benzene) in the range of (5-150 \( \mu l \)) was added to each tube and shaken for a minute. The walls of the tube were washed down with 1 ml of benzene, and the total volume was made up to 3 ml and left for several hours for equilibration. The supernatant liquid was decanted and preserved for estimating the concentration of the unadsorbed dye and the residual samples dried under vacuum and stored in a dry vacuum desiccator containing a small amount of \( \text{P}_2\text{O}_5 \) until spectral measurements were made. The spectra of these samples were used for monitoring the linearity of the PA signal strength with the amount of adsorbed dye.

About 50 mg of the solid catalyst was taken as in the previous case and the exact weight of the sample determined. The required amount of the indicator in benzene was added, maintaining the same amount of the indicator (ca. 125 \( \mu l / 60 \) mg of the solid) per unit weight of the solid. Varying amounts of (0 to 12 \( \mu l / mg \) in 1 \( \mu l / mg \) steps) the titrant (0.04 mM/ml, n-butyliamine in benzene) were added, the tubes shaken, and left for 2k hours for equilibrium. The supernatant liquid was decanted, the samples were dried under vacuum, and stored in a vacuum desiccator over \( \text{P}_2\text{O}_5 \). The samples were transferred to the PA cell in a dry box.
All the spectra were corrected for blank absorption and normalized using a prerecorded carbon black spectrum. This normalization corrects the observed spectrum for the power variation of the source over the spectral region of interest. A high modulation frequency of 300 Hz was used to avoid problems of nonlinearity due to PA saturation, if any. The spectra were recorded with 2.0 mm slits, giving a spectral band width of 8 nm, and at a scan speed of 100 nm/min. The optical density of the supernatant liquids were measured on a Schimadzu 200S u v-vis spectrophotometer.

2.4 Results and Discussion

Methyl red adsorbed on the solid surface was found to absorb at 515 nm in the acidic form and at 410 nm in its basic form. As the surface is neutralized, the absorption, and hence the PA signal strength at 515 nm decreases, while the signal strength at 410 nm increases. The sample that shows no band at 515 nm is the one that is fully neutralized and the amount of the titrant butylamine added in this case is the volume required to neutralize the surface. The acidity of the surface is then expressed as milli-equivalent of the titrant per gram of the catalyst.

As discussed before, this method requires that PA signal strength should vary linearly with the amount of the chromophore adsorbed on the surface. Figure 2.1 shows the plot of PA signal strength at 515 nm versus the amount of methyl red adsorbed on the sample. The amount of the methyl red absorbed on the sample is determined by equilibrating the solid with a methyl red solution of known concentration and estimating the unadsorbed dye in the supernatant. The PA signal varies linearly with the amount of the adsorbed dye, at low concentrations and becomes independent at higher concentrations. This could be due
Figure 2.1 PA signal intensity at 515 nm versus amount of methyl red on silica-alumina.
to PA saturation or due to the complete coverage of all the acidic sites on
the surface and hence further absorption of indicator causes very little or
no increase in the absorption at 515 nm. (Methyl red adsorbed on chromatography
grade neutral alumina samples (Sigma and BDH) does not absorb at 515 nm.
Methyl red adsorbed on neutral silica gel also does not absorb at 515 nm.)

In the case of highly absorbing samples, most of the radiation will
be absorbed within one optical absorption length $\mu_s = 1/\beta$, where $\beta$ is the
optical absorption coefficient) small compared to the thickness of the sample, 1. If the thermal diffusion length $\mu_s$ (given by $(2\kappa / \omega)$; where $\kappa$ is the
thermal diffusivity and $\omega$ the modulation frequency) is more than the sample
thickness, $\lambda$ and optical absorption length $\mu_s$, then the sample is photoacoustically opaque and signal becomes independent of $\beta$ and varies as $\omega^{-1}$ (Case
2(i) of Table 1.1). Signal saturation can be overcome by increasing the modulation
frequency which will decrease $\mu_s$. When $\mu_s < \beta/\omega$ and less than 1, than the PA
signal will be proportional to $\beta/\mu_s$ and vary as $10^{3/2}$ (case 2(iii) of Table 1.1).
In the case of finely divided powder samples as the present ones, the thickness
of the sample is equal to the diameter of the particle and since the particle
diameter is much smaller than $\mu_s$, PA signal saturation is seldom encountered
for fine powders. Figure 2.2 shows a plot of the logarithm of PA signal strength
at 515 nm versus the logarithm of $\omega$, the modulation frequency. The slope
is found to be -1.0 and does not vary even at 550 Hz. Taking the thermal
diffusivity of alumina to be 0.083 cm $^2$s$^{-1}$ (TPRC Data Series Volume 10, Thermal
diffusivity, Y.S. Toulkian (Ed.), Plenum, New York, 1970) and assuming that
5% silica does not alter the thermal properties of alumina significantly, the
thermal diffusion length for silica-alumina can be calculated. The calculated
values for $\mu_s$ vary from 2.5 x 10$^{-2}$ cm at 40 Hz to 6.9 x 10$^{-3}$ cm at 550 Hz.
Figure 2.2 A log-log plot of the PA signal for methyl red adsorbed on silica-alumina versus modulation frequency, showing the $\omega^{-1}$ dependence.
If the near plateau region of Figure 2.1 is due to the onset of PA saturation, one would expect a change of slope to \(-1.5\) at high frequencies. Thus it is clear from Figure 2.2 that the situation is not due to PA saturation. The independence of the PA signal with respect to the amount of adsorbed methyl red can be attributed to a complete coverage of all the acidic sites. Thus, the plot also provides an estimate of the concentration of the indicator dye required to completely cover the acidic sites on the given solid surface.

Figure 2.3 shows the PA spectra of a few samples of the catalyst neutralised to varying extents by the amine. It can be seen that the band at 515 nm due to acidic form of the indicator decreases while the band at 410 nm due to basic form of the indicator increases progressively with the surface neutralization. An interesting feature of the figure is the presence of an isosbestic point near 445 nm through which most of the curves pass. It can however be seen that two curves deviate a little from the isosbestic point. This deviation, we believe, is due to the presence of trace amounts of water in the two samples, which will decrease the PA signal by robbing the thermal energy deposited in the sample due to the nonradiative deexcitation process. Also, possible differences in the surface concentration, if any, of the indicator may lead to deviations. In this connection Figure 2.4 shows the effect of exposure of the sample to the atmosphere on the PA signal strength. The first spectrum is of the sample transferred to the PA cell in a dry box. The second spectrum is also of the same sample transferred to the PA cell in the open, exposing the sample to the atmosphere (25°C and 60% RH) for about 2 minutes. It can be seen that there is a reduction in the peak height and also a slight change in the band shape. This difference is observed only for the samples that are neutralised to some extent. The peak heights at 515 nm were measured after
Figure 2.3 PA spectra of methyl red adsorbed on silica alumina containing increasing amounts of n-butylamine in \( \mu L/mg \). Curve (1) 1.0; Curve (2) 2.0; Curve (3) 3.0; Curve (4) 4.0; Curve (5) 9.0; Curve (6) 10.0.
Figure 2.4 PA spectra of methyd red on neutralized silica-alumina showing the effect of sample exposure to the atmosphere.
normalization at 445 nm, where all the spectra should have the same signal strength; this accounts for small variations of signal strengths from sample to sample if any.

The PA signal strength at 515 nm is plotted against the volume of the titrant added, in order to determine the neutralization point. Interestingly the plot shows three inflection points; an observation that has been confirmed by six independent experiments. The surface of silica-alumina is known to have at least three different groups of acidic sites with varying acid strengths (25). This point is reflected in our titration plots. Figure 2.5 is plot of the quotient \( \Delta S/\Delta \delta \) versus \( \bar{V} \), where \( \Delta S \) is the difference in the signal strength at 515 nm between two consecutive volumes \( (v_1, v_2) \) of the added amine, and \( \Delta \delta = v_1 - v_2 \) and \( \bar{V} \) is the average volume \( (v_1 + v_2)/2 \) of the amine added. Such a derivative plot is made to accentuate the inflection points and shows two distinct peaks and a shoulder. The relative amounts of the strong, moderately strong and the weak acid sites on the surface under investigation are found to be 1.0:1.3:1.09 respectively, on the basis of the relative amounts of the titrant. And the total acidity is found to be 0.39 milli-equivalent per gram of the solid.

2.5 Conclusion:

The work reported here, though preliminary in nature, demonstrates for the first time the potential of PA spectroscopy in the study of surface acidity of catalysts. Apart from the surface acidity, it has also been possible to monitor the distribution of various acidic sites on the surface. Because of its simplicity, this method appears particularly suitable for screening catalysts prepared in the laboratory and for making rapid surveys of the catalysts used in some industrial processes, where the surface acidity is the key factor.
Figure 2.5 Derivative plot of the titration of catalyst surface with n-butylamine.
We have used here a single indicator that allows the measurements of the total (or at least all the sites of interest) acidity. The extension of this work, with the use of a series of Hammett indicators, as reported by Benesi (15) in his visual titration method, is evident. Such a study should be able to provide precise information not only regarding the total acidity and the distribution of acidic sites but also acid strengths of each group of sites. Indeed, such a study has been reported by Ganguly and Rao (26) and more extensively by Jagannathan et al. (27). The IR spectra of certain organic bases coordinated to the surface are markedly different from that of the protonated species. It should be also possible to distinguish between Lewis and Bronsted acid sites by extending the study into the near infrared and infrared spectral regions.
References:


