# A New Method for Measuring Surface Acidity. The Titration of Silica–Alumina with the Indicator Itself[1]

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(Received July 23, 1976)

A new method has been proposed for measuring the surface acidity of solid acids. The method involves the titration of a solid acid with the indicator itself in a nonpolar solvent; it determines the number of acid sites from the amount of the indicator chemisorbed at saturation. The titration of silica–aluminas with 4-anilinoazobenzene ($pK_a = 1.5$) itself yielded an acid content smaller than the butylamine titration method with the same indicator. This difference in acid content was ascribed to the difference in the base strength of the titrants. Similarly, titration with *trans*-azobenzene ($pK_a = -2.9$)itself produced an acid content smaller than that with 4-anilinoazobenzene itself.

Walling's[3] and the butylamine titration (or Benesi's)[4] methods have been employed for measuring the acidic properties of solid acid surfaces in nonpolar solvents. The former is for measuring the acid strength from the color change in indicators adsorbed on surfaces. The latter method, for measuring the acid-strength distributions, can be interpreted in the following way: it is primarily designed to determine the number of acid sites capable of chemisorbing each $H_0$ indicator on the basis of the amount of butylamine which must be added until the chemisorbed indicator changes in color. In our recent studies[5–7] it was pointed out that the assumption underlying the latter method is not valid from a practical point of view. This argument is based on the fact that neither the amine nor the any indicator reaches an adsorption equilibrium with the acid sites under the conventional conditions of operation.

Since butylamine is much more basic than the usual indicators, it may reasonably be inferred that the acid sites capable of chemisorbing the amine are not all capable of chemisorbing indicators, and also that the amine chemisorbed is less mobile than the chemisorbed indicators. The former inference is equivalent in essence to the generalized one that acid sites on a solid acid vary in number depending on the base strength of the base used. When no asdorption equilibrium is attained, a substantial part of the amine added may be chemisorbed on acid sites incapable of chemisorbing an indicator, and thus wasted. Consequently, the butylamine titration method may overestimate the number of acid sites.

Therefore, if solid acid surfaces are titrated with indicators themselves different in base stregth, accurate information may be obtained on acid-strength distributions from both the amount chemisorbed at saturation and the base strength of each indicator. The amount of a chemisorbed indicator at saturation will correspond to the number of acid sites capable of chemisorbing the indicator. The base strength of the indicator (*e.g.*, its $pK_a$ value) will determine an arbitrary scale of the acid strength of the acid sites. Also this method will not require, in principle, that the adsorption be at equilibrium, if only the amount of a chemisorbed indicator itself is measurable even in the presence of the physically adsorbed indicator.

The present study was undertaken in order to see whether or not the titration of solid acid surfaces worked out in practice with an indicator itself, and also to examine whether or not the above inference was valid. This attempt was carried out with silica–alumina catalysts as solid acids, silica gel as an inert diluent of the catalysts, and 4-anilinoazobenzene or *trans*-azobenzene as an indicator.

## Experimental

*Materials.* The original and Na-poisoned silica–alumina catalysts (SA-1, SA-1-Na-2 and -3) were described elsewhere.[8] The additional catalyst (SA-1-Na-4) was prepared by the impregnation of SA-1 with an aqueous solution of sodium hydroxide. Its surface area and $Na^+$- content were 452 $m^2/g$ and 0.807 mg-ion/g respectively. The silica gel (S-3) was taken from the same batch as was used earlier.[6] The 4-anilinoazobenzene (BADA, $pK_a = 1.5$) and *trans*-azobenzene (TAB, $pK_a = -2.9$) were of a GR and an EP grade respectively, and both were purified by recrystalization from ethanol. Their solutions in cyclohexane were prepared in the way described previously.[6] Thoroughly purified cyclohexane was sealed in a small Y-shaped glass ampoule under a vacuum;[6] its volume (around 3 ml) was determined from the difference in the weight of the ampoule before and after sealing. Gaseous nitrogen from a cylinder was also purified.[6]

*Apparatus.* The specially designed UV-cell, which provides two light-paths rectangular to each other, was shown in a previous paper.[6] A single wafer was used in each of the present runs, so that concurrent spectral measurements were possible of both the wafer and the liquid phase. The spectra were recorded on a Shimadzu multipurpose recording spectrophotometer, Model MSP-50L, at room temperature. The control was atmospheric air.

*Procedures.* Most of the procedures have been described in detail earlier.[6] In most experiments, the powdered catalysts were diluted with inert S-3 powder (for a reason to be stated later) by mixing them well for 2—5 min in a mixing grinder; they were then pressed into self-supporting wafers.

A wafer was activated in the cell at 450 °C and at pressures of $10^{-4}$ to $10^{-5}$ mmHg for 2 h after pretreatment in air at 550 °C for 5 h. After the introduction of the sealed cyclohexane, the background spectra were recorded of both the liquid phase and the wafer, plus the liquid phase. The background spectra of the wafer itself were obtained as a difference between the two spectra. A known, small amount of each indicator solution (around 0.3 or 0.5 ml) was added to the cell, and then the cell was allowed to stand at 60 °C for at least 4 days before spectral measurements. This addition was repeated until the amount of a chemisorbed indicator became virtually constant. A previous study[6] showed that the BADA adsorbed on non-acidic sites transmigrated

effectively onto acid sites when it was allowed to stand as above. In the present titration, therefore, the added indicator can be regarded as being approximately in an adsorption equilibrium.

## Results

*Spectra of BADA and Molar Absorption Coefficients.* BADA shows a band at 386 nm in cyclohexane, at 440 nm on S-3, and at 545 nm on SA-1. The bands at 440 and 545 nm are ascribable to species hydrogen-bonded to non-acidic sites and chemisorbed on acid sites respectively.[6] The molar absorption coefficients were determined for each species from the Beer plots. They are listed in Table 1. The values for adsorbed species were obtained with undiluted wafers (*ca.* 25 mg). For each species, an excellent linearity was confirmed up to an absorbance of at least 2 at an absorption maximum. This critical absorbance corresponded to surface concentrations of around $3.5\times10^{-3}$ and of around $7\times10^{-3}$ mmol/g for chemisorbed and hydrogen-bonded BADA respectively.

Table 1. Molar absorption coefficients of BADA

| System | Molar absorption coefficient | |
|---|---|---|
| | Symbol | $\varepsilon\times10^{-4}$ |
| In cyclohexane | $\varepsilon_{l,386}$ | 2.78 |
| On S-3 | $\varepsilon_{p,440}$ | 2.00 |
| | $\varepsilon_{p,545}$ | 0.07 |
| On SA-1 or | $\varepsilon_{c,545}$ | 3.72 |
| SA-1-Na-4 | $\varepsilon_{c,440}$ | 0.29 |

With S-3 wafers, the BADA remained in part unadsorbed in the liquid phase, even on the first addition (about $3\times10^{-5}$ mmol). Also, no spectral evidence was found to indicate the presence of chemisorbed BADA, not even at the above critical surface concentration. The adsorption isotherm of hydrogen-bonded BADA followed the Freundlich equation well. With undiluted SA-1 wafers, the spectra showed not only the presence of chemisorbed BADA alone on the surface, but the absence of BADA in the liquid phase, even at a surface concentration of about $8\times10^{-3}$ mmol/g, indicating that the chemisorption was far from saturation even at this surface concentration. The same things were noted with undiluted SA-1-Na-4 wafers. Therefore, it was necessary for the titration of the catalysts with BADA itself to reduce greatly the amount of acid sites in a wafer. For this purpose, it seemed advisable to dilute the catalysts with inert S-3. This is the reason for the use of a diluted wafer.

*Evaluation of the Amount of Chemisorbed BADA.* The spectra of diluted wafers showed the coexistence of both chemisorbed and hydrogen-bonded BADA, even on the first addition of $3\text{—}5\times10^{-5}$ mmol. When the addition was repeated, the BADA increased gradually in both the liquid-phase and surface concentrations. Hence, the material balance is given by the following equations:

$$m_0 = m_a + m_l, \tag{1}$$

$$m_a = m_p + m_c, \tag{2}$$

where $m$ is the amount of BADA; the 0, a, l, p, and c subscripts denote the BADA added, adsorbed, remaining in the liquid phase, hydrogen-bonded, and chemisorbed respectively. The $m_l$ quantity is readily determinable from the data on both the liquid-phase concentration of BADA and the cumulative volume of cyclohexane added; hence, the $m_a$ can be determined from Eq. 1. The absorbances at the absorption maxima of both adsorbed species ($A_{\lambda_m}$) are given by Eqs. 3 and 4:

$$A_{545} = \frac{1}{S}(\varepsilon_{c,545}m_c + \varepsilon_{p,545}m_p), \tag{3}$$

$$A_{440} = \frac{1}{S}(\varepsilon_{c,440}m_c + \varepsilon_{p,440}m_p), \tag{4}$$

where $S$ is the cross section of a wafer; $\varepsilon$, the molar absorption coefficient, and $m$, in mmol.[6]

It is well known that molar absorption coefficients often vary at high concentrations.[9] When diluted wafers were titrated, the chemisorbed BADA increased in the net surface concentration by a factor of 10 to 50 over the critical concentration below which the Beer law was valid. On the other hand, the concentration of hydrogen-bonded BADA was never beyond the range of the validity of the Beer law. Then, it does not seem to be reasonable to evaluate the amount of chemisorbed BADA directly from Eqs. 3 and 4 with the $\varepsilon_c$ and $\varepsilon_p$ values given in Table 1. With the assumption that the ratio of $\varepsilon_{c,440}$ to $\varepsilon_{c,545}$ is constant over an extended range of surface concentrations (Eq. 5), Eq. 6 is derived from Eqs. 2, 3, and 4:

$$\frac{\varepsilon_{c,440}}{\varepsilon_{c,545}} = \alpha \text{ (constant value)}, \tag{5}$$

$$m_c = m_a - m_p = m_a - \frac{S(A_{440}-\alpha A_{545})}{\varepsilon_{p,440}-\alpha\varepsilon_{p,545}}. \tag{6}$$

This assumption seems to be reasonable and much more practical than the assumption of the Beer law over an extended range of surface concentrations. For BADA, the value of $\alpha$ was as low as 0.078. Also, the second term ($\alpha\varepsilon_{p,545}$) in the denominator of Eq. 6 was neglected because of its negligibly small value. Thus, the amount of chemisorbed BADA was determined according to Eq. 6.

*Adsorption Isotherms of Chemisorbed BADA.* The adsorption isotherms were obtained by plotting the amount chemisorbed on a catalyst of a unit weight, $M_c$ (mmol/g), against the liquid-phase concentration, as is exemplified in Fig. 1. Each isotherm conformed well to the Langmuir equation, as is illustrated in Figs. 1 and 2. The solid lines in Fig. 1 denote isotherms derived from the Langmuir equation. Figure 2 shows the Langmuir plots of the isotherm data given in Fig. 1. The isotherm data at zero concentration were excluded from the Langmuir plots because the lower limit for the detectable liquid-phase concentration was about $3\times10^{-4}$ mmol/l. The amount of chemisorbed BADA at saturation (*i.e.*, the number of acid sites capable of chemisorbing BADA) was determined from the Langmuir plots in the usual way. The results are listed in Table 2. Acid contents determined by other methods were also collected in this table for comparison.

*Spectra and Adsorption Isotherms of TAB.* Titration

TABLE 2. ACID CONTENTS OF SILICA-ALUMINA CATALYSTS

| Catalyst | Dilution ratio[b] (Cat : S-3) | Acid contents[a] This work BADA | This work TAB | Amine method with BADA[c] | IR-Py method[d] (L+B) |
|---|---|---|---|---|---|
| SA-1 | 1 : 19.0 | $0.12_5$, $0.07_4$ | — | | |
| | | $0.08_9$[e] | | 0.23 | $0.09_7$ |
| | 1 : 6.24 | $0.06_7$ | $0.01_0$ | | |
| | 1 : 0 | — | $0.01_1$ | | |
| SA-1-Na-2 | 1 : 5.54 | $0.06_7$ | — | 0.16 | $0.07_7$ |
| SA-1-Na-3 | 1 : 9.58 | $0.09_3$ | — | 0.13 | $0.06_0$ |
| SA-1-Na-4 | 1 : 9.24 | $0.04_3$, $0.05_8$ | — | | |
| | | $0.05_0$[e] | | — | $0.04_6$ |

a) mmol/g. b) Ratio by weight. c) The butylamine titration method, Ref. 8. d) IR spectroscopic method with pyridine (Ref. 10); L+B, Lewis plus Brønsted acid sites; see text. e) Values averaged over the indicated two or three independent titration data.

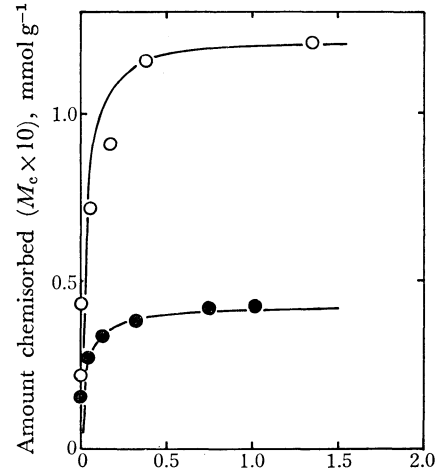


Fig. 1. Adsorption isotherms of chemisorbed BADA.
○: SA-1, ●: SA-1-Na-4.

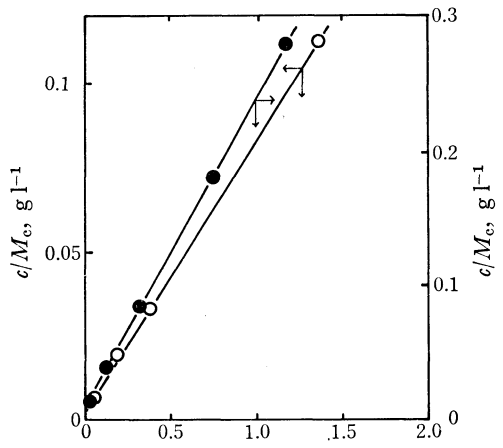


Fig. 2. Langmuir's plots of BADA chemisorption.
○: SA-1, ●: SA-1-Na-4.

with TAB, less basic than BADA, was preliminarily examined. Table 3 summarizes the absorption spectra of TAB, together with the relevant molar absorption coefficients determined from the Beer plots. An inspection of this table leads to the conclusion that the strong bands at 435 nm on SA-1 and at 318 nm on S-3 are due to TAB chemisorbed on acid sites and adsorbed in the neutral (probably, hydrogen-bonded) form on non-acidic sites respectively. The amount of chemisorbed TAB was determined according to the equation corresponding to Eq. 6. For TAB, $\alpha$ was 0.21 and the second term ($\alpha\varepsilon_{p,435}$) in the denominator was again neglected.

TABLE 3. UV SPECTRA OF TAB AND MOLAR ABSORPTION COEFFICIENTS

| System | Absorption at[a] | | | Molar abs. coef. Symbol | $\varepsilon \times 10^{-4}$ |
|---|---|---|---|---|---|
| In cyclohexan | 230(s) | 317(vs) | 450(vw, b) | $\varepsilon_{1,317}$ | 2.50 |
| In ethanol | 230(s) | 318(vs) | 420(vw, b) | | |
| On S-3 | 230(s) | 318(vs) | 420(vw, b) | $\varepsilon_{p,318}$ | 1.65 |
| | | | | $\varepsilon_{p,435}$ | 0.16 |
| In aq $H_2SO_4$ | 255(s) | 295(vw) | 425(vs) | | |
| On SA-1 | 245(s) | 305(vw) | 435(vs) | $\varepsilon_{c,435}$ | 1.57 |
| | | | | $\varepsilon_{c,318}$ | 0.34 |

a) nm; (vs), very strong; (s), strong; (vw), very weak; (b), broad.

When a diluted SA-1 wafers was titrated, even the first addition of TAB (about 5 mmol) effected the saturation of the chemisorption, as evidenced by the fact that repeated additions brought about no increase in the amount of chemisorbed TAB. The amount of chemisorbed TAB in each addition was, therefore, taken as the amount of acid sites for TAB. The value listed in Table 2 is the one averaged over four additions.

The adsorption isotherm of chemisorbed TAB was determined with an undiluted SA-1 wafer (Fig. 3). In this titration, TAB was detected in the liquid phase, even at a low surface concentration. In addition, no spectral evidence was observed to show the presence of hydrogen-bonded TAB at any stage of the titration. Figure 3 also shows that the isotherm fits the Langmuir equation. The acid content evaluated from the Langmuir plot is also listed in Table 2.

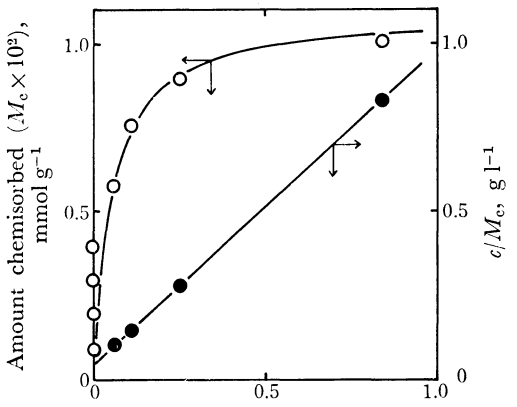


Fig. 3. Adsorption isotherm (○) and Langmuir's plot (●) for TAB chemisorption on SA-1.

## Discussion

Table 2 indicates that there are fewer acid sites on SA-1 when TAB is used than when BADA is used, as was expected. This difference can be explained in terms of the difference in the base strength of the two indicators, since TAB is smaller in molecular size than BADA. A similar phenomenon was observed with S-3. Silica gel S-3 behaved as a non-acid to BADA. but as an acid to 4-(1-naphthylamino)azobenzene ($pK_a=4.0$), which is more basic than BADA. This is also very similar to the well-known fact that even alcohols such as 1-butanol behave as acids toward potasium hydroxide, yielding alkoxide anions. Thus, the present observations substantiate the inference that acid sites on a solid acid vary in number depending on the base strength of the base used.

Also, Table 2 points out that the present titration with BADA itself gives an acid content smaller than the butylamine titration method with BADA for every catalyst used. Two explanations may be offered for this difference. The first is that the observed difference results from the difference in molecular size between BADA and butylamine as titrants. If the acid sites were present mainly in small surface pores which are accessible to butylamine molecules, but inaccessible to BADA molecules larger than the amine, or if such pores were predominant in the surfaces, titration with BADA itself would yield an acid content smaller than the butylamine titration method with BADA. The second is in terms of the difference in the base strengths of the two titrants, as has been described in the Introduction.

The acid-content data shown in the last column of Table 2 give a clue for determining which explanation is valid. These values (for Lewis plus Brønsted acid sites) were determined from the integrated IR absorption intensities for the Lewis-bound pyridine (1455 cm$^{-1}$) and Brønsted-bound pyridine (1540 cm$^{-1}$) bands,[10] using the apparent integrated molar absorption coefficients reported by Hughes and White.[11] The IR spectra were recorded after a catalyst wafer had been exposed to pyridine vapor and then evacuated at 150 °C for 1 h.[10] When an undiluted SA-1 wafer was pretreated with pyridine in the same way as above, its UV spectra revealed that such a wafer was capable of chemisorbing only a small amount of BADA. This fact implies that the prechemisorbed pyridine has occupied almost all the acid sites capable of chemisorbing BADA. It should be noted here that pyridine is substantially the same in molecular size as butylamine. According to the first explanation, therefore, the IR-pyridine method would produce an acid content larger than the present titration method. On the other hand, according to the second explanation, almost the same acid contents will be obtained by both methods. Table 2 shows clearly that the two methods yielded almost the same acid content for each catalyst except for SA-1-Na-3. This fact proves the second explanation and, hence, our inference to be valid, although the cause of the exceptional value for SA-1-Na-3 is not clear at present.

Tiration with TAB produced the same acid content for both diluted and undiluted SA-1 wafers, as is shown in Table 2. In the case of the former wafer, its acid content was obtained without the determination of the adsorption isotherms, as has been described above. These facts imply that the present titration method does not necessarily require the time-consuming determination of adsorption isotherms.

The authors are grateful to Mr. Akira Watanabe for his help in part of the measurements, and to Dr. Yasukazu Saito for his valuable discussion.

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