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Measurements of Acid-strength Distribution beyond $H_0=-8.2$ of Sillca-Alumina Catalysts by UV-Spectrophotometric *n*-Butylamine Titration Method[1]

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A new UV-spectrophotometric *n*-butylamine titration method was proposed for measuring acid-strength distribution of acid sites on solid acid catalysts. The method can provide information on acid-strength distribution of acid sites beyond $H_0=-8.2$, which can not be obtained by the conventional visual *n*-butylamine titration method. Acid-strength distributions were measured for a series of silica-alimina catalysts differing in sodium content, using 4-benzeneazodiphenylamine ($pK_a=1.5$), *trans*-benzalacetophenone ($pK_a=-5.6$), 4-nitrotoluene ($pK_a=-10.5$), and 2,4-dinitrotoluene ($pK_a=-12.8$) as indicators. The results revealed that about one-half of the acid sites on an unpoisoned silica-alumina catalyst lay in the H_0 region from -10.5 to -12.8, and the strongest ones in the H_0 region beyond -12.8. The strong acid sites were eliminated with the modification of acid-strength distribution as the catalyst was poisoned with sodium ions. UV spectra of the above indicators in adsorbed state were discussed.

Various methods have been developed for the measurement of acid-strength distributions of solid surfaces. The method frequently referred to as the Benesi or *n*-butylamine titration method[4,5] has been widely employed. In this method, solids suspended in a nonpolar solvent such as benzene are titrated with *n*-butylamine and a series of visible H_0 indicators, the end-point being determined by the naked eye. Benesi[5] revealed, using this method, that most of the acid sites on silica-alumina lay in the region $H_0\leq-8.2$. Information on acid-strength distributions in this region is indispensable for the study of solid acid catalysis. No such information, however, can be provided by the conventional *n*-butylamine titration method, since anthraquinone is the least basic ($pK_a=-8.2$) of well-known visible H_0 indicators. Available H_0 indicators having a pK_a lower than -8.2 change color in the ultraviolet region, and thus UV-spectrophotometric titration becomes essential. Moreover, such titration is superior to the conventional method by the naked eye in determining the end-point.

From the viewpoint of homogeneity of acid sites in acid strength, Kobayashi[6] has recently analyzed the data on silica-alumina that were obtained by UV-spectrophotometric titration using visible dimethyl yellow ($pK_a=3.3$) or methyl red ($pK_a=4.8$) as an indicator. Durshel and Sommers[7] showed ultraviolet and visible absorption spectra of several visible H_0 indicators in adsorbed state in order to examine their suitability for the conventional titration of surface acidity.

We have applied UV-spectrophotometry to the conventional method using 4-benzeneazodiphenylamine, the use of which was recommended by Drushel and Sommers.[7] The method was then extended to titration using other indicators, especially 4-nitrotoluene ($pK_a=-10.5$) and 2,4-dinitrotoluene ($pK_a=-12.8$), both of which respond to very strong acid sites with color change in the ultraviolet region. The use of these indicators furnished new information on acid-strength distributions in the H_0 region beyond -8.2 of acid sites on silica-alumina catalysts.

Experimental

Materials. The silica-alumina catalysts listed in Table 1 were taken from batches used in previous studies,[8] and were calcined at 550°C for 8 hr in atmosphere. Silica gel (WAKOGEL Q-12 for chromatography) was also used. The indicators, 4-benzeneazodiphenylamine (BADA), *trans*-benzalacetophenone (BAP), 4-nitrotoluene (NT), and 2,4-dinitrotoluene (DNT), were of EP or GR grade and were dissolved in decaline after repeated recrystallization. Their pK_a values are 1.5 for BADA, -5.6 for BAP, -10.5 for NT, and -12.8 for DNT.[9] A 0.1 N decaline solution of *n*-butylamine, purified by distillation, was used as a titrant. Decaline used as a nonpolar solvent was passed through two chromatographic columns containing freshly activated silica gel and alumina[10] in order to remove water, aromatics and other impurities. The water content was reduced to below 10 ppm.

Titration Procedure. The catalyst sample was activated at 450°C overnight in a vacuum. After ten to twenty 20 m*l* conical flasks with ground glass stoppers had been weighed, roughly one gram of the sample was placed in each in a dry box replaced with dried nitrogen. The tightly stoppered flasks were reweighed, and about 10 m*l* of decaline was then added to each in the dry box. A solution of *n*-butylamine was introduced into the sample slurries so that they differed in amine content. After vigorous shaking, the tightly stoppered sample slurries were placed in a desiccator at 30°C for two days for equilibration, and then an indicator was added to each. They were put to stand in the desiccator for additional three or four days for reaction of the indicator. The result-

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[4] O. Johnson, *J. Phys. Chem.*, **59**, 827 (1955).

[5] H. A. Benesi, *ibid.*, **61**, 970 (1957).

[6] J. Kobayashi, *Nippon Kagaku Zasshi*, **84**, 25 (1963).

[7] H. V. Drushel and A. L. Sommers, *Anal. Chem.*, **38**, 1723 (1966).

[8] I. Mochida and Y. Yoneda, *J. Catal.*, **7**, 393 (1967); H. Matsumoto, J. Take, and Y. Yoneda, *ibid.*, **11**, 211 (1968).

[9] M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957).

[10] J. Take, N. Kikuchi, and Y. Yoneda, *J. Catal.*, **21**, 164 (1971).

TABLE 1. CATALYSTS

No	Symbol	Surface area[a] (m^2/g)	Remarks
1	SA-1	540	Silica-alumina, 13%Al_2O_3, Nippon Cat, a cracking catalyst of the Shokubai Kasei Co.
2	SA-1-Na-1	450	0.048 meq Na/g, by impregnation of SA-1 with NaOH aq. soln.
3	SA-1-Na-2	480	0.087 meq Na/g, by impregnation of SA-1 with NaOH aq. soln.
4	SA-1-Na-3	480	0.168 meq Na/g, by impregnation of SA-1 with NaOH aq. soln.
5	SA-Na-HCl	...	0.119 meq Na/g, by treatment of SA-Na (another lot of silica-alumina impregnated with NaOH) with HCl
6	SA-Na-HAcO	...	0.200 meq Na/g, by treatment of SA-Na with HAcO

a) Measured by the BET method with N_2.

ing sample slurry was transferred to a conventional 10 mm absorption cell with a 9 mm quartz spacer to provide a light-path length of 1 mm.

No indicators were detected in the supernatant layer of decaline. The following amounts of indicators were used: 0.3 for BADA, 1 for BAP, and 1.5 to 2.0 for NT and DNT, in μmol/g-catalyst.

Evaluation of Molar Absorptivities. Ultraviolet and visible absorption spectra were recorded against reference cell containing fresh sample slurries (not treated with amine) on Hitachi Recording Spectrophotometer (Model EPS-2). The molar absorptivity ε of an adsorbed indicator was evaluated by the equation

$$\varepsilon = \frac{Av}{mwl}, \tag{1}$$

where A is absorbance, v the volume of a sample slurry in an absorption cell (liter), m the amount of an adsorbed indicator (mol/g-catalyst), w the amount of a sample in an absorption cell (g), determined after decaline has been removed by evaporation, l the light-path length (cm).

Results and Discussion

The relevant UV absorption spectra of the indicators are summarized in Table 2.

4-Benzeneazodiphenylamine (BADA). A decaline solution of BADA (yellow) shows absorption at 390 mμ. This is slightly red-shifted (415 mμ) in a polar solvent such as ethanol because of the interaction between indicator and solvent. An absorption band at 535 mμ (purple) in acidified aqueous solution is evidently due to the conjugate acid of BADA. Adsorption of BADA on every fresh silica-alumina catalyst gave a band at 550 mμ alone, in good agreement with the spectrum obtained by Drushel and Sommers,⁷⁾ showing that all the adsorbed molecules were in the conjugate-acid form. As the level of neutralization of the surface was raised, the band decreased in intensity with the development of an absorption band near 450 mμ due to the physically adsorbed neutral indicator, and finally only the band near 450 mμ remained. The slight red-shift to 450 mμ from 440 mμ for silica gel seems to be due to a stronger physical adsorption of the indicator. The presence of an isosbestic point was also observed in a series of spectra, each being determined for a catalyst at a different level of neutralization, indicating that none other than the simple acid-base reaction took place on the solid surface.¹¹⁾ The above behavior is very similar to that observed in a series of aqueous sulfuric acid solutions, each having a different acidity.

TABLE 2. ABSORPTION SPECTRA OF INDICATORS[a]

Indicator	In solution		On solid surface		
	Acidic	Neutral	Fresh SA-1	Neutralized SA-1	Silica gel
BADA	535	415	550	450	440
BAP	320 (w) 400—430 (s)	315	320 (sh) ~400	320	315
NT	380	310	300 (w,sh) 340 (s) ~500 (w)	300	295
DNT	280 (m) 340 (s)	260	260 (s) 320 (sh) ~500 (w)	260	255

a) λ in mμ; (s), strong; (m);, medium (w), weak; (sh), shoulder.

Changes in the level of neutralization of solid surfaces may therefore be followed quantitatively by observing the concentration of BADA adsorbed either in tht conjugate-acid form c_A or in the neutral form c_P. Spectrophotometric determination of the concentration requires data on the following molar absorptivities: (1) ε, the molar absorptivity at a selected wavelength of the adsorbed indicator, generally containing both the conjugate-acid species and the neutral one, (2) ε_A and ε_P, the molar absorptivity at the same wavelength of the pure species adsorbed in the conjugate-acid form and that in the neutral form, respectively. These are connected with c_A or c_P by the equation

$$\frac{c_A}{c_0} = \frac{\varepsilon - \varepsilon_P}{\varepsilon_A - \varepsilon_P} \text{ or } \frac{c_P}{c_0} = \frac{\varepsilon - \varepsilon_A}{\varepsilon_P - \varepsilon_A} \tag{2}$$

only when $c_A + c_P = c_0$, where c_0 is the total concentration of the adsorbed indicator and can be determined from the amount of addition. Since the relation, $c_A + c_P = c_0$, holds evidently for adsorbed BADA, a titration curve can be obtained by plotting the color change ratio $x_A = c_A/c_0$ or $x_P = c_P/c_0$ of BADA against

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11) H. H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, New York (1962), p. 563.

Table 3. Molar absorptivities of adsorbed BADA at 550 mμ

Amount of *n*-butylamine$^{a)}$	Catalysts									
	SA-1			SA-1-Na-1			SA-1-Na-2	SA-1-Na-3	SA-Na-HCl	SA-Na-HAcO
	$\varepsilon \times 10^{-4\,b)}$		$n^{c)}$	$\varepsilon \times 10^{-4\,b)}$		$n^{c)}$	$\varepsilon \times 10^{-4}$	$\varepsilon \times 10^{-4}$	$\varepsilon \times 10^{-4}$	$\varepsilon \times 10^{-4}$
0	4.20	(6.7%)	9	4.04	(0.4%)	2	3.85	4.46	4.49	4.31
0.05	...	...	..	3.63	(3.0%)	2	3.60	3.52	4.47	4.38
0.10	4.08	(12.4%)	3	2.20	(16.8%)	2	3.25	2.78	3.74	3.65
0.15	3.67	(13.7%)	3	2.48	(13.7%)	2	3.30	1.69	3.06	3.28
0.20	3.12	(5.6%)	3	0.92	(58.7%)	2	0.44	0.31	0.72	1.48
0.25	1.49	...	1	...	...	..	...	0.18	0.14	0.37
0.30	0.69	(18.9%)	3	0.07	(19.2%)	2	0.15	0.02	...	...
0.35	...	...	..	...	...	..	...	...	0.10	0.18
0.40	0.26	(19.2%)	2	0.12	(94.3%)	2	0.12	0.01	...	...
0.50	0.04	...	1	...	...	..	...	...	...	...

a) meq/g catalyst. b) Quantity in parentheses is the relative standard deviation.
c) Number of separate spectral measurements.

the amount of *n*-butylamine added.

The ε values at 550 mμ are given in Table 3, each being for a different level of neutralization of each silica-alumina catalyst. The reproducibility of the ε values is considerably good when it is taken into account that a specimen for spectral measurement is in slurry form.

We see that each fresh catalyst provides the same ε value within experimental error, and also that a few fresh catalysts including SA-1 remain practically unchanged even upon addition of the 0.05 or 0.1 meq/g-catalyst of *n*-butylamine. Thus the ε value for each fresh catalyst can be taken as the ε_A value of the indicator. This is also in line with the fact that a band appears only at 550 mμ on each fresh catalyst. The average ε_A value, $(4.3 \pm 0.4) \times 10^4$, is in accordance with that (3.8×10^4) determined from a linear relationship between the absorbance at 550 mμ of adsorbed BADA and its amount with a thin wafer of SA-1.[12] It is lower than that in an aqueous sulfuric acid solution, 5.88×10^4 at the maximum peak position of 535 mμ, by a factor of about 1.4. A similar observation was reported for dimethyl yellow and methyl red adsorbed on silica-alumina catalyst by Kobayashi.[13] Molar absorptivity ε for each catalyst sufficiently neutralized corresponds to ε_P. It can be neglected since its value is very small compared with the ε_A value.

Titration curves are shown in Fig. 1. In the calculation of the color change ratio, ε for each fresh catalyst was taken as ε_A for the corresponding one. The color change of an indicator is visually observed when the surface concentrations of the neutral and the conjugate-acid species become equal. The point of color change or the end-point therefore corresponds to the intersection of a titration curve with a horizontal line at $x_A = 0.5$.

According to Benesi,[5] acid strength of solid surfaces can be expressed with the Hammett and Deyrup H_0 function

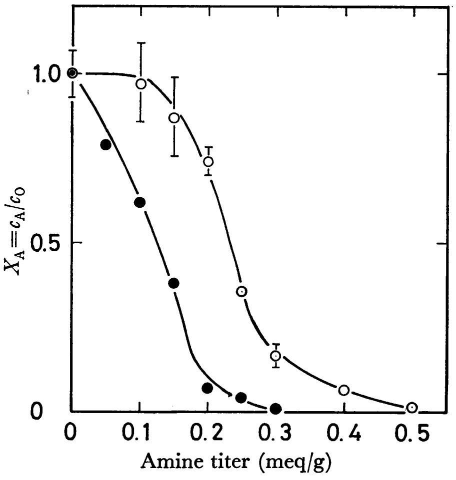

Fig. 1. Titration curves with BADA for SA-1(○) and SA-1-Na-3 (●).

$$H_0 = -\log(a_{H^+}f_B/f_{BH^+}) = pK_a + \log(c_B/c_{BH^+}). \qquad (3)$$

The value of abscissa of the intersection therefore gives the amount of acid sites having an H_0 equal to or lower (stronger) than the pK_a of the indicator used. The amount of acid sites so determined for each silica-alumina catalyst is shown in Table 4. The acid content ($H_0 \leq 1.5$) of SA-1 decreases to about two-thirds of its original value on treatment with aqueous sodium hydroxide solution, but those for the set of the SA-1-Na and SA-Na catalysts scarcely differ from each other.

Table 4. Acid contents$^{a)}$

Catalyst	Indicators			
	BADA pK_a= 1.5	BAP pK_a= −5.6	NT pK_a= −10.5	DNT pK_a= −12.8
SA-1	0.23	0.18	0.13	0.02
SA-1-Na-1	0.16	0.12	0.03	0
SA-1-Na-2	0.15_5	0.10_5	0.01_5	0
SA-1-Na-3	0.12_5	0.08	0	0
SA-Na-HCl	0.15	0.10	0	0
SA-Na-HAcO	0.18	0.07	0	0

a) In meq/g catalyst.

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[12] J. Take, H. Kawai, and Y. Yoneda, presented at the 25th Symposium on Catalysis of the Catalysis Society of Japan, Fukuoka, Oct. 1969.

[13] J. Kobayashi, *Nippon Kagaku Zasshi*, **82**, 288 (1961).

TABLE 5. MOLAR ABSORPTIVITIES[a] FOR SA-1 AT DIFFERENT LEVELS OF NEUTRALIZATION

Amount of n-butylamine[b]	Indicators								
	BAP			NT			DNT		
	$\varepsilon \times 10^{-3}$		n[c]	$\varepsilon \times 10^{-3}$		n[c]	$\varepsilon \times 10^{-3}$		n[c]
0	11.8	(18.7%)	10	10.2	(19.6%)	13	5.09	(20.4%)	14
0.025	...	...	..	10.9	(25.7%)	3	...	...	..
0.05	11.2	(18.7%)	4	7.57	(31.4%)	4	2.90	(18.3%)	3
0.10	10.2	(19.5%)	4	7.19	(18.5%)	5	2.75	(9.5%)	3
0.15	8.07	(37.1%)	4	5.97	(31.0%)	5	1.87	(47.1%)	3
0.20	4.77	(79.2%)	4	4.65	(58.3%)	4	1.36	(25.7%)	3
0.25	...	...	..	2.98	(87.0%)	2	...	...	..
0.30	0.86	(105%)	4	3.93	(59.3%)	4	0.29	(114%)	2
0.40	0.06	(66.7%)	2	2.09	(70.8%)	6	0.79	(65.8%)	3

a) Quantity in parentheses is the relative standard deviation. b) In meq/g catalyst.
c) Number of separate spectral measurements.

TABLE 6. MOLAR ABSORPTIVITIES[a] FOR FRESH CATALYSTS

Catalyst	Indicators								
	BAP			NT			DNT		
	$\varepsilon \times 10^{-3}$		n[b]	$\varepsilon \times 10^{-3}$		n[b]	$\varepsilon \times 10^{-3}$		n[b]
SA-1	11.8	(18.7%)	10	10.2	(19.6%)	13	5.09	(20.4%)	14
SA-1-Na-1	12.9	(29.5%)	2	7.08	(8.3%)	3	4.39	(7.7%)	2
SA-1-Na-2	10.4	...	1	5.85	...	1	...	...	..
SA-1-Na-3	10.0	...	1	3.88	...	1	1.52	...	1
SA-Na-HCl	12.2	...	1	4.83	...	1	3.13	...	1
SA-Na-HAcO	8.04	...	1	1.91	...	1	1.45	...	1

a) Quantity in parentheses is the relative deviation. b) Number of separate spectral measurements.

Thus UV-spectrophotometric titration is useful for measuring an acid-strength distribution of acid sites on catalyst surfaces.

trans-*Benzalacetophenone (BAP).* A protonated BAP molecule in a concentrated sulfuric acid solution exhibits a strong band at 400—430 mμ depending upon acidity of the solution and a weak one near 320 mμ, as shown by Noyce and Jorgenson.[14] The former decreases in intensity with the development of the latter as acidity of the solution is reduced, and finally disappears.

The spectrum of BAP adsorbed on fresh SA-1, where a strong band near 400 mμ and a weak one near 320 mμ (shoulder) appear, shows that the conjugate-acid species is formed on the fresh surface of SA-1. Recent workers[7] observed that BAP adsorbed on silica-alumina gave a strong band at 390 mμ and a weak one at 310 mμ. They attributed the former mainly to the strongly adsorbed neutral species, presumably, on the basis of the difference between the wavelength of absorption on the silica-alumina (390 mμ) and that in concentrated sulfuric acid solution (430 mμ). Our assignment is also based on the fact that the intensity of the strong band near 400 mμ decreases as n-butylamine is added. The spectra in the ultraviolet region below 340 mμ varied in a somewhat complicated manner upon titration. No isosbestic point was observed. This suggests that some reactions besides the simple acid-base reaction take place in the system under investigation. When the complicated behavior of the spectra is ignored, an increase in the extent of neutralization of solid surfaces may be followed by observing a decrease in the intensity of the band near 400 mμ, as was the case in the titration using BADA.

The ε values at 400 mμ are summarized for different levels of neutralization of SA-1 in Table 5, and their variations with fresh catalysts in Table 6. They decrease with increasing amount of n-butylamine. Reproducibility is fair but not so good as that for adsorbed BADA. The value for fresh SA-1 does not change upon addition of the 0.05 meq/g-catalyst of n-butylamine (Table 5). This is also the case for SA-1-Na-1. The ε values for the fresh catalysts other than SA-Na-HAcO do not differ within experimental error (Table 6). These findings support the conclusion that the ε_A value of BAP corresponds to the ε value for each fresh catalyst except for SA-Na-HAcO. All the ε values for catalysts sufficiently neutralized, on which only the physically adsorbed neutral species is probably present, are very small compared with the ε_A value. Accordingly, in the calculation of the color change ratio, the ε_P was neglected for all the catalysts, and ε for each fresh catalyst was taken as ε_A for the corresponding one, except for SA-Na-HAcO. For the latter, the average ε value for other fresh catalysts, $(11.5 \pm 1.2) \times 10^3$, was taken as the ε_A value. The value is lower than that in an aqueous sulfuric acid solution of $H_0 = -7.3$ by a factor of about 3.4. The decrease in absorption intensity exceeds that observed for BADA.

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[14] D. S. Noyce and M. J. Jorgensen, *J. Amer. Chem. Soc.*, **84**, 4312 (1962).

Further study has revealed that this remarkable decrease in absorption intensity resulted from contamination with the *cis*-isomer produced by light-induced *trans-cis* isomerization of BAP either in adsorbed state or in solvent, and that the ε_A value of the *trans*-isomer adsorbed on SA-1 corresponded to about 56% of that in a sulfuric acid solution of $H_0=-7.3$.[15] Since the *cis*-isomer is almost as basic as the *trans*-isomer,[14] the use of the spectral data obtained without consideration for contamination with the *cis*-isomer are not likely to lead to a serious error.

A typical titration curve is shown in Fig. 2. Such a curve furnishes the amount of acid sites having an H_0 equal to or lower than −5.6 (Table 4). The acid contents ($H_0 \leq -5.6$) decrease with an increase in sodium content.

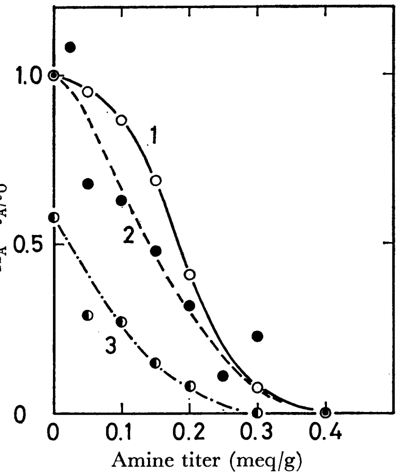

Fig. 2. Titration curves with (1) BAP, (2) NT, and (3) DNT for SA-1.

4-Nitrotoluene (NT). In dilute oleum protonated NT molecules show strong absorption only at 380 mμ. On successive dilution, the band decreases in intensity with the development of a band at 310 mμ due to the solvated neutral molecules, and finally disappears. In the spectrum of NT adsorbed on fresh SA-1, three bands appear near 300, 340, and 500 mμ. In most cases, the band near 300 mμ behaved in a complicated manner upon successive titration: that is, its absorption intensity decreased in an early stage and subsequently increased. On silica gel and silica-alumina catalysts sufficiently neutralized, NT gives only a band at 300 mμ. Thus it is apparent that the physically adsorbed molecules show absorption near 300 mμ, but it is difficult to conclude that the band is due only to the physically adsorbed molecules because of its complicated behavior during the course of titration. On the other hand, the strong band near 340 mμ, with a similar wavelength of absorption to that in acidic solutions, decreased in intensity without exception upon successive titration. This indicates that the band near 340 mμ is due to the species adsorbed in the conjugate-acid form. The very weak band near 500 mμ, which disappears on addition of excess *n*-butylamine, can be attributed to the anion radical of NT.

The absorbance of the band near 340 mμ was determined at 357 mμ, slightly longer than the wavelength of absorption maximum, in order to reduce the contribution from the band around 300 mμ (see Table 5 and 6). The ε value for fresh SA-1 appears to decrease slightly on addition of the 0.05 meq/g-catalyst of *n*-butylamine even when experimental error is considered (Table 5). The ε values for the fresh catalysts vary with catalyst (Table 6), showing that the fresh silica-alumina catalysts differ in their ability to adsorb NT molecules in the conjugate-acid form. Both facts imply that a new criterion is required for the determination of the ε_A value of the indicator.

Neither non-empirical nor empirical methods have been established for the estimation of the molar absorptivity of a certain species in adsorbed state from that in solution. With BADA and BAP, the molar absorptivity of the adsorbed conjugate-acid species has proved to fall to about 70% and to about 56% of that in acidic solution, respectively. If these correlations hold for NT, ε_A will be estimated to be 10.7×10^3 (60%) to 12.5×10^3 (70%) for the adsorbed conjugate-acid species of NT. These values are equal to the ε value observed for fresh SA-1 within experimental error. The assumption may be reasonable in view of the fact that the ε value for fresh SA-1 is substantially constant even on addition of the 0.025 meq/g-catalyst of *n*-butylamine (Table 5). The ε value for fresh SA-1 was therefore taken as the ε_A value for all the silica-alumina catalysts. As the ε_P value for each catalyst, the ε value for the corresponding one neutralized sufficiently with the 0.35—0.4 meq/g-catalyst of *n*-butylamine was taken, since it was not negligible as compared with the ε_A value.

In the calculation of the color change ratio, the complicated behavior of the band near 300 mμ was ignored as in the case of BAP (see Fig. 2 and Table 4). The acid contents ($H_0 \leq -10.5$) decrease with ε for fresh catalyst. The difference of acidity between SA-1-Na-3, SA-Na-HCl, and SA-Na-HAcO may become apparent by using an indicator slightly more basic than NT.

2,4-Dinitrotoluene (DNT). The spectral data in solutions were taken from literature.[16] Protonated DNT absorbs strongly at 340 mμ and moderately near 280 mμ. A band due to strongly solvated neutral DNT appears near 260 mμ. In the spectrum of DNT adsorbed on fresh SA-1, three bands appear: a strong one near 260 mμ, and weak ones near 320 (shoulder) and 500 mμ. On silica gel and SA-1 poisoned sufficiently with *n*-butylamine, DNT shows absorption only near 260 mμ. The intensity of the band near 320 mμ decreased upon successive titration, indicating that it was due to the adsorbed conjugate-acid species, while the band 260 mμ behaved in a similar manner to one near 300 mμ of adsorbed NT. Thus no isosbestic point was observed. The very weak band near 500 mμ can be attributed to the anion radical of DNT.

The absorbance of the band near 320 mμ was deter-

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[15] Presented at the 19th Annual Meeting of the Chemical Society of Japan, Yokohama, April 1966.

[16] J. C. D. Brand, W. C. Horing, and M. B. Thornley, *J. Chem. Soc.*, **1952**, 1374.

mined at 340 mμ in order to reduce the contribution from the band near 260 mμ (see Tables 5 and 6). We see from these tables that an assumption is required for the calculation of the color change ratio of DNT as in the case of NT. The ε_A value for each catalyst was estimated to be 8.2×10^3, which corresponded to 60% of the value in oleum (1.37×10^4),[16] according to the criterion used for NT. The ε value for each catalyst sufficiently neutralized was taken as the ε_P value for the corresponding one (see Fig. 2 and Table 4).

Acid-strength Distribution. The acid strength distributions of acid sites on all of the silica-alumina catalysts are shown in Table 7. They are obtained from Table 4 as the difference of acid contents with two adjacent indicators.

TABLE 7. ACID-STRENGTH DISTRIBUTION[a],[17]

Catalyst	H_0			
	1.5 to −5.6	−5.6 to −10.5	−10.5 to −12.8	≤ -12.8
SA-1	0.05	0.05	0.11	0.02
SA-1-Na-1	0.04	0.09	0.03	0
SA-1-Na-2	0.05	0.09	0.01_5	0
SA-1-Na-3	0.04_5	0.08	0	0
SA-Na-HCl	0.05	0.10	0	0
SA-Na-HAcO	0.11	0.07	0	0

a) In meq/g catalyst.

The original unpoisoned silica-alumina catalyst SA-1 has the largest amount of strong acid sites ($-12.8 < H_0 \leq -10.5$) along with relatively small amounts of the strongest ones ($H_0 \leq -12.8$), moderately strong ones ($-10.5 < H_0 \leq -5.6$), and weak ones ($-5.6 < H_0 \leq 1.5$). This is qualitatively in line with the results of Benesi,[5] who found that the strength of most acid sites on synthetic silica-alumina lies beyond an H_0 of −8.2. Apparently strong acid sites ($H_0 \leq -10.5$) on SA-1 are eliminated as it is poisoned with sodium ions. The effect of alkali-treatment on surface acidity, however, is not a mere disappearance of acid sites but a modification of acid-strength distribution where strong acid sites are eliminated and replaced in some manner with sites of lower acid strength. A similar effect was found for more severely alkali-poisoned silica-alumina by Hirschler[18] using H_R indicators.

Anion Radicals. Reducing ability of alumina and silica-alumina catalysts has recently been demonstrated with tetracyanoethylene[19] and various aromatic nitrocompounds.[20] For example, the latter compounds formed stable anion radicals on these catalysts, giving a three-line ESR spectrum insensitive to molecular oxygen. Adsorption of NT and DNT on fresh SA-1 gave ESR spectra (g value=2.004) similar to that of the adsorbed trinitrobenzene anion radical[20] and insensitive to molecular oxygen. This indicates that stable NT anion radical is formed on the catalyst surface. There seems to be no publication on UV spectra of NT anion radical. Comparison of the UV and ESR data on two different kinds of "free radicals" produced from NT in strongly basic solution[21] with another publication on ESR data[22] shows that one absorption at 538 mμ may be due to the anion radical (the other, 517 mμ). In the light of this and the fact that the surface of alumina became reddish-purple when it adsorbed trinitrobenzene,[20] the very weak bands near 500 mμ for NT and DNT (Table 2) can be attributed to their anion radicals. Accordingly, the wavelength employed for analysis of adsorbed NT or DNT is free from the band due to its anion radical. The concentration of reducing sites on the surface of SA-1 with alumina content of 13% is estimated to be 1×10^{-5} meq/g-catalyst from literature,[20] corresponding to about 1% of that of NT or DNT added. It is therefore concluded that the material balance, $c_A + c_P = c_0$, for each indicator is hardly affected by ignoring the formation of its anion radical. This is also given at least qualitative support by the fact that a reduction of absorptivity observed for the adsorbed conjugate-acid species of NT is not unusual.

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[17] Numerical data before revision was presented by one of the authors (Y.Y.) at the plenary lecture of the 4th International Congress on Catalysis, Moscow, 1968.

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