Acidic Nature of Chemisorption Sites on Silica-Alumina and Alumina Catalysts. Characterization by UV Spectra of Adsorbed *p*-Nitroaniline

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Chemisorbed *p*-nitroaniline (PNA) gives two bands at 245 and 445 nm on silica-alumina and one band at 450 nm on alumina. The present paper deals with the nature of these chemisobed species and of the chemisorption sites. Kinetic studies of PNA chemisorption onto silica-alumina from cyclohexane solution revealed that the chemisorbed species responsible for the 245 nm band was formed with an activation energy by 0.9 kcal/mol smaller than that responsible for the 445 nm band. The two bands on silica-alumina are due conclusively to two different chemisorbed species. Comparison among UV absorption spectra of PNA in various solutions and on various solid surfaces led to the conclusion that the 245 nm band is ascribable to PNA chemisorbed on Brønsted acid sites and the 445 and 450 nm bands to PNA chemisorbed on Lewis acid sites (*i.e.* surface Al^{3+} ions).

The characterization of the surface acid sites of solid catalysts has provided information useful for the clarification of solid acid catalysis. A variety of techniques have been proposed for determining acid properties.[1] Most of them, however, scarcely give information on the type of surface acid sites (Brønsted or Lewis acid). Such information must also be required for the elucidation of reaction mechanism. In recent years, the distinguishment between both types of surface acid sites has been attempted in IR spectroscopic studies of chemisorbed bases. Ammonia,[2] pyridine,[3] and 2,6-dimethylpyridine[4] were employed successfully because their protonated species exhibit IR absorption bands definitely different from those of the species coordinated to Lewis acid sites.

If an indicator is available which shows UV absorption bands distinct from each other when it interacts with Brønsted and Lewis acids, all of the acid strength of acid sites, their content, and their type are possibly determined as an extension of the butylamine titration method. In a previous study,[5] we found that *p*-nitroaniline (PNA) shows two bands at 245 and 445 nm upon chemisorption on silica-alumina catalyst and concluded that these two bands may be due to two different chemisorbed species.

The present study was undertaken in order to confirm further the previous conclusion and to understand the nature of the chemisorbed species and hence of the chemisorption sites. Kinetic studies of PNA chemisorption onto silica-alumina from cyclohexane solution revealed that the chemisorbed species responsible for the 245 nm band was formed with an activation energy by 0.9 kcal/mol smaller than that responsible for the 445 nm band, demonstrating that these two bands are due unambiguously to two different chemisorbed species. Comparison among UV absorption spectra of PNA in various systems (*i.e.*, in solutions and on surfaces) led to the conclusion that the 245 and 445 nm bands are ascribable to PNA coordinated to Brønsted acid sites and to Lewis acid sites (*i.e.* surface Al^{3+} ions), respectively.

Experimental

Materials. The silica-alumina (SA-1, 13% Al_2O_3) and the silica gel (S-3) were used earlier.[6] Alumina (A-1) was prepared by the neutral hydrolysis of aluminum isopropoxide distilled twice immediately before use.[7] Its surface area was 170 m^2/g. Silica gel impregnated with sulfuric acid (SS-3) was prepared by soaking a thin S-3 wafer calcined in air at 550 °C for 4 h in a diluted aqueous solution of sulfuric acid (20%) and then dried in air at about 80 °C overnight. *p*-Nitroaniline (PNA) was a GR grade reagent and dissolved in cyclohexane without further purification. Cyclohexane used was exhaustively dried and degassed as previously described.[6]

Kinetic Adsorption and UV Studies. Procedures were essentially the same as in a previous study,[6] except that a single wafer was used in all experiments.

A wafer of SA-1, after mounted on the rectangular quartz cage, was treated in a dry oxygen stream at 550 °C for 2.5 h and then in a wet oxygen stream at 150 °C for 0.5 h. The wafer was activated at 450 °C and 10^{-4} mmHg for 2 h in the specially designed UV-cell which is transparent in all sides. Back-ground spectra were determined for both the wafer and the solvent, after introduction of cyclohexane (about 3 ml) followed by that of dry nitrogen. A small amount of PNA (2×10^{-7} mol) was added in a dry nitrogen stream onto frozen cyclohexane in the cell kept at 0 °C, in order to prevent the chemisorption of PNA onto the wafer during the course of addition. The capped cell was rapidly warmed on a water bath thermostatted at temperatures of 10 to 80 °C under stirring with a magnetic stirrer. Separate experiments proved that the frozen PNA almost instantaneously reached adsorption temperature with this procedure. The change of PNA concentration with time was followed by UV spectrophotometry for both the wafer and the solvent.

Wafers of A-1 and S-3 were treated in a dry oxygen stream at 500 °C for 2 h and then activated *in situ* under identical conditions with those employed for SA-1 wafers. A wafer of SS-3 was evacuated briefly *in situ* at room temperature immediately after preparation.

UV spectra over the range of 220 to 600 nm were recorded on a Shimadzu multipurpose recording spectrometer Model MPS-50L at room temperature with a control of atmospheric air.

ESR Studies. A 494 mg sample of powdered SA-1 was activated in an adsorption vessel equipped with a conventional ESR-tube. Experimental conditions for oxygen-treatment and activation were the same as employed in kinetic studies. After addition of cyclohexane and PNA (3.9×10^{-6} mol), the vessel was kept at 62 °C for 2 h. The solvent was removed by evaporation under a vacuum, and then the catalyst was transferred into the ESR-tube. ESR spectra were recorded on a JES-3BS-X spectrometer at room temperature.

Results and Discussion

UV Spectra of PNA. UV absorption spectra of PNA on various solid surfaces are shown in Fig. 1 and, together with those in various solutions, are summarized in Table 1. PNA chemisorbed on SA-1 shows two bands at 245 (Band I) and 445 nm (Band II), whereas PNA adsorbed on A-1, S-3 and SS-3 gives a single band.

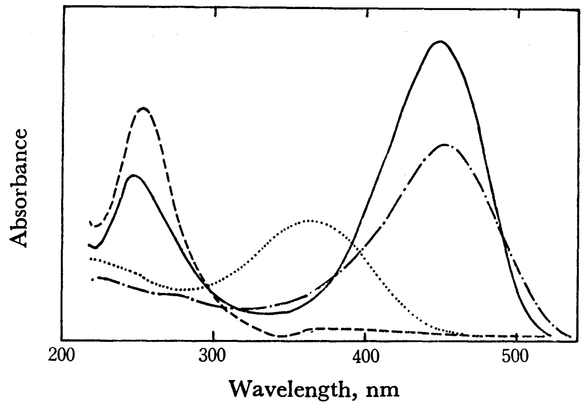

Fig. 1. UV spectra of PNA adsorbed on SA-1 (——), A-1 (-·-), SS-3 (------), and S-3 (······).

TABLE 1. UV ABSORPTION SPECTRA OF PNA ON VARIOUS CATALYSTS AND IN VARIOUS SOLUTIONS (nm)

System		Species		
	Acidic nature	Protonated	Neutral	Coordinated to Al^{3+} ion
on SA-1	L[a] and B[a]	245 (Band I)		445 (Band II)
on A-1	L			450
in $AlBr_3$–$(C_2H_5)_2O$	L			440[b]
in $AlCl_3$–$(C_2H_5)_2O$	L			440[c]
on SS-3	B	252		
in aq H_2SO_4 (20%)	B	255		
on S-3	Nonacidic		365	
in C_2H_5OH	Nonacidic		370	
in cyclo-C_6H_{12}	Nonacidic		322	

a) L and B stand for Lewis and Brønsted acidity, respectively. b) Ref. 8. c) Ref. 9.

Chemisorption of PNA onto SA-1 from Cyclohexane. Chemisorption of PNA onto SA-1 from cyclohexane solution was kinetically investigated in order to determine whether Bands I and II over SA-1 are due to two different chemisorbed species. Figure 2 shows an example of the change of PNA concentration with time. Both Bands I and II increased in intensity with decreasing intensity of the 322 nm band due to PNA in cyclohexane. After initial 2—3 h the 322 nm band completely disappeared and both Bands I and II reached stationary intensities, indicating that the chemisorption was completed. The disappearance of PNA from cyclohexane solution obeyed well a first-order kinetics with respect to the concentration of PNA, as shown in Fig. 3. From the temperature dependence of rate constants for the disappearance of PNA, the overall activation energy was evaluated to be 1.4 kcal/mol for the chemisorption from cyclohexane.

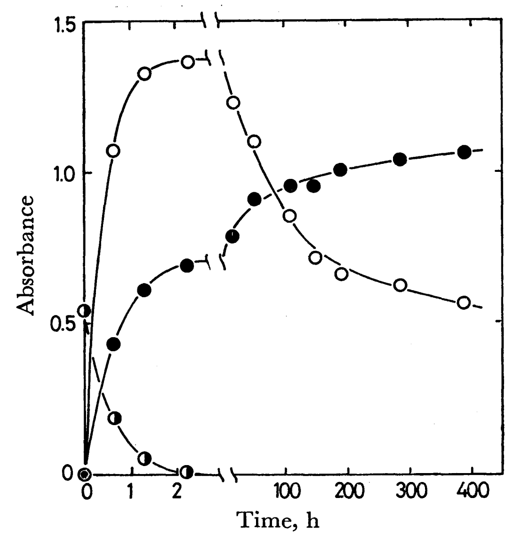

Fig. 2. Change of absorption intensity during chemisorption at 70 °C.
245 (●), 322 (◑), and 445 nm (○) band.

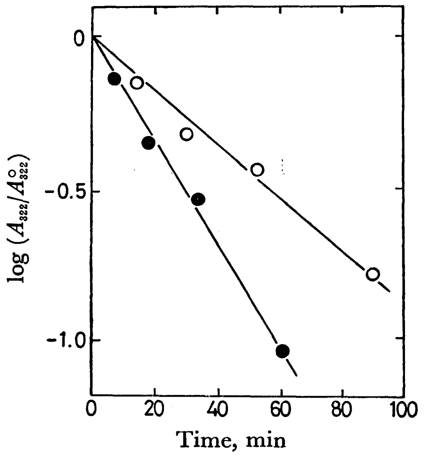

Fig. 3. Disappearance rates of PNA from cyclohexane at 10 (○) and 65 °C (●).

At every temperature, linear correlations were observed between the increment in intensity of both Bands I and II and the decrement in intensity of the 322 nm band: *i.e.*, $\Delta A_{\mathrm{I}} = -\alpha_{\mathrm{I}}\Delta A_{322}$ and $\Delta A_{\mathrm{II}} = -\alpha_{\mathrm{II}}\Delta A_{322}$, where ΔA_{i} is the increment in absorbance of Band I, α_{i} its proportionality constant, as exemplified in Fig. 4. The ratio of the proportionality constants ($\alpha_{\mathrm{II}}/\alpha_{\mathrm{I}}$) *i.e.*, the ratio of the increments in intensity of Bands I and II ($\Delta A_{\mathrm{II}}/\Delta A_{\mathrm{I}}$) at a given time, however, changed depending upon adsorption temperature, as is shown in Fig. 5. If Bands I and II were ascribed to identical chemisorbed species, this ratio would correspond simply to the ratio of the molar extinction coefficients of Bands I and II independent of adsorption temperature. Therefore, the temperature dependence observed demonstrates that Bands I and II are ascribable unambiguously to two different chemisorbed species. As will be described in

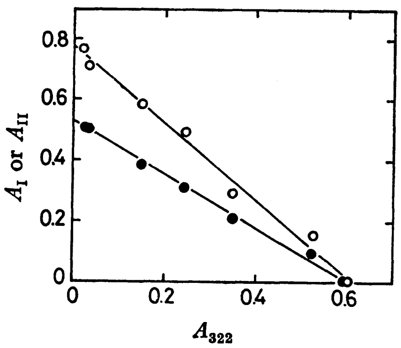

Fig. 4. Ratio of increment in absorbance of Band I (●) or II (○) over decrement in absorbance of 322 nm band (40 °C).

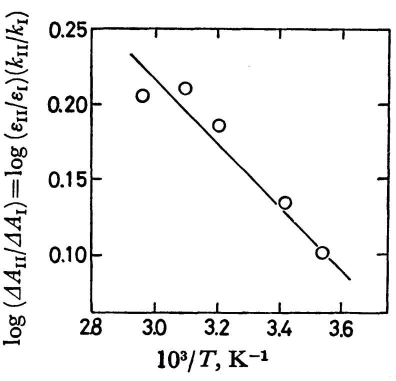

Fig. 5. Difference between activation energies for chemisorption of PNA onto Brønsted acid sites and onto Lewis acid sites.

detail later, these two chemisorbed species correspond to PNA chemisorbed on two types of acid sites different in nature (Sites I and II).

After the completion of chemisorption above 40 °C, the intensity of Band II decreased very slowly with an accompanying increase in intensity of Band I (see Fig. 2), indicating that Band II was just replaced by Band I. This observation provides additional evidence supporting the conclusion that there exist two different chemisorbed species. The observed slow replacement of Band II by Band I is best explained by the following postulation: because the apparent stationary state is far from an equilibrium, the system gradually approaches a true adsorption equilibrium by the migration of less stable chemisorbed species on Site II (responsible for Band II) onto Site I, producing more stable chemisorbed species responsible for Band I. This explanation is in line with the expectation by Polanyi's rule that less stable species become less unfavorable at kinetically controlled stage than at equilibrium. Also, the explanation is consistent with our previous conclusion that the establishment of an adsorption equilibrium of indicators and *n*-butylamine is seriously difficult under the ordinary conditions employed in the butylamine titration method.[10]

Accordingly, the ordinate of Fig. 5 corresponds to the product of the ratio not of equilibrium constants but of the rate constants for chemisorption onto Sites I and II (k_{II}/k_I) and the ratio of molar extinction coefficients for Bands I and II ($\varepsilon_{II}/\varepsilon_I$). The temperature dependence in Fig. 5 thus indicates that the activation energy of the chemisorption of PNA is by 0.9 kcal/mol higher for Site II than for Site I.

Nature of Chemisorption Sites. Inspection of Table 1 will provide interesting information on the nature of the chemisorbed species on SA-1 and hence of the chemisorption sites. The solutions and solid acids employed in the present study can be devided into four groups according to their acidic nature.

As regards the solutions, it has been well established that the acidity of a diluted aqueous solution of sulfuric acid is of the Brønsted type, whereas aluminum bromide and chloride in diethyl ether behave as Lewis acids, and also that ethanol having hydrogen-bonding ability and cyclohexane are both nonacidic. With regard to the solid except for SS-3, the characterization of the surface acidity by means of the IR spectra of adsorbed pyridine indicated that SA-1 has both Lewis and Brønsted acid sites while on A-1 only Lewis acid sites are present, and that S-3 is nonacidic though it has hydrogen-bonding ability,[12] in accord with the results in the literature.[3] SS-3 probably has Brønsted acidity alone.

A noteworthy feature in UV absorption spectra of PNA is that maximal absorption takes place in one or two of three different wavelength regions, depending upon the acidic nature of environments: the first region (240—260 nm), the second (320—370 nm), and the third (440—450 nm) are characteristic for environments of Brønsted acidity, for nonacidic environments, and for environments containing Al^{3+} ions as a Lewis acid, respectively. The second region can be further classified in two subregions: one is the 370 nm region characteristic for environments having hydrogen-bonding ability and the other the 320 nm region characteristic for nonpolar environments.

These considerations lead reasonably to the conclusion that Bands I and II on SA-1 are due to PNA chemisorbed on the Brønsted acid sites and Lewis acid sites (surface Al^{3+} ions), respectively. The 450 nm band on A-1 is ascribed, of course, to PNA chemisorbed on the Lewis acid sites. Reportedly the bathochromic shift from 322 nm in cyclohexane to 370 nm in ethanol is due to the formation of intermolecular hydrogen bonds with the solvents.[12] The 365 nm band on S-3 is therefore ascribed to PNA hydrogen-bonded with the surface, probably with surface hydroxyl groups and oxide ions.

From spectral and reaction-mechanistic evidence, it has been established that besides acidic sites, various sites such as an oxidizing, reducing, and basic site coexist on silica-alumina and alumina surfaces.[13—16] On oxidizing and reducing sites PNA may be converted to radical cations and anions, respectively, by one-electron transfer. In strongly basic media, PNA which is a weak acid of $pK_a = 18.9$ is ionized with the loss of a proton from the amino group to produce an anion giving rise to absorption at 467 nm.[17] This wavelength is close to that of Band II or of the 450 nm band on A-1. Such an ionization may also take place over basic sites on SA-1 and A-1. However, we ruled out the formation of either ionic radicals or anions as a main chemisorbed species responsible for Band II on the following grounds: (a) the presumption that a system of $AlBr_3$ (or $AlCl_3$)–$(C_2H_5)_2O$ has neither a strong basicity nor the ability of oxidation or reduction is quite reasonable, (b) Band II, as well as Band I, was unaffected by the introduction of gaseous oxygen, which enhances the ability of oxidation of silica-alumina and alumina,[18)] (c) the surface concentration of the chemisorbed species responsible for Band II on SA-1 was estimated to amount to about 500 times that of reducing sites of silica-alumina with an alumina content of 13%,[14)] (d) the ESR spectrum of PNA chemisorbed on SA-1 (g-value$=2.00$) indicates that the surface concentration of radical species amounts to 5×10^{15} spins/g and corresponds to about one thousandth of that of chemisorbed PNA, and (e) the surface basicities of SA-1 and A-1 are both too weak to ionize PNA, as evidenced by the experimental fact that both catalysts exhibited no absorption peaks around 500 nm upon adsorption of 2,4-dinitroaniline,[19)] which is a less weak acid of $pK_a=15.0$ and produces in strongly basic media an anion giving rise to absorption at 388 and 535 nm.[20)] This statement is also applicable to Band I characteristic of an anilinium-ion type of species.

Mohammad and Satchell[8)] have attributed the 440 nm band observed in their system, PNA–$AlBr_3$ (or $AlCl_3$)–$(C_2H_5)_2O$, to a charge-transfer type of absorption by the complex, and proposed a structural model in which the aluminum ion coordinates weakly to the amino nitrogen atom of PNA. Consistent with this model is our interpretation that the chemisorbed species on Lewis acid sites (*i.e.*, surface Al^{3+} ions) is less stable than that on Brønsted acid sites. It is not obvious why Lewis acid sites of SA-1 should interact less strongly with PNA than do Brønsted acid sites, in contrast with the fact that pyridine coordinates more strongly to Lewis acid sites than to Brønsted acid sites of SA-1.[11)]

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