The Existence of Acid Centers of a Lewis Type on Silica-Alumina Surface

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Recently, attention has been paid to the nature of acid centers on silica-alumina surface[1]. In order to study this problem spectroscopically, we have measured electronic spectra of some reagents adsorbed from their cyclohexane solutions on silica-alumina according to a procedure described by Robin[2].

A sample of silica-alumina was kindly supplied by Professor Shiba of Tokyo Institute of Technology and stated to contain approximately 13% alumina and no ferric ion. This sample was used as an adsorbent without further heat treatment (SA-1), or after heat treatment for 3 hr. at 110°C (SA-2), for 3 hr. at 430°C (SA-3) in dry air.

By using benzeneazodiphenylamine (pK_a: 1.52) as Walling's acid-base indicator, it was found that the adsorbent shows surface acidity. As is clearly seen from Fig. 1, benzeneazodiphenylamine adsorbed exhibits the two absorption bands at 440 mμ and 538 mμ, which are evidently associated with the free base of the dye and its conjugated acid respectively. The latter specimen is produced by the reaction of the free base with a proton of protonic acid or aluminum atom as Lewis acid. The heat treatment of adsorbents increases the intensity of the acid band, indicating the increase of the amount of acid centers on the silica-alumina surface.

To obtain some information on whether or not these acid centers involve those of a Lewis type, *p*-phenylenediamine, which is a typical electron donor and is suitable for detecting electron accepting ability of the opponent entity, was adsorbed on silica-alumina adsorbents and its absorption spectrum was examined. The absorption spectrum of *p*-phenylenediamine adsorbed showed two characteristic bands at 324 mμ and 468 mμ, as shown in Fig. 2. The former band was identified with that of *p*-phenylenediamine in alcohol (λ_{max}: 312 mμ)[3] and the latter band with that of its semiquinone

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[3] L. C. Anderson and J. W. Steedly, Jr., *J. Am. Chem. Soc.*, 76, 5144 (1954).

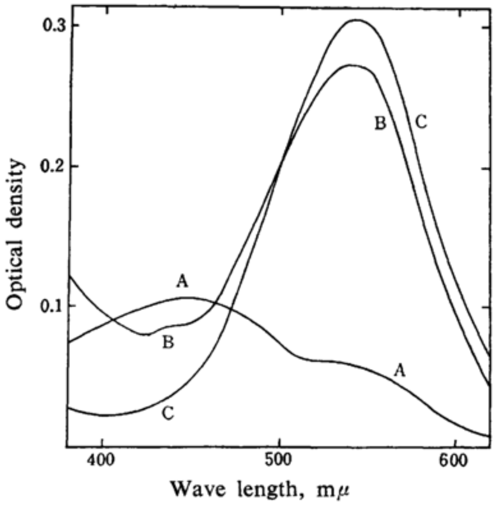

Fig. 1. Absorption spectra of benzeneazodiphenylamine adsorbed on silica-alumina (A, SA-1; B, SA-2; C, SA-3).

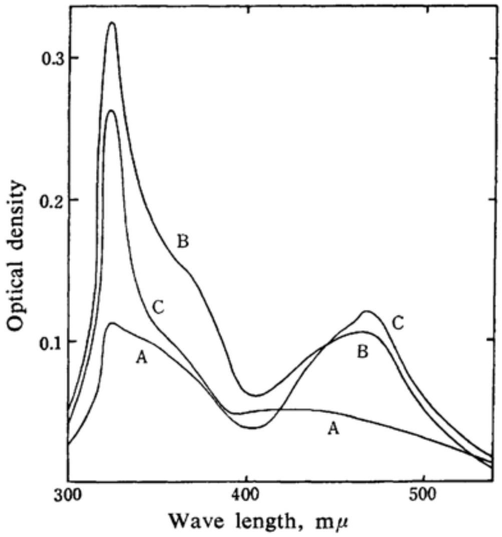

Fig. 2. Absorption spectra of p-phenylenediamine adsorbed on silica alumina (A, SA-1; B, SA-2; C, SA-3.)

cation radical $(NH_2C_6H_4NH_2)^+$ in water (λ_{max}: 462 mμ)[4]. Fig. 2 shows also that the intensity of absorption band of semiquinone increases with the increasing temperatures of heat treatment of adsorbent. The existence of semiquinone radicals on the adsorbent was also confirmed by the appearence of electron spin resonance spectrum. On the other hand, semiquinone radical could not be observed with the absorption spectrum of p-phenylenediamine adsorbed on a silica gel sample containing protonic acid.

The present results lead us to consider that the vacant $3p$ orbital of the aluminum atom on silica-alumina surface accepts one electron from the highest occupied π orbital of the p-phenylenediamine molecule adsorbed and, therefore, aluminum atoms react with a base as Lewis acid centers, the structure of which has been proposed by Mills et al.[5]. It was also shown that the amount of Lewis acid centers increases with the temperature of heat treatment of the silica-alumina sample. The method of electronic spectra studied by us has given a more direct evidence for the existence of Lewis acid centers on silica-alumina sample than that obtained by other methods hitherto reported[1].

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[4] L. Michaelis, M. P. Schubert and S. Granick, ibid., **61**, 1981 (1939).

[5] T. H. Milliken, Jr., G. H. Mills and A. G. Oblad, *Disc. Faraday Soc.*, No. 8, 279 (1950).