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The Estimation of the Surface Properties of Metal Oxides by the Use of TCNQ Adsorption. II. The Electron-donor Property of Silica-Alumina, Silica-Titania, and Alumina-Titania System Surfaces

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The electron-donor property of silica–alumina, silica–titania, and alumina–titania system surfaces was investigated by means of TCNQ adsorption. When TCNQ was adsorbed on the surfaces of the metal oxide systems from its acetonitrile solution, the surfaces of the metal oxides acquired the coloration characteristic of each oxide. The coloration was caused by the formation of TCNQ anion radicals on the metal oxide surfaces. The presence of the TCNQ anion radicals was confirmed by studying the ESR absorption and the electronic spectrum. The silica–alumina, silica–titania, and alumina–titania systems showed lower radical-ion-forming activity (electron-donating power) than the parent oxides-silica, alumina, and titania. The change in the activity with the composition was characteristic of each metal oxide system.

The presence of electron-transfer sites on the surface of certain metal oxides is well known.[1–6] Recently, it has been reported that the formation of TCNQ anion radicals takes place on some metal oxide surfaces, and that the electron-donor property of metal oxides can be estimated by the use of 7,7,8,8-tetracyanoquinodimethane (TCNQ) adsorption.[6]

The present paper will describe the electron-donor property of silica–alumina, silica–titania, and alumina–titania systems as studied by means of TCNQ adsorption.

Experimental

Materials. The samples of the silica–alumina, silica–titania, and alumina–titania systems were prepared by the co-hydrolysis of silicon ethoxide and aluminium butoxide mixtures, silicon ethoxide and titanium butoxide mixtures, and aluminium butoxide and titanium butoxide mixtures, respectively, in different molar ratios. Excess aqueous ethanol was vigorously stirred into the alcoholic solution of alkoxides. Stirring was continued for 10 hr at a temperature near the boiling point. The precipitate was then separated by

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[4] B. D. Flockhart, J. A. N. Scott, and R. C. Pink, *Trans. Faraday Soc.*, **62**, 730 (1966).

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[6] H. Hosaka and K. Meguro, This Bulletin, **44**, 2616 (1971).

centrifuging, thoroughly washed with water and methanol, finely ground, and then evacuated at 100°C until the residual pressure was less than 10^{-5} Torr. The complete hydrolysis of these alkoxides was confirmed by studying the infrared spectra. The dried products were calcined for 2 hr at 500°C.

The composition of the metal oxide systems was measured with a Rigaku Denki X-ray vacuum spectrograph by means of X-ray fluorometry. The abbreviations used are as follows: S, silica; A, alumina; T, titania; 4SA, SA, and S4A, silica–aluminas containing 35, 64, and 81% alumina; 4ST, ST, and S4T, silica–titanias containing 21, 55, and 83% titania; 4AT, AT, and A4T, alumina–titanias containing 28, 62, and 83% titania, respectively.

The crystal features as determined by X-ray diffractometry, and the surface areas as determined by studying the nitrogen adsorption of the metal oxides, are set out in Table 1.

TCNQ was synthesized from the condensation product of 1,4-cyclohexanedione and malononitrile.[7] This was purified by repeated recrystallization. The purity was checked by elemental analysis, by the measurement of the melting point, and by spectrophotometry.[6]

Apparatus and Procedure. The metal oxide was placed in a flask which was attached to a high-vacuum line and outgassed at 10^{-5} Torr for 1 hr at 100°C, and then cooled to 25°C *in vacuo* prior to the TCNQ adsorption. A solution of TCNQ in acetonitrile (10 mM) was then poured into the flask through a stop cock. Subsequently, the contents of the flask were transferred into an L-type test tube and then shaken for 2 hr at 25°C. After this shaking, the metal oxide was collected by centrifuging and dried at room temperature *in vacuo*. The dried sample was used for the measurement of the electronic spectrum and was evacuated at 10^{-5} Torr for the ESR measurement.

The ESR spectra were measured by means of a Japan Electrons Optics Laboratory JES-3BS-Xtype ESR spectrometer operating at a cavity resonance frequency of 9400 Hz with 100 kHz modulation. The g-value was obtained by comparison with the value for Mn^{2+}. The radical concentration (spin conc.) was estimated by comparing the peak-to-peak height on the first derivative curves with that of an internal-standard Mn^{2+} sample.

The electronic spectra of the samples were measured by means of a diffuse-reflectance spectrophotometer.

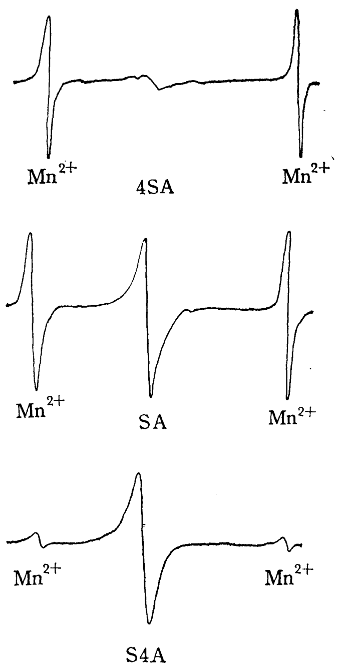

Fig. 1. ESR spectra from TCNQ adsorbed on the silica–alumina systems.

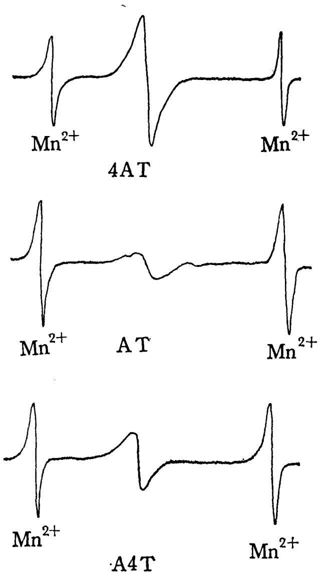

Fig. 2. ESR spectra from TCNQ adsorbed on the alumina–titania systems.

Results and Discussion

When TCNQ was adsorbed on the surfaces of the silica–alumina, silica–titania, and alumina–titania from its acetonitrile solution at room temperature, the surfaces of the metal oxides acquired the colorations characteristic of each oxide, as is shown in Table 1. The same colorations were observed when the metal oxides were ground with TCNQ crystal. The colorations of the metal oxide surfaces suggest that new adsorbed species are formed on the surfaces. This suggestion was confirmed by the evidence that the colored metal oxides showed ESR absorptions, indicating the presence of free radical species. The spectra are unresolved (Figs. 1—2; g-values, 2.011), which can be explained by the fact that the anisotropy of the hyperfine structure arises from the lack of motional degrees of freedom. The state of the adsorbed species was studied by means of the electronic spectra in addition to the ESR spectra. The electronic spectra of the colored samples are illustrated in Figs. 3—5. The bands appearing below 400 mμ are common to all the metal oxides and may be supposed to correspond to the physically-adsorbed state of neutral TCNQ, which has its absorption band at 395 mμ.[8] In the case of the silica–titania and alumina–titania systems, this assignment does not hold completely because the titania has its characteristic band in the same region. The absorption bands in the visible region observed in the cases of the silica–alumina, silica–titania, and

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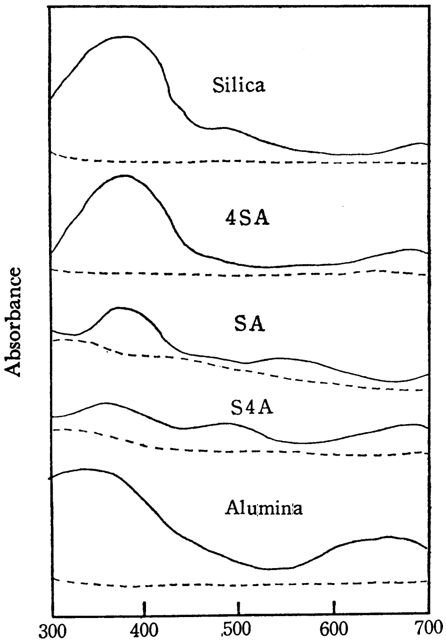

Fig. 3. Electronic spectra from TCNQ adsorbed on the silica–alumina systems. Dotted line, silica–aluminas prior to adsorption.

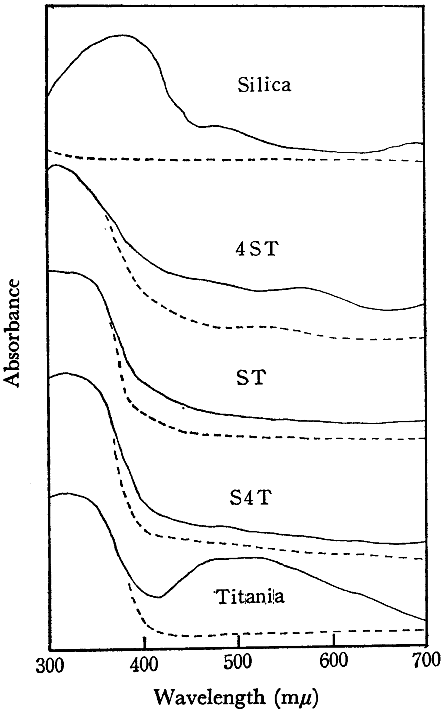

Fig. 4. Electronic spectra from TCNQ adsorbed on the silica–titania systems. Dotted line, silica–titanias prior to adsorption.

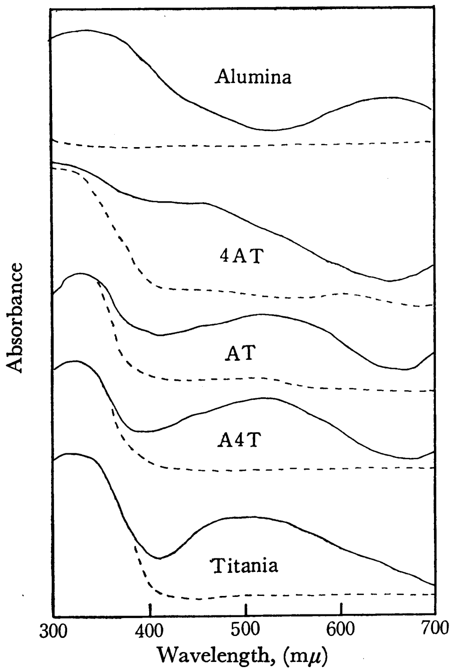

Fig. 5. Electronic spectra from TCNQ adsorbed on the alumina–titania systems. Dotted line, alumina–titanias prior to adsorption.

alumina–titania systems can be attributed to neither TCNQ nor the metal oxides. The bands near 600 mμ probably stem from the dimer TCNQ anion radical, which absorbs light at 643 mμ.[9] They are very broad and have not been assigned with certainty, but support is given by the characteristic features that neutral TCNQ absorbs only at 395 mμ, that TCNQ has a high electron affinity, and that the TCNQ anion radical derivatives are stable even at room temperature.[10–13]

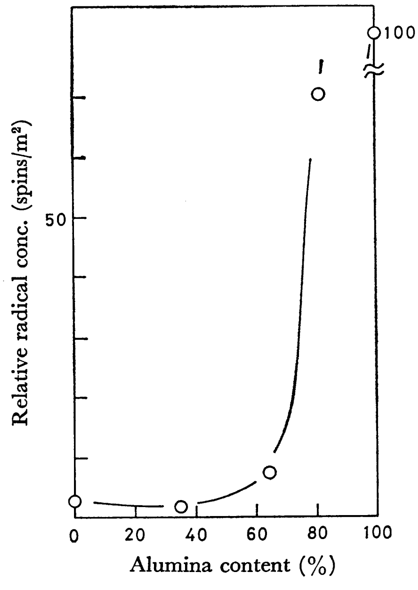

Fig. 6. The change in TCNQ anion radical forming activity of the silica–alumina systems with composition.

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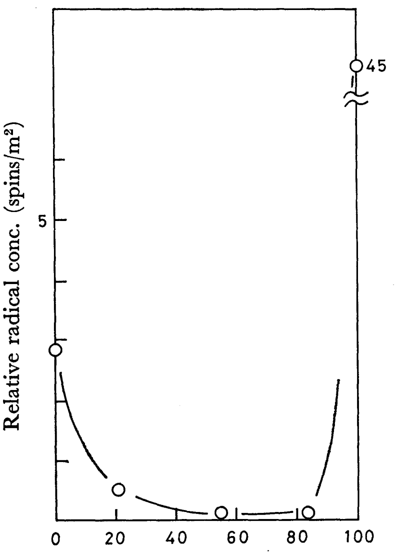

Fig. 7. The change in TCNQ anion radical forming activity of the silica-titania systems with composition.

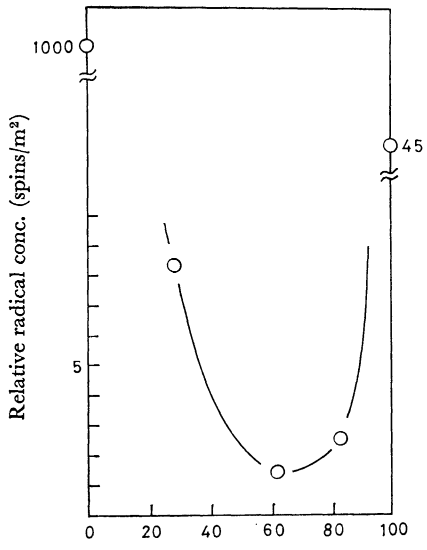

Fig. 8. The change in TCNQ anion radical forming activity of the alumina-titania systems with composition.

In view of the ESR and the electronic spectra, it is confirmed that radical ions are formed from TCNQ on the metal oxide surfaces as a result of electron transfer to TCNQ from the metal oxide surfaces.

The TCNQ anion-radical-forming activity of the metal oxide surfaces is shown in Table 1 and Figs. 6—8. The activity is reflected in the saturation of the color of TCNQ on the metal-oxide surfaces and the increase in absorbance at C–T band. The activity sequence and the color of the samples were found to be: S4A (greenish light grey)>SA (light brown)>4SA (brown tinged white); 4ST (pink)>S4T (brown tinged white)>ST (colorless); 4AT (orange)>A4T (deep pink)>AT (red brown).

The silica–alumina, silica–titania, and alumina–titania systems showed much less activity than the parent oxides-silica, alumina, and titania. The systems exhibit surface properties (surface area, heat of immersion, hydrophilicity, and surface acidity) which would not be qualitatively predicted from a consideration of the independent properties of the parent oxides.14–16)

Flockhart *et al.*5) have reported that typical silica–alumina cracking catalysts have negligible reducing (electron donating) power and that silica–aluminas of a higher alumina content possess an appreciable reducing activity, but this may be associated with the presence, in the conglomerate, of a pure alumina phase. It is well known that the –Si–O–Al– structure forms a strong acid site,17–28) but the formation of an electron-donor site can not be expected. In the present work, all of the silica–alumina systems (4SA, SA, and S4A) showed appreciable radical-forming activity and the activity increased with an increase in the alumina content. However, the silica–alumina systems had much less activity than the alumina. The steep fall in the activity between the silica–alumina system and the alumina suggests that the pure alumina phase is present only a little on the silica–alumina surfaces. The activity increases gradually between 4SA and SA, and then increases steeply between SA and S4A. This suggests the existence of a small part of a pure alumina phase on the surface of S4A. The existence of the pure alumina phase is confirmed by the appearance of the weak band at about 650 mμ in S4A corresponding to the C–T band of TCNQ adsorbed on the alumina.

The surface hydroxyl ion may be one of the electron-donor sites.5,6) Hall *et al.*29) reported that the greater part of surface hydroxyls on silica–alumina catalyst consisted of SiOH. SiOH is much more stable than AlOH,30) and shows little radical-forming activity.6) The low activity of the silica–alumina systems agreed with Hall's results.

The change in the activity of the silica–alumina systems with the alumina content was approximately inverse to that of the surface acidity.15)

The silica–titania systems had negligible radical-

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Table 1. Summary of the TCNQ adsorption

Sample	Composition	Crystal features by X-ray diffraction	Surface area (m^2/g)	The color of the metal oxide surface after TCNQ adsorption	The relative radical concentration (radical conc./m^2)
silica		amorphous	600	yellow	2.8
alumina		weak γ-Al_2O_3 lines	263	blue green	1000
titania		weak anatase lines	64	violet	45
4SA	35% Al_2O_3	amorphous	263	brown tinged white	1.3
SA	64% Al_2O_3	amorphous	279	light brown	7.2
S4A	81% Al_2O_3	amorphous	367	greenish light grey	70
4ST	21% TiO_2	amorphous	348	pink	0.5
ST	55% TiO_2	amorphous	343	colorless	0.14
S4T	83% TiO_2	weak anatase lines	239	brown tinged white	0.2
4AT	28% TiO_2	amorphous	331	orange	8.3
AT	62% TiO_2	amorphous	377	red brown	1.4
A4T	83% TiO_2	weak anatase lines	195	deep pink	2.5

forming activity, and the C–T band scarcely appeared at all. This result suggests that the pure titania phase is present only a little on the silica–titania surfaces. It is noteworthy that a weak anatase line in the X-ray diffraction pattern of the S4T suggests the presence, in the conglomerate, of a pure titania phase, but the S4T had negligible radical-forming activity.

The alumina–titania systems showed much less radical-forming activity than the parent oxides-alumina and titania. The TCNQ adsorbed on the alumina–titania systems showed the C–T band at about 500 mμ corresponding to the TCNQ adsorbed on the titania. This observation suggests the presence of a pure titania phase and the absence of a pure alumina phase on the alumina–titania system surfaces. The radical-forming activity decreases steeply between the alumina and 4AT, decreases gradually between 4AT and AT, increases between AT and A4T, and increases markedly between A4T and the titania. The AT has showed the most characteristic surface properties among the alumina–titania systems.[14)]

The TCNQ anion radical-forming activity has been proposed as a convenient method for estimating the electron-donor property of metal oxide surfaces.[6)] In the present paper, the electron-donor property of silica–alumina, silica–titania, and alumina–titania systems has been revealed and information regarding the surface structure of the mixed-oxide systems has been obtained by means of studying the radical-forming activity and the wavelength of the C–T band.