The Estimation of the Surface Properties of Metal Oxides by the Use of TCNQ Adsorption

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The electron-donor properties of metal oxides (magnesia, alumina, silica, titania, zinc oxide, and nickel oxide) were investigated by means of TCNQ adsorption. When TCNQ was adsorbed on the surfaces of the metal oxides from its acetonitrile solution, the surfaces of the metal oxides acquired the colorations 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 on the colored metal oxide surfaces was confirmed by studying the ESR absorption and electronic spectra. The radicals were formed as a result of electron transfer to TCNQ from the metal oxide surfaces. The order of the radical-forming activity, determined by ESR, was as follows: magnesia> zinc oxide>alumina>titania>silica>nickel oxide. The electron-donor property of the metal oxide surfaces might be dependent on the natures of the semiconductor and the surface hydroxyl ion.

During the past decade, there has been much discussion about the natures of the acid and base present on metal oxide surfaces, and their relevance in catalysis has been extensively investigated. Spectroscopic studies have established the existence of strong electrophilic centers on the silica-alumina surface and the formation of cation radical from hydrocarbons at the same centers.[1–3] On the assumption that cation radicals are formed on Lewis-acid sites, the formation of radical ions at the surface of the silica-alumina catalyst, *i.e.*, the electron-accepting property of the silica-alumina surface, has been widely studied.[1–3] The nature of the site responsible for the electron transfer process is of wide interest. Recently, Flockhart *et al.*[4] studied the formation of the TCNE anion radical at alumina surfaces, *i.e.*, the electron-donor properties of aluminas; however, there have been few reports about the electron-donor properties of metal oxides. In this work, it was demonstrated that when 7,7,8,8-tetracyanoquinodimethan (TCNQ), which was one of the strongest electron acceptors, was adsorbed onto magnesia, alumina, silica, titania, zinc oxide, and nickel oxide, TCNQ anion radicals were formed as a result of electron transfer to TCNQ from the metal oxide surfaces. Comparing the radical-forming activity of the metal oxides, we revealed the electron-donor properties of the metal oxides.

Experimental

Materials. The titania, alumina, and silica were prepared by the hydrolysis of titanium tetra-butoxide, aluminium *s*-butoxide, and silicon ethoxide, purified by distillation. Excess aqueous ethanol was vigorously stirred into the alcoholic solution of alkoxide. Stirring was continued for 10 hr at a temperature near the boiling point. The precipitate was then separated by centrifuging, thoroughly washed with alcohol, 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 infrared spectra. The dried products were calcined for 2 hr at 500°C.

The magnesia, zinc oxide, and nickel oxide were obtained by the thermal decomposition of their carbonates (G. R.) at 500°C for 2 hr in an electric furnace.

The crystal structures of the metal oxides, as determined by X-ray diffractometry, were as follows: the titania, anatase; the alumina, γ-alumina; the silica, amorphous. The X-ray diffraction patterns of the magnesia, zinc oxide, and nickel oxide showed typical lines.

The surface areas of the metal oxides, as determined by nitrogen adsorption, were as follows: the titania, 64; the alumina, 263; the silica, 600; the magnesia, 134; the zinc oxide, 7.10 m^2/g.

TCNQ was synthesized from the condensation product of 1,4-cyclohexanedione and malononitrile.[5] This was the purified by repeated recrystallization. The purity was checked by elemental analysis (Found: C, 70.22; H, 2.60; N, 27.8%, Calcd.: C, 70.59; H, 1.97; N, 27.42%), measurement of the melting point (280.0—283.0°C), and spectrophotometry.

Apparatus and Procedure. The metal oxide was placed in a flask which was attached directly 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 content in the flask was transferred into an L-type test tube and then shaken for 2 hr at 25°C. After 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-X-type 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.) were estimated by comparing the peak-to-peak heights on the first derivative curves with those of an internal-standard Mn^{2+} sample.

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

Results and Discussion

When TCNQ was adsorbed on the surfaces of the magnesia, alumina, silica, titania, and zinc oxide

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from its acetonitrile solution at room temperature, the surfaces of the metal oxides acquired the coloration characteristic of each oxide. The colors were as follows: magnesia, blue green; alumina, blue green; silica, yellow; titania, violet; zinc oxide, greyish green. 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 show ESR absorptions, indicating the presence of free radical species. The spectra are unresolved (Figs. 1—5; *g*-values, 2.011); this 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. 1—5. The bands appearing below 400 mμ are common to all the oxides and may be supposed to correspond to the physically-adsorbed state of neutral TCNQ, which has the absorption band at 395 mμ.[5] In the cases of titania and zinc oxide, this assignment does not hold completely because the titania

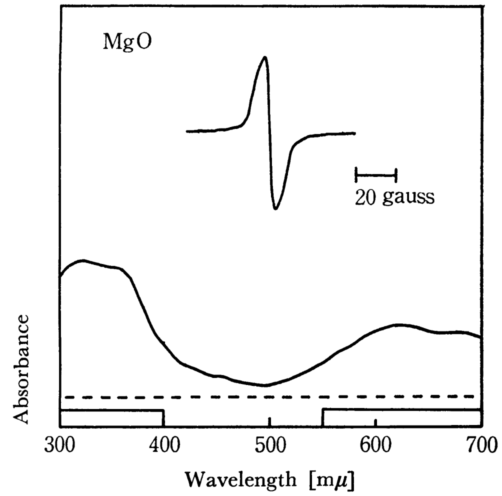

Fig. 1. ESR and electronic spectra from TCNQ adsorbed on the magnesia. Dotted line, MgO prior to adsorption.

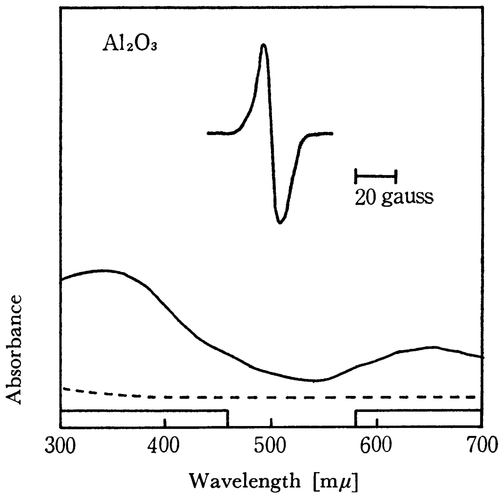

Fig. 2. ESR and electronic spectra from TCNQ adsorbed on the alumina. Dotted line, Al_2O_3 prior to adsorption.

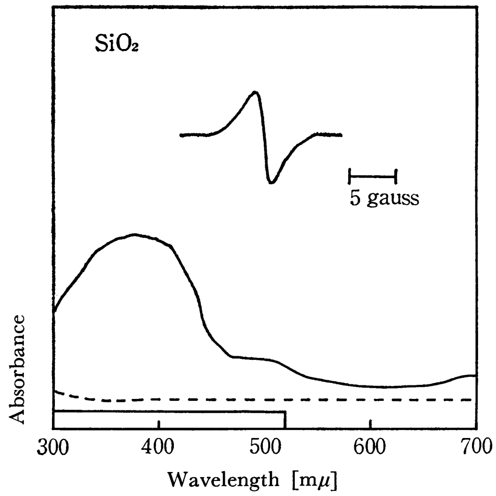

Fig. 3. ESR and electronic spectra from TCNQ adsorbed on the silica. Dotted line, SiO_2 prior to adsorption.

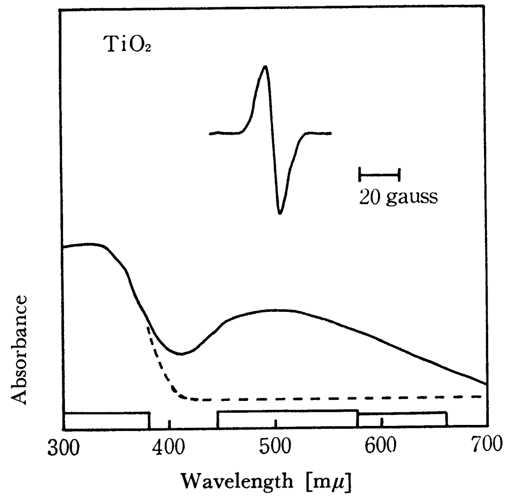

Fig. 4. ESR and electronic spectra from TCNQ adsorbed on the titania. Dotted line, TiO_2 prior to adsorption.

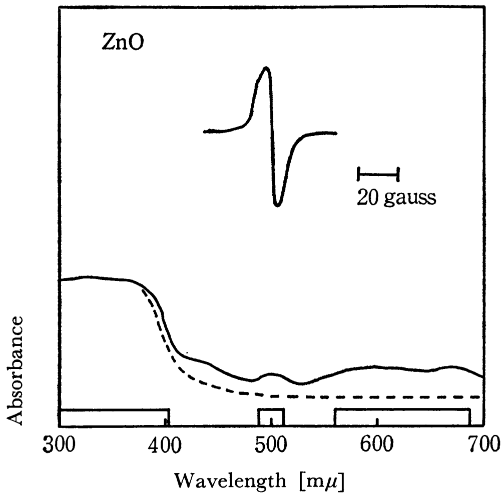

Fig. 5. ESR and electronic spectra from TCNQ adsorbed on the zinc oxide. Dotted line, ZnO prior to adsorption.

TABLE 1. SUMMARY OF THE TCNQ ADSORPTION

	Type of semiconductor	The color of the metal oxide surface after TCNQ adsorption	The relative radical concentration (radical conc./m^2)
MgO	insulator	blue green	100
Al_2O_3	insulator	blue green	38
SiO_2	insulator	yellow	0.11
TiO_2	*n*-type semiconductor	violet	1.6
ZnO	*n*-type semiconductor	greyish green	47
NiO	*p*-type semiconductor		0.00

and zinc oxide have characteristic bands in the same region. The absorption bands in the visible region observed in the cases of magnesia, alumina, silica, titania, and zinc oxide 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.[6] They are very broad and have not been assigned with certainty, but this tentative attribution is supported 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.[7–10] The ESR and the electronic spectra confirm that radical ions are formed as a result of electron transfer to TCNQ from the metal-oxide surfaces.

The radical-forming activities of the metal oxide surfaces, estimated by means of the relative radical concentration (spin number/m^2), are as follows: magnesia, 100; zinc oxide, 47; alumina, 38: titania, 1.6; silica, 0.11; nickel oxide, 0.00. The nature of the site responsible for the electron-transfer process is not well understood. However, it may be suggested that two types of active sites exist on the surfaces. One of these has an anion deficiency (*n*-type semiconductor), and the other has a hydroxyl ion on the oxide surface.

The type of surface complex by the mechanism of electron transfer from a semiconductor was found in titania, zinc oxide, and nickel oxide. A major way of introducing donors and acceptors into semiconductors arises from the nonstoichiometry in compounds.[11] The nonstoichiometry can arise either by virtue of vacant lattice sites for one component of the compound, or because of an excess of one component located in interstitial sites. A donor center can result from the trapping of one or more electrons in an anion vacancy. Semiconductors which have an excess of conduction electrons over holes are normally called "*n*-type", because their conductivity arises from negative-current carriers. Those with an excess of holes are called "*p*-type," as the carriers are positive. *n*-Type semiconductors have anion deficiencies (or cation excesses), while *p*-type semiconductors have anion excesses (or cation deficiencies). For example, zinc oxide,[12,13] titania,[14] and nickel oxide are as follows;

$$ZnO \rightleftarrows O_v{}^{+} + \ominus + 1/2\,O_2(g)$$

$$ZnO \rightleftarrows O_v{}^{2+} + 2\ominus + 1/2\,O_2(g)$$

where O_v is an O vacancy and where $\ominus$ is a free electron. An O_v in zinc oxide is a donor.

$$2TiO_2 \rightleftarrows Ti_2O_3 + (O_v{}^{2+}\cdot 2\ominus)^{\circ} + 1/2\,O_2(g)$$

$$(O_v{}^{2+}\cdot 2\ominus)^{\circ} \rightleftarrows (O_v{}^{2+}\cdot\ominus)^{+} + \ominus$$

where $(O_v{}^{2+}\cdot 2\ominus)^{\circ}$ is a neutral, charged O vacancy.

$$1/2\,O_2(g) \rightleftarrows NiO + Ni_{(v)}{}^{2-} + 2\oplus$$

$$1/2\,O_2(g) \rightleftarrows NiO + Ni_{(v)}{}^{2-}\cdot\oplus + \oplus$$

where $Ni_{(v)}$ is a Ni vacancy and where $\oplus$ is a positive hole. A Ni vacancy in nickel oxide is an acceptor. From this fact, it is reasonable that nickel oxide has no radical-forming activity. If TCNQ radical ions are formed by interaction with free electrons derived from the intrinsic or extrinsic defects present on the surface or in the bulk of the solid, magnesia, alumina, and silica, which are insulators, they would not normally be expected to participate in a charge-transfer adsorption process because of the lack of a free electron. Flockhart *et al.*[4] have suggested that the electron-donor defect site on the surface of alumina was created at activation temperatures of above 500°C.

The second active site may be the surface hydroxyl ion. Surface hydroxyl groups can be expected on all metal oxides.[15] The ionization potential of hydroxyl ions is comparatively small ($\sim$2.6 eV in the gas phase[16]); therefore, the possibility of its participation in oxidation-reduction processes of the type:

$$OH^- + A \rightarrow OH + A^-$$

where A is an electron-acceptor, can not be excluded. Indeed, Fomin *et al.*[17] have shown that electron

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transfer from the hydroxyl ion can and does occur in certain solvent systems provided a suitable acceptor molecule is present. Flockhart *et al.*[4] have reported that the electron-donor site on the alumina surface might be associated with the presence on the surface of unsolvated hydroxyl ions. As alumina, magnesia, and silica surfaces are usually covered with hydroxyl groups,[18] the charge-transfer adsorptions of TCNQ on alumina, magnesia, and silica may result from the electron-transfer from surface hydroxyl. Stöber[15] found that, even after thorough outgassing at 100°C, one molecule of externally tightly adsorbed water is retained for each two silanol groups in the amorphous silica. This surprising result was confirmed by Boehm *et al.*[19] using chemical reactions as well as deuterium exchange. Lee and Weller[20] confirmed the existence of surface hydroxyl groups on alumina which had been dehydrated at 500°C. It is reasonable to assume that these electron-transfer from hydroxyl ions on the metal oxides which have been calcined at a high temperature such as 500°C. Surface hydroxyls may exist on all of the samples. However, surface hydroxyls on metal oxides are shown to differ in chemical properties. Surface silanol groups are much more stable than Al–OH groups.[18] Differences in acidity among the hydroxyl groups of several oxide surfaces have been reported.[21] These results suggest that the hydroxyl ions of the metal oxide surfaces have different electron-donor properties (radical-forming activities).

The radical-forming activity, *i.e.*, the electron-donor property of the metal oxide surfaces, may be associated with the natures of the semiconductor and the surface hydroxyl ion. The radical-forming activity determined by TCNQ adsorption is a new convenient method of estimating the electron-donor property of metal oxide surfaces.

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