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OH^- as a Possible Cause of the Electron-donor Property of the ZrO_2-TiO_2 System

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Synopsis. The electron-donor property of the zirconia-titania system was investigated by means of the adsorption of TCNQ. The TCNQ anion radicals were formed as a result of electron transfer to adsorbed TCNQ from the zirconia-titania surface. The radical concentration on the zirconia-titania system decreased with a increase in the titania content, reached a minimum point at a titania content of 38%, and then increased with the further increase in the titania content. This behavior can explained by the relative amount of OH^- sites, which must be proportional to both, or either one, the relative contents of the pure zirconia phase or the pure titania phase existing on the surface of the zirconia-titania system.

The formation of anion-radical ions on electron-donor sites of some simple metal oxide surfaces has been reported, these electron-donor sites have been also associated with the surface hydroxide ions and the surface oxide ions.[1-5] On the other hand, Flockhart *et al.*[1] studied the electron-donor property of two-component metal oxide systems, they found that silica-aluminas had negligible electron-donating power at low alumina contents, but silica-aluminas of high alumina contents possessed strong electron-donor properties. Hosaka *et al.*[6] studied the electron-donor property of silica-alumina, silica-titania, and alumina-titania systems in the base of the results of the adsorption of 7,7,8,8-tetracyanoquinodimethane (TCNQ), they found that the difference in electron-donor properties among metal oxide systems can be characterized by the change in the concentration of TCNQ anion radicals formed.

These studies are of metal oxides in the Group IV elements. This group, starting with silica, is of interest with respect to changes in size of the metal, coordination, and bonding type. In the present work, the electron-donor property of the zirconia-titania system, estimated by means of the TCNQ adsorption, will be reported.

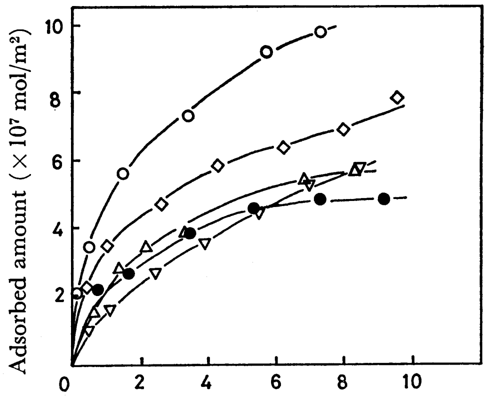
The preparation of zirconia-titania samples was carried out as follows: Zirconium tetrachloride and titanium one mixtures, in different molar ratios, were dissolved in distilled water, and then, to these solutions, diluted aqueous ammonia was added under vigorous stirring. The precipitates formed were washed with distilled water until free from Cl^- ions. The products were then dried for 48 h at 120 °C. The dried products were calcined in air for 2 h at 500 °C in an electric furnace, followed by cooling *in vacuo*.

The composition of zirconia and titania in each product was determined by means of X-ray fluorometry. The compositions were, respectively, 0, 13, 38, 80, and 100 in the weight-percentage ratio: $TiO_2/(TiO_2+ZrO_2)$. The abbreviations used here are as follows: Z, zirconia; T, titania; Z4T, ZT, and ZT4, zirconia-titania containing 13, 38, and 80% titania.

The surface areas of the zirconia-titania system, as determined by nitrogen adsorption, were as follows: Z, 88; Z4T, 224; ZT, 282; ZT4, 140; T, 69 m^2/g.

The TCNQ was supplied by Dainippon Ink Chemical, Ltd. It was recrystallized from acetonitrile for purification. The acetonitrile used as the solvent was of a reagent grade.

The apparatus and procedure used in this study have been previously described.[7]

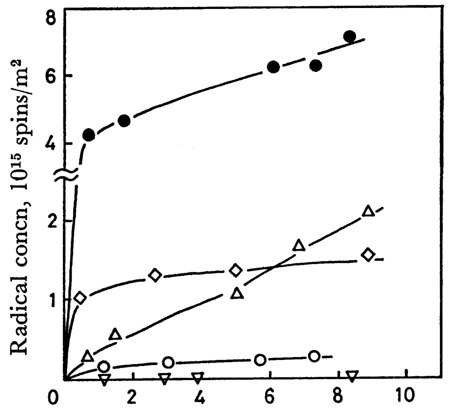


Equil. concn (mmol/l)

Fig. 1. Adsorption isotherms of TCNQ on zirconia-titania system (at 25 °C): zirconia, △; Z4T, ○; ZT, ▽; ZT4, ◇; titania, ●.

Figure 1 shows the adsorption isotherms of TCNQ from the acetonitrile solution at 25 °C on the zirconia-titania surfaces. All the isotherms follow Langmuir plots.

The radical concentration formed on the surfaces of



Equil. concn (mmol/l)

Fig. 2. Radical concentration on zirconia-titania system *vs.* equilibrium concentration of TCNQ: zirconia, △; Z4T, ○; ZT, ▽; ZT4, ◇; titania, ●.

zirconia-titania, plotted against the equilibrium concentration of TCNQ, is shown in Fig. 2.

When TCNQ was adsorbed from a solution in acetonitrile on the surfaces of zirconia-titania, the surfaces of zirconia-titania showed a remarkable coloration, such as violet. The colored samples gave an unresolved ESR spectra with a *g*-value of 2.003, that of TCNQ anion radicals.[6,7] These TCNQ anion radicals were formed as a result of electron transfer from the electron-donor sites of the zirconia-titania surface to adsorbed TCNQ. In the ZT sample, however, the ESR absorption was scarcely observed at all. The unresolved ESR spectra can be explained by the decrease in the freedom of the TCNQ anion radicals adsorbed and by the hyperfine structure becoming obscure of the spectra.

The half-values of the saturated amounts of TCNQ adsorbed, as estimated from the Langmuir plots, are given in the second column of Table I. As can be seen, the half-values are almost the same in all the samples except the Z4T. This indicates that the half-values which consist of neutral TCNQ and TCNQ anion radicals are little affected by the change in the composition of the zirconia-titania system.

For the evaluation of the change in the radical concentration on the surface of zirconia-titania with the composition, the amount of the radical concentration corresponding to the half-values of adsorbed TCNQ in saturation is employed, as is shown in the third column of Table 1. The zirconia-titania (Z4T, ZT, and ZT4) had a much lower radical concentration than titania only. The same tendency has been reported by Hosaka *et al.*[6] in the silica-alumina, silica-titania, and alumina-titania systems. The radical concentration decreased gradually between zirconia and Z4T, but decreased remarkably between Z4T and ZT. On the other hand, in the crystal features of the zirconia-titania system, the pure zirconia phase was present until Z4T, but it became amorphous, as is shown in the fourth column of Table 1. From these results, it may be supposed that the amount of the pure zirconia phase present on the surface of the zirconia-titania system plays an important role in determining the radical concentration. However, the increase in the radical concentration from ZT to ZT4 can be related to the pure titania phase present slightly on the surface of ZT4. It is noteworthy that a weak anatase pattern of ZT4 suggests the presence, in the conglomerate, of a pure titania phase. The steep increase in the radical concentration from ZT4 to the titania corresponds to the increase in the amount of the pure titania phase on the surface.

Table 1. Data of TCNQ adsorption

Sample	Half-values of saturated amounts ($\times 10^7$ mol/m^2)	Radical concn to corresponding half-values of saturated amounts 10^{14} spins/m^2	Phase
Zirconia	3.6	6.8	M*+T(w)
Z4T	5.8	1.7	T(w)
ZT	3.9	negligible	A
ZT4	3.9	11.9	An(w)
Titania	2.8	48.0	An

* M=monoclinic, T=tetragonal, A=amorphous, An=anatase, (w)=weak.

The electron-donor sites of two-component metal oxides are not well known. However, the electron-donor sites of titania, one of the parent oxides in the zirconia-titania system, have been associated with surface hydroxide ions and Ti^{3+} ions.[2,8] Infrared spectroscopy of zirconia has shown that the surface of zirconia contains hydroxide ions.[9] Indeed, Fomin *et al.*[10] have reported that electron transfer from the hydroxide ion can occur in certain solvent systems, provided a suitable acceptor molecule is present. The electron-transfer adsorption of TCNQ on the zirconia-titania system may result from surface hydroxide ions and Ti^{3+} ions. The other product of the electron-transfer adsorption is mainly the OH radical, although only the TCNQ anion radicals are observed in the ESR spectra. The change in the radical concentration of the zirconia-titania system, shown in Table 1, depends on the amount of the pure zirconia phase or the pure titania phase present on the surface of the zirconia-titania system. From the above considerations, it can be expected that the electron-donor sites are surface hydroxide ions(Zr–OH^-) in zirconia-titania of a higher zirconia content, and surface hydroxide ions(Ti–OH^-) and Ti^{3+}ions in the case of zirconia-titania of a higher titania content.

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