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The Electron-donor Property of Zirconia

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Synopsis. The electron-donor property of zirconia 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 surface. The radical concentration decreased with an increase in the calcining temperatures, reached a minimum value at 700 °C, and then increased. This behavior can be explained by a change in the electron-donor site number and the strength of the electron-donor site.

The adsorption of electron acceptors on metal oxides has been investigated, in order to characterize the electron-donor properties of the metal-oxide surfaces. Flockhart *et al.*[1] attempted the adsorption of tetracyanoethylene (TCNE) for the estimation of the electron-donor properties of the alumina surface. In this respect, they associated the electron-donor sites with the unsolvated hydroxide ions and the defect centers involving oxide ions. Meguro and Esumi,[2] carrying out a study of the adsorption of electron acceptors with electron affinities ranging from 1.26 to 2.84 eV on the surface of alumina, have shown that the limit of electron transfer from the alumina surface to the electron acceptors ranged between 1.77 and 1.26 eV in the affinity of the electron acceptor. Thus, the utility of electron-acceptor adsorption for the study of the electron-donor properties of metal oxides has been established.

Zirconia is an important promoter of various dispersed catalysts. To characterize zirconia catalysts, it is necessary to study the surface properties of zirconia. Already, works involving the adsorption of gases, the heat of immersion, and infrared spectroscopy for zirconia have been reported.[3–5] The present study will discuss the electron-donor property of zirconia when 7,7,8,8-tetracyanoquinodimethan (TCNQ) adsorption is used.

Zirconia was prepared by the hydrolysis of zirconium tetrachloride, which had been dissolved in distilled water. The solution was neutralized by ammonium hydroxide, and the precipitate thus formed was washed with distilled water until free from chloride ions. The precipitate was dried for 48 h at 120 °C. The final products were then obtained by calcination in air for 2 h at temperatures between 300 and 1000 °C in an electric furnace, followed by cooling *in vacuo*. The pertinent properties of these samples are given in Table 1.

The TCNQ was supplied by Dainippon Ink Chemical Ltd., and was recrystallized from an acetonitrile solution. The acetonitrile used was of a reagent grade. The apparatus and procedure used in this study have been described elsewhere.[2]

Table 1. Pertinent properties of zirconia

Sample	Calcining temp/°C	Phase[a]	Surface area[b] m^2/g^{-1}
A	300	A[c] + T(tr)	276.9
B	500	M + T(tr)	88.1
C	700	M	60.1
D	900	M	42.8
E	1000	M	34.5

a) From X-ray analysis. b) From the nitrogen adsorption at 77 K after outgassing at 100 °C. c) A = amorphous, T = tetragonal, M = monoclinic, (tr) = trace.

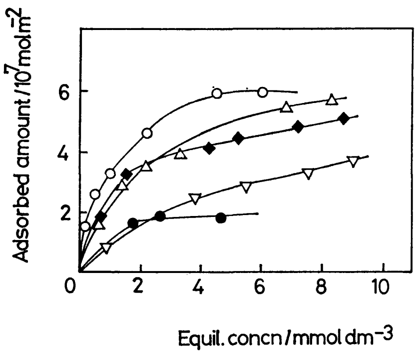

Fig. 1. Adsorption isotherm of TCNQ on zirconia (at 25 °C). Calcination temperature; ○: 300 °C, △: 500 °C, ◆: 700 °C, ▽: 900 °C, ●: 1000 °C.

The adsorption isotherms of TCNQ at 25 °C from a solution in acetonitrile on the surface of zirconia calcined between 300 and 1000 °C are shown in Fig. 1. All of the isotherms are convex to the concentration axes, and all follow the Langmuir plots. The half-value of the limiting amount of TCNQ adsorbed on the zirconia surfaces, as estimated from the Langmuir plots, is given in the first column of Table 2. As shown in Table 2, it can be seen that the amount of TCNQ adsorbed on the ziconia surfaces increases with an increase in the calcining temperature, reaches a maximum value at 500 °C, and then decreases.

When TCNQ was adsorbed from a solution in acetonitrile on the surfaces of zirconia, the zirconia surfaces developed a remarkable coloration. The color was violet in all of the samples. It has previously been reported[2,6,7] that the adsorption of electron acceptors onto metal oxides produces a surface coloration. The samples colored by the TCNQ adsorption gave unresolved ESR spectra with a *g*-value of 2.003. These spectra can be attributed to the hindered freedom of the adsorbed species, which obscures the hyperfine structure of the spectra. The spectra have been identified as being those of TCNQ anion radicals.[2]

The above results support the idea that the TCNQ anion radicals are formed as a result of electron transfer from the zirconia surfaces to the TCNQ adsorbed.

The TCNQ-radical concentration formed on the surface of zirconia is plotted against the equilibrium

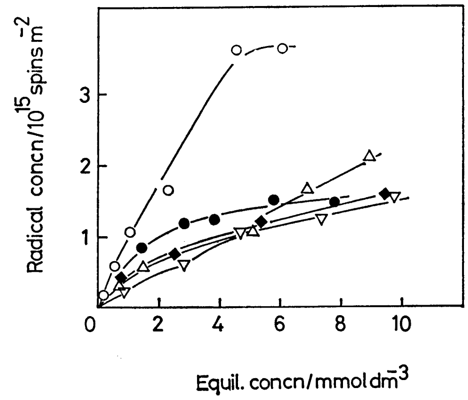

Fig. 2. Radical concentration on zirconia *vs.* equilibrium concentration of TCNQ (at 25 °C). Calcination temperature; ○: 300 °C, △: 500 °C, ◆: 700 °C, ▽: 900 °C, ●: 1000 °C.

concentration of TCNQ at 25 °C in Fig. 2. Many of the isotherms were of a Langmuir type. Therefore, to compare the TCNQ-radical concentration on the surface of zirconia as a function of the calcination temperature, the TCNQ-radical concentration corresponding to the half-value of the limiting amount of TCNQ adsorbed is employed, it is given in the second column of Table 2. It is found that the TCNQ radical concentration decreases with an increase in the calcining temperatures, reaches a minimum value at 700 °C, and then increases.

The nature of the electron-donor sites responsible for the electron-transfer process is not well understood. However, it has been proposed[5,6] that the electron-donor sites of metal oxides, such as alumina and titania, are associated with surface hydroxide ions at lower calcining temperatures and with surface oxide ions at higher temperatures. In the case of zirconia, it is also expected that the electron-donor sites are correlated with the two different sites described above. Indeed, it has been observed by infrared spectroscopy[7] that the surface of zirconia contains hydroxide ions.

The change in the TCNQ radical concentration as a function of the calcination temperatures might be interpreted as follows. At the calcining temperature of 300 °C, the electron-donor sites are surface hydroxide ions. The decrease in the TCNQ radical concentration between 300 and 700 °C corresponds to a reduction in the number of hydroxide ions on the surface. Above 900 °C, surface oxide ions play an important role as electron-donor sites.

Table 2. Data of TCNQ adsorption on zirconia

Sample	Adsorbed amount	Radical concn	Radical concn / adsorbed amount
	10^{-7} mol m^{-2}	10^{4} spins m^{-2}	10^{21} spins mol^{-1}
A	3.4	10.0	3.2
B	3.6	6.8	1.9
C	2.9	5.3	1.8
D	2.5	8.5	3.4
E	1.1	6.4	5.8

The ratio of the transformation from the TCNQ adsorbed into the TCNQ radical on the surface of zirconia is important to an understanding of the strength of the electron-donor sites. That is, the larger the ratio, the stronger the electron-donor sites. This ratio can be estimated by dividing the TCNQ radical concentration by the corresponding half-value of the limiting amount of TCNQ. The values are given in the third column of Table 2. This ratio decreases with an increase in the calcining temperatures, reaches a minimum value at 700 °C, and then increases. This result suggests that, in the electron-transfer process, the surface oxide ions are much stronger electron-donor sites than the surface hydroxide ions.

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