# Adsorption of Electron Acceptors on Titania

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**Synopsis.** Four electron acceptors with electron affinities ranging from 1.26 to 2.84 eV were adsorbed from acetonitrile solution on to a titania sample. On adsorption, radical anions were formed on the titania surface as a result of electron transfer to the acceptors from the surface of the titania. The concentration of radical anions thus formed decreased with the decreasing electron affinity of the acceptors; the decrease is steep between 1.26 and 1.77 eV. These results suggest that the limit of electron transfer from the titania surface to the acceptor ranges between 1.77 and 1.26 eV in the electron affinity of the acceptor.

Recently, the adsorption of electron acceptors on metal oxides has been investigated to estimate electron donor properties of metal oxides and their characterization.[1-3] Flockhart *et al.*[4] studied the electron donor properties of alumina surface by the adsorption of tetracyanoethylene (TCNE) and they concluded that the electron donor sites originated from unsolvated hydroxide ions for the samples activated at lower temperatures, but from defect centers involving oxide ions for the samples activated at higher temperatures.

In this work we report the adsorption of some electron acceptors on titania in order to evaluate the limit of the electron transfer. For this purpose, the following electron acceptors were employed as adsorbates: 7,7,8,8-tetracyanoquinodimethan (TCNQ), 2,5-dichloro-*p*-benzoquinone (DCQ), *p*-dinitrobenzene (PDNB), and *m*-dinitrobenzene (MDNB), whose electron affinity ranges between 2.84 and 1.26 eV.

The preparation of titania has been described elsewhere.[3] The specific surface area of the sample measured by the BET method was about 47 $m^2/g$. The sample was found to be anatase by X-ray diffractometry. TCNQ was supplied by Dainippon Ink Chemical, Ltd, and recrystallized from acetonitrile. DCQ, PDNB and MDNB were supplied by Tokyo Kasei, Ltd., and were purified by recrystallization from ethanol, chloroform and carbon tetrachloride, respectively. The acetonitrile used as solvent was of reagent grade supplied by Kokusan Chemical Works, Ltd. The apparatus and procedure used in this study have been described previously.[1]

Figure 1 shows the adsorption isotherms of TCNQ, DCQ, PDNB, and MDNB from their acetonitrile solutions at 25 °C on the titania surface. All the isotherms except MDNB are of Langmuir type. In the case of MDNB, the amount adsorbed was so small that it was hard to estimate. The limiting amounts of TCNQ, DCQ and PDNB adsorbed on the surface estimated from the Langmuir plots, are given in the second column of Table 1. As shown in Table 1, it is noticeable that the limiting amount decreases with the decreasing electron affinity[5,6] of the acceptors.

When the electron acceptors were adsorbed from the solution in acetonitrile on the surface of titania, the surface showed a remarkable coloration characterized with the kind of acceptors: violet for TCNQ, brown for DCQ and PDNB, and colorless for MDNB. It has been reported by some workers[1-4] that the adsorption of acceptors on metal oxides produces a surface coloration due to the interaction between acceptor molecules adsorbed and metal oxide surfaces. To study the nature of the interaction the electronic spectrum of colored samples was measured, as illustrated in Fig. 2. The bands appearing below 400

Table 1. Summary of the electron acceptor adsorption

| Electron acceptor | Electron affinity / eV | Adsorbed amount / mol $m^{-2} \times 10^{-7}$ | Radical concentration / spins $m^{-2}$ |
|---|---|---|---|
| TCNQ | 2.84 | 6.0 | $3.1 \times 10^{16}$ |
| DCQ | 2.30 | 5.0 | $1.5 \times 10^{15}$ |
| PDNB | 1.77[a] | 2.0 | $7.1 \times 10^{13}$ |
| MDNB | 1.26 | Negligible | 0 |

a) The value given by Briegleb[5] plus 1.07 eV.

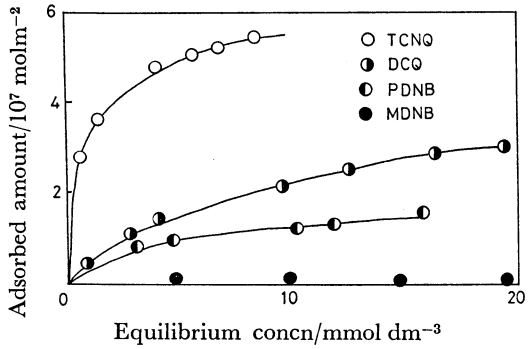


Fig. 1. Adsorption isotherms of electron acceptors on titania (at 25 °C).

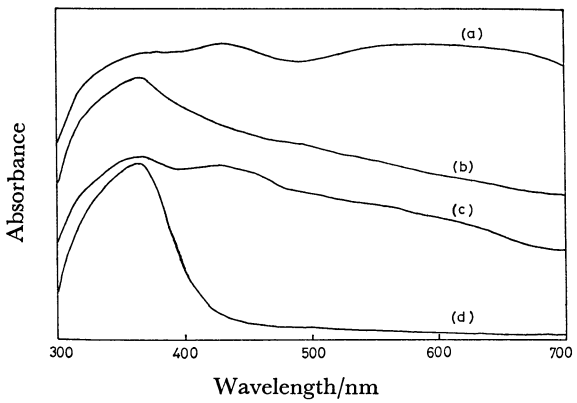


Fig. 2. Electronic spectra from electron acceptors on titania: (a) TCNQ; (b) DCQ; (c) PDNB; (d) MDNB.

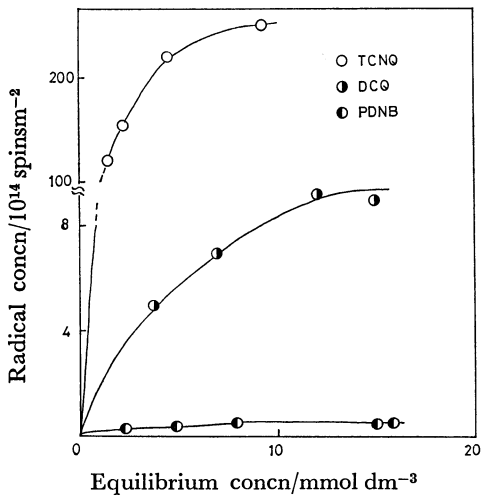


Fig. 3. Radical concentration on titania *vs.* equilibrium concentration of electron acceptor (at 25 °C).

nm are common to all the samples and could not be assigned specifically to any adsorption state because titania alone has a characteristic band in the same region. The absorption band near 600 nm observed in Fig. 2(a) can be attributed to the dimer TCNQ anion radical which absorbs light at 643 nm.[7] In Fig. 2(b), a broad tail band extending to 700 nm was observed and may be supposed to correspond to the DCQ anion radical.[8] The spectrum shown in Fig. 2(c) has a maximum absorption at about 420 nm and the band may be attributed to the PDNB anion radical. In the case of MDNB as shown in Fig. 2(d), no new band was observed on adsorption. If the acceptor anion radicals are formed by the adsorption on the titania surface, the adsorbed species obtained will show ESR signals. Indeed, the colored species gave an unresolved ESR spectrum with a g-value of 2.003 for TCNQ, 2.005 for DCQ and 2.004 for PDNB, respectively. However, the sample of adsorbed MDNB showed no ESR signal. These phenomena confirm the formation of TCNQ, DCQ, and PDNB anion radicals as a result of electron transfer from titania surface to each acceptor.

The nature of the sites responsible for the electron transfer process is not well understood. However, it might be suggested that two possible electron sources exist on the titania surface. One of these is $Ti^{3+}$ ions and the other is surface hydroxide ions.[9]

Figure 3 shows the radical concentration on the surface of titania plotted against the equilibrium concentration of electron acceptor. All the isotherms are of Langmuir type. The limiting radical concentration of TCNQ, DCQ, and PDNB adsorbed on the titania surface estimated by the Langmuir plot is given in the third column of Table 1. It is found that the limiting radical concentration decreases with decreasing electron affinity of the acceptors and steeply between PDNB and MDNB. This suggests that adsorption sites of titania act as electron donors to the adsorbed molecules with electron affinity larger than 1.77 eV but not to those smaller than 1.26 eV. Accordingly, the limit of electron transfer from electron donor sites of titania to electron acceptor molecules is located between 1.77 and 1.26 eV in the electron affinity of the acceptors.

## References

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