

Electron donor sites on Y_2O_3 catalyst as a function of the activation temperature

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The adsorption of electron acceptors on metal oxides has been investigated to study and characterize the electronic properties of metal oxides [1-3]. Two possible electron sources exist on the metal oxide responsible for the electron transfer. One of these has electrons trapped in intrinsic defects and the other has hydroxyl ions [4]. It was reported that the free-electron defect site on the metal oxide surface was created at an activation temperature of above 500 °C [5]. The other site may be the hydroxyl ion and the participation of oxidation-reduction processes of the type $OH^- + A \rightarrow OH + A^-$ (where A is an electron acceptor) can be included. Electron transfer from hydroxyl ions occurs in certain solvent systems, provided a suitable acceptor molecule is present. It has been reported that the electron donor site of an alumina surface might be associated with the presence of unsolvated hydroxyl ions on the surface [6]. As the activation temperature increases, the OH^- concentration should decrease and the number of free-electron defect sites should increase.

In this letter we report the electron-donating properties and the limit of electron transfer from the surface as a function of the activation temperature of the catalyst. For this purpose we studied the adsorption of electron acceptors of varying electron affinity on yttrium oxide activated at 300, 400, 500, 600 and 800 °C. The electron acceptors used were 7,7,8,8-tetracyanoquinodimethane (TCNQ), 2,3,5,6-tetrachloro-1,4-benzoquinone (chloranil), *p*-dinitrobenzene (PDNB) and *m*-dinitrobenzene (MDNB). Since the adsorption of electron acceptors is dependent on the basicity of the medium, studies were carried out in acetonitrile and 1,4-dioxan.

Rare-earth oxides are widely used in industry as catalysts for polymerization, oxidation, desulfurization, pollution control, etc. They are also used as promoters and supported catalysts.

Yttrium oxide was regenerated from the oxide obtained from Indian Rare Earths Ltd, Udyogamandal, by the hydroxide method [7]. It was heated in air for 3 h at the required temperature. The specific surface areas of the samples were determined by the Brunauer-Emmett-Teller (BET) method as 46.3, 41.3, 81.5, 42.4 and 38 m²g⁻¹, respectively, for oxides activated at 300, 400, 500, 600 and 800 °C.

TCNQ, PDNB and MDNB were obtained from Merck-Schuchardt and from Koch Light Laboratory, and were purified by repeated recrystallization from acetonitrile, chloroform and carbon tetra-

chloride, respectively [8]. Chloranil was obtained from Sisco Research Laboratory, and was purified by repeated recrystallization from toluene [9]. The solvents acetonitrile and 1,4-dioxan used were obtained from Merck and were further purified [10, 11]. In the case of MDNB the adsorption was so negligible that the amount was hardly estimated. The adsorption of PDNB from acetonitrile could be estimated only on yttrium oxide activated at 800 °C. In all other cases the adsorption of PDNB was negligible.

When TCNQ and chloranil were adsorbed from solution on the surface of yttrium oxide the surfaces showed remarkable coloration characteristics with the kind of acceptors like bluish green for TCNQ and slight pink for chloranil. These colorations are due to the interaction between the acceptor adsorbed and the oxide surface [12]. The concentration of electron acceptor in solution was determined with a Hitachi 200-20 ultraviolet-visible spectrophotometer by measuring the absorbance at 393.5, 289, 262 and 237 nm, each of which was due to TCNQ, chloranil, PDNB and MDNB in acetonitrile, and at 403 and 286 nm due to TCNQ and chloranil in dioxan, respectively. The amount of electron acceptor adsorbed on the metal oxide was determined by the method of Esumi *et al.* [9] from the concentration difference of electron acceptor in solution before and after adsorption.

The values of the limiting amounts of TCNQ, chloranil and PDNB adsorbed on yttrium oxide at different activation temperatures are given in Table I against the electron affinity of the electron acceptors. The adsorption of MDNB was negligible in all of the systems studied. The data would correspond to the Langmuir adsorption isotherm. This was confirmed by plotting the linear form of the Langmuir adsorption isotherm. The limiting amount of electron acceptor adsorbed on the surface decreased with decrease in electron affinity of the acceptor and increase in basicity of the solvent. The limiting amount also increased with increasing activation temperature. On yttrium oxide activated at lower temperatures, the surface hydroxyl ions may be responsible for the adsorption of electron acceptors. It was reported that two types of surface sites are responsible for adsorption. At lower activation temperature surface sites may be associated with the presence of unsolvated hydroxyl ions, and at higher activation temperature an electron defect centre is produced [13]. We found that the limiting amount of

TABLE I Limiting amount of electron acceptors adsorbed

Temperature (°C)	Solvent	Electron acceptor	Electron affinity (eV)	Limiting amount adsorbed (mol m^{-2})
300	Acetonitrile	Chloranil	2.40	1.783×10^{-5}
300	Acetonitrile	TCNQ	2.84	5.721×10^{-5}
300	Dioxan	Chloranil	2.40	1.167×10^{-5}
300	Dioxan	TCNQ	2.84	1.914×10^{-5}
400	Acetonitrile	Chloranil	2.40	1.790×10^{-5}
400	Acetonitrile	TCNQ	2.84	6.087×10^{-5}
400	Dioxan	Chloranil	2.40	1.057×10^{-5}
400	Dioxan	TCNQ	2.84	1.929×10^{-5}
500	Acetonitrile	Chloranil	2.40	2.462×10^{-5}
500	Acetonitrile	TCNQ	2.84	7.218×10^{-5}
500	Dioxan	Chloranil	2.40	1.260×10^{-5}
500	Dioxan	TCNQ	2.84	2.460×10^{-5}
600	Acetonitrile	Chloranil	2.40	3.389×10^{-5}
600	Acetonitrile	TCNQ	2.84	7.912×10^{-5}
600	Dioxan	Chloranil	2.40	1.258×10^{-5}
600	Dioxan	TCNQ	2.84	3.710×10^{-5}
800	Acetonitrile	Chloranil	2.40	4.107×10^{-5}
800	Acetonitrile	TCNQ	2.84	9.405×10^{-5}
800	Dioxan	Chloranil	2.40	1.369×10^{-5}
800	Dioxan	TCNQ	2.84	5.823×10^{-5}
800	Acetonitrile	PDNB	1.77	7.860×10^{-5}

electron acceptors adsorbed remained almost constant at an activation temperature below 500 °C. Above 500 °C the limiting amount of electron acceptors adsorbed increased considerably with increasing activation temperatures. Fig. 1 shows the increase in the limiting amounts of TCNQ and chloranil in both dioxan and acetonitrile with increasing activation temperature. Since the concentration of surface hydroxyl ions decreased with increasing temperature and the concentration of trapped electrons increased with increasing temperature, it might be expected that the trapped electrons are solely responsible for the adsorption of electron acceptors on the surface of yttrium oxide activated at higher temperatures. The limiting amount decreased steeply between PDNB and MDNB in the case of yttrium oxide activated at 800 °C in acetonitrile. This suggests that adsorption sites in yttrium oxide activated at 800 °C act as electron donors to the adsorbed molecules with electron affinity > 1.77 but not smaller than 1.26 eV in acetonitrile. Accordingly, the limit of electron transfer from the electron donor site of yttrium oxide to the electron-acceptor molecule is located between 1.26 and 1.77 eV in acetonitrile. In dioxan on yttrium oxide activated at 800 °C it is between 2.40 and 1.77 eV. In all other cases the limit is between 2.40 and 1.77 eV in both acetonitrile and dioxan.

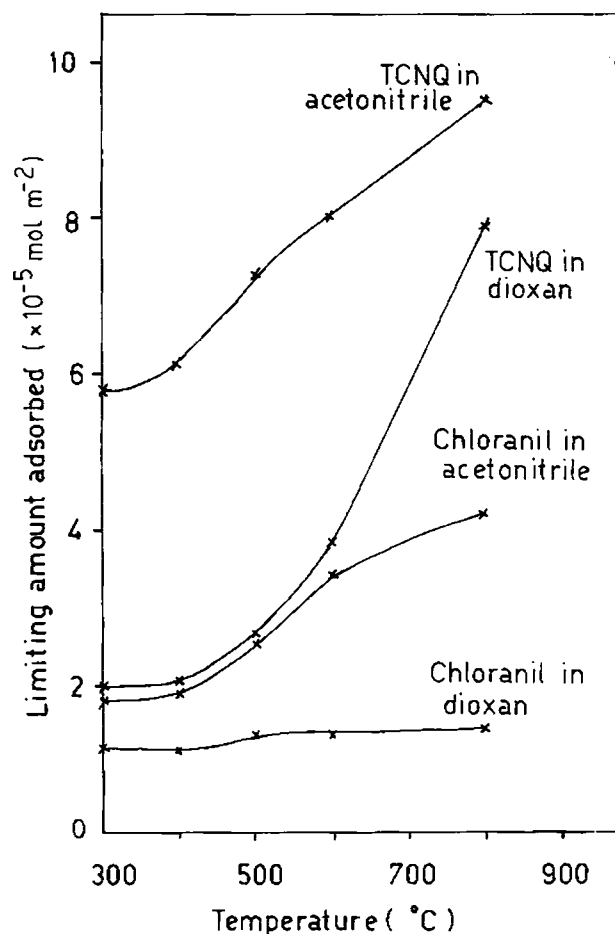


Figure 1 Effect of activation temperature on the limiting amount of electron acceptor adsorbed on Y_2O_3 .

References

1. H. P. LEFTIN and M. C. HOBSON, *Adv. Catal.* **14** (1963) 163.
2. A. TERENIN, *ibid.* **15** (1964) 256.
3. R. P. PORTER and W. K. HALL, *J. Catal.* **5** (1966) 366.
4. K. MEGURO and K. ESUMI, *J. Colloid Interf. Sci.* **59** (1973) 93.
5. J. B. PERI, *J. Phys. Chem.* **69** (1965) 211.
6. *Idem*, *ibid.* **69** (1965) 220.
7. D. S. FOSTER and S. E. LESLIE, in "Encyclopaedia of industrial chemical analysis" Vol. 15. (Interscience, New York, 1972) p. 152.
8. K. ESUMI and K. MEGURO *Bull. Chem. Soc. Jpn.* **55** (1982) 1647.
9. K. ESUMI, K. MIYATA, F. WAKI and K. MEGURO, *ibid.* **59** (1986) 3363.
10. A. I. VOGEL, in "A Textbook of practical organic chemistry" (ELBS, London, 1973) p. 407.
11. *Idem*, *ibid.* p. 177.
12. M. CHE, C. NACCACHE and B. IMELIK, *J. Catal.* **24** (1972) 328.
13. B. D. FLOCKHART, I. R. LEITH and R. C. PINK, *Trans. Faraday Soc.* **65** (1969) 542.

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