The Dipolar Nature of the Alumina Surface. Electron-donor Properties of Aluminas

By B. D. FLOCKHART, C. NACCACHE, J. A. N. SCOTT, and R. C. PINK

[*Department of Chemistry, The Queen's University, Belfast, Northern Ireland* (*B.D.F.*, *J.A.N.S.*, *and R.C.P.*), *and Institut de Recherches sur la Catalyse, Villeurbanne, France* (*C.N.*)]

INTEREST in the nature of catalytic aluminas has centred mainly on the electron-deficient sites on the alumina surface. Thus, the acidity of active aluminas has generally been characterised as of the Lewis type as distinct from Bronsted acidity,[1] whilst the presence on strongly dehydrated alumina surfaces of electron-deficient centres sufficiently powerful to promote the formation of positive

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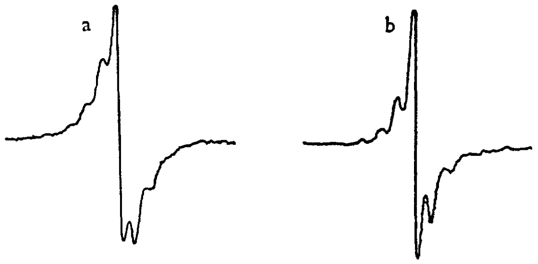
[1] J. B. Peri, *Actes* 2^e^ *Congr. Intern. Catalyse, Paris*, 1960 (Editions Technip, Paris, 1961), Vol. 1, p. 1333; A. J. deRosset, C. G. Finstrom, and C. J. Adams, *J. Catalysis*, 1962, **1**, 235; E. P. Parry, *J. Catalysis*, 1963, **2**, 371; W. K. Hall, H. P. Leftin, F. J. Cheselske, and D. E. O'Reilly, *J. Catalysis*, 1963, **2**, 506.

radical-ions from aromatic hydrocarbons in the presence of molecular oxygen has been demonstrated.[2]

We have now obtained experimental evidence for the presence of *electron-donor* sites on the surface of aluminas by the electron spin resonance (e.s.r.) technique. Tetracyanoethylene (TCNE) has a pronounced electron affinity, centred in the ethylenic π-bond. This is evidenced by the ease with which it forms complexes with aromatic hydrocarbons,[3] and by the formation of the corresponding radical anion in the presence of suitable electron-donors[4] or by irradiation,[5] the radical being readily identified by its nine-line e.s.r. spectrum with hyperfine splitting of 1·56 gauss. This splitting results from interaction of the unpaired electron with the four equivalent nitrogen atoms of the cyano-groups. A similar partially resolved spectrum is observed (Fig. a) when TCNE is adsorbed from the vapour phase on the surface of partially dehydrated aluminas from which oxygen has been removed by prolonged evacuation at 10^{-5} mm. Hg. The nine-line spectrum is also obtained when TCNE is adsorbed from solution in hexane or benzene on samples of gibbsite, γ-alumina or η-alumina activated at temperatures between 100° and 450°, or on gibbsite samples which have been kept at room temperature and 10^{-5} mm. Hg for one hour (Fig. b). The development of the e.s.r. signal is accompanied by the appearance of a yellow colour on the oxide surface similar to that given by the TCNE radical anion in solution. When the radical is prepared by adsorption from solution, the spectrum decays slowly with loss of resolution, possibly due to the formation of polymeric radical products. For a gibbsite sample heated at 420° for 2·5 hr. the concentration of electron-donor sites was estimated to be $\sim 7 \times 10^{10}$ per cm.^{2} of surface, which is not greatly different from the concentration of electron-acceptor sites on some partially dehydrated aluminas[2] and silica–aluminas.[6] The number of electron-donor sites decreases with increasing temperature of activation between 100° and 450°. Less well-resolved e.s.r. signals are obtained when TCNE is adsorbed on aluminas dehydrated above 500° and the colour developed on the catalyst surface varies between yellowish green and dark green. It may be significant that the loss of resolution in the TCNE radical-ion spectrum and the development of the green colour occur in samples activated at temperatures above which the strong oxidising properties of the aluminas become apparent.[2] In these cases the adsorption and subsequent processes are probably complex. No e.s.r. signal was observed when TCNE was adsorbed on fully dehydrated catalytically-inactive α-alumina (corundum).

With chloranil, an electron-acceptor with weaker π-acid character than TCNE,[3] e.s.r. signals were also obtained when the compound was adsorbed on a range of partially dehydrated aluminas. No hyperfine splitting is to be expected with this adsorbate.

Although the electron-donor properties of the alumina surface may be modified by the presence of impurity metal ions. it seems unlikely that the present results can be wholly accounted for in this way. The gibbsite used in these experiments was a high purity sample with an iron content of < 20 p.p.m. and a sodium content of < 10 p.p.m. The other aluminas which were commercial samples of the γ- and η-modifications behaved in a similar manner to the pure gibbsite. Present findings are more easily explained on the assumption that the presence of numerous electron-donor sites is an intrinsic property of the surface of catalytic aluminas. Since the presence of electron-acceptor or oxidising centres on catalytic aluminas has previously been shown,[2] the results now reported provide an experimental demonstration of the dipolar nature of the alumina surface. They offer support therefore for the conclusions reached by Peri[7] from a theoretical study of the dehydration



(a) *Tetracyanoethylene adsorbed from the vapour phase on gibbsite dehydrated at* 200°.

(b) *Tetracyanoethylene adsorbed from benzene on gibbsite dehydrated at* 200°.

J. A. N. Scott, B. D. Flockhart and R. C. Pink, *Proc. Chem. Soc.*, **1964**, 139.

[3] R. E. Merrifield and W. D. Phillips, *J. Amer. Chem. Soc.*, 1958, **80**, 2778.

[4] W. D. Phillips, J. C. Rowell, and S. I. Weissman, *J. Chem. Phys.*, 1960, **33**, 626.

[5] R. L. Ward, *J. Chem. Phys.*, 1963, **39**, 852.

[6] J. J. Rooney and R. C. Pink, *Trans. Faraday Soc.*, 1962, **58**, 1632.

[7] J. B. Peri, *J. Phys. Chem.*, 1965, **69**, 220.

process. The possibility that both electron-donor and electron-acceptor sites are present on the surface of doped aluminas has also been suggested recently by Schwab and Kral.[8]

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[8] G. M. Schwab and H. Kral, *Proc. Third Internat. Congr. Catalysis, Amsterdam,* 1964 (North-Holland Publ. Co., Amsterdam, 1965), Vol. 1, p. 433.