

Evidence for the Redox Nature of the Surface of Catalytic Aluminas

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Oxidation of polynuclear aromatic hydrocarbons to the radical-cation form occurs readily on partially dehydrated aluminas, the surface of which has previously been saturated with a polynitrobenzene. Conversely, reduction of mono- and polynitrobenzenes to the radical-anion form occurs on a surface previously saturated with anthracene or perylene. Different surface sites are therefore responsible for the oxidation and reduction processes. Direct electron transfer between the donor and acceptor molecules is not involved. Under certain conditions superimposed electron spin resonance spectra of the radical-cation and the radical-anion may be obtained from the same alumina sample. A marked enhancement of the radical-anion signal results when perylene is adsorbed on the alumina surface and similarly the radical-cation signal is reinforced by adsorption of trinitrobenzene. This indicates that the active sites responsible for oxidation and for reduction are to some degree mutually dependent. These results are interpreted using the Peri model for the surface of partially dehydrated catalytic aluminas.

INTRODUCTION

The acid-base properties of aluminas are well known and their relevance in catalysis has been extensively investigated (1). More recently, attention has been drawn (2) to the one-electron transfer or redox reactions that occur at the surface of partially dehydrated aluminas. In the presence of molecular oxygen, which appears to be necessary as an electron acceptor, certain aromatic hydrocarbons and amines are readily oxidized to the corresponding radical-cation and subsequently to oxygenated products (3). The intermediate radical-cations can be detected, in suitable cases, by their electron spin resonance (ESR) spectra. Using the same technique, reduction of certain acceptor molecules such as tetracyanoethylene, and mono- and polynitrobenzenes to the corresponding radical-anion at the surface of catalytic aluminas has been demonstrated (4, 5).

The nature of the active sites on the alumina surface that participate in these

electron-transfer processes is not well understood and the relationship between the redox activity of a particular alumina sample and its catalytic activity remains uncertain. Examination of a model of the alumina surface (6) suggests however that both electron-deficient and potential electron-donor sites might occur together at some stage of the dehydration process. This paper presents direct experimental evidence that this is the case and, further, that the sites responsible for oxidation and for reduction are to some degree mutually dependent.

EXPERIMENTAL

Materials. The aluminum hydroxide (97% gibbsite, 3% bayerite) had a particle size in the range 20 — 600 nm and a total impurity content of ~200 ppm, the principal contaminants being Na (<10 ppm), Si (<20 ppm), and Fe (<20 ppm). It was activated by heating in a stream of oxygen for 30 min and subsequently in air for 3 hr

at 750°C in an electric muffle furnace, and was allowed to cool *in vacuo* over phosphoric oxide. High-purity platinum crucibles were used to minimize contamination with silicon. The calcined material had an impurity content similar to that of the untreated trihydroxide and a BET surface area, measured by nitrogen adsorption, of ~ 150 m²/g.

Anthracene (Hopkin and Williams' microanalytical standard) and perylene (Rutgerswerke-Aktiengesellschaft) were used without further purification. The remaining chemicals were reagent grade, purified by standard procedures. Benzene (AR) was allowed to stand over active alumina for 48 hr and was filtered before use.

Apparatus and Procedure. The ESR spectrometer has been described previously (3). The minimum detectable number of spins was below 10^{13} spins/gauss. Radical-ion concentrations were estimated by comparison of the areas obtained by double integration of the first derivative curves for the sample and standard solutions of 1,1-diphenyl-2-picrylhydrazyl in benzene. The error in the determination of radical concentration was less than $\pm 10\%$.

Samples for ESR measurements were contained in 5-mm OD glass tubes. These were joined to wider glass tubing that could be attached directly to a high-vacuum system; the wider tubing incorporated a sidearm for holding either solids or liquid solutions which could be subsequently

transferred to the main stem of the ESR tube. When required, solutions were degassed by three to five freeze-evacuate-thaw cycles; solids were degassed by prolonged pumping at room temperature. The concentrations of the benzene solutions of perylene and 1,3,5-trinitrobenzene (TNB) used were $\sim 5 \times 10^{-4}$ M and $\sim 10^{-2}$ M, respectively. All spectra were recorded at room temperature.

RESULTS

When the surface of the activated alumina was saturated by adsorption of TNB from benzene solution at room temperature, the catalyst developed a reddish brown color and gave the three-line spectrum shown in Fig. 1(a), which can be attributed to the radical-anion of TNB (5). Subsequent adsorption of perylene from benzene on the same sample, without precautions to exclude oxygen, caused a color change to reddish purple and the development of well-marked resolution in the central feature of the TNB spectrum [Fig. 1(b)]. This resolution, which decreased slowly over a period of several hours, gave a measured hyperfine splitting of 3.3 gauss, in good agreement with the value for the perylene radical-cation (7). Adsorption of TNB on an alumina surface previously saturated with perylene gave the same spectrum as in Fig. 1(b). An immediate golden-yellow color developed when the benzene solutions of perylene and TNB were mixed, but the

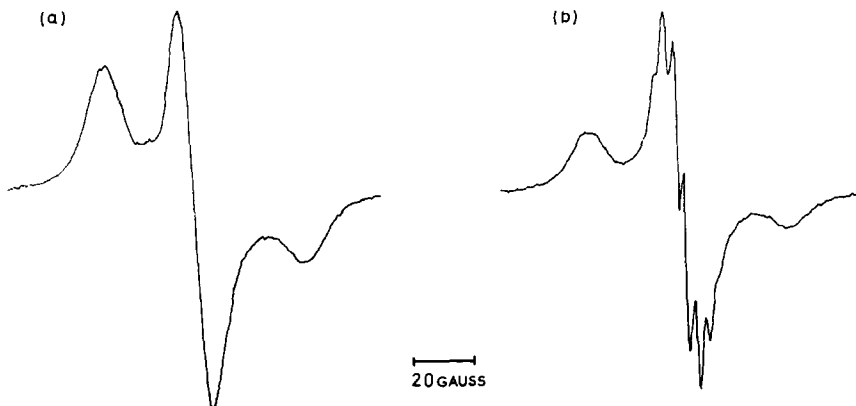


FIG. 1. Electron spin resonance spectra (first derivative): (a) 1,3,5-trinitrobenzene (TNB) on alumina; (b) TNB and perylene on alumina.

resulting solution showed no ESR absorption even at maximum spectrometer sensitivity, although when active alumina was added the superimposed spectra of Fig. 1(b) were again obtained.

Previous work (3) has shown that molecular oxygen plays an essential role in the electron transfer from aromatic hydrocarbons to acceptor sites on the alumina surface. Adsorption of TNB on alumina, however, produced the same ESR spectrum in the absence of oxygen as was obtained when the gas was present. On the addition of activated alumina to mixed deaerated solutions of perylene and TNB, the surface of the catalyst developed a blue-black color and the system gave only the TNB radical-ion spectrum. When the solvent was removed and oxygen admitted, the color and the spectrum remained unchanged. The addition of alumina to mixed solutions of perylene and TNB in the presence of oxygen, followed by thorough degassing of the system, caused the hyperfine structure due to the perylene radical-cation to disappear, and this was not restored by the readmission of oxygen.

The order of addition of the adsorbate molecules to the alumina surface apparently determines whether the superimposed spectra or the anion spectrum only is observed. The results of experiments designed to investigate this problem are summarized in Table I. Superimposed spectra were *not* obtained if both the perylene and TNB were adsorbed on the alumina surface before oxygen was added. The order in which the perylene and TNB were adsorbed on the surface was not important. A significant

finding was that the addition of perylene to the alumina + TNB system, irrespective of whether oxygen was present or absent, produced a marked increase in the intensity of the TNB radical-ion spectrum.

Experiments similar to those described above but substituting anthracene for perylene gave broadly similar results, as did substitution of nitrobenzene for TNB. With the weaker acceptor molecule of nitrobenzene, however, intense radical-anion spectra were only obtained after the system had been irradiated for a short period (3–5 min) with ultraviolet light. Also, addition of perylene to the irradiated alumina + nitrobenzene system, with oxygen present, caused no noticeable color change on the catalyst surface and the ESR spectrum remained unchanged, although when the order of addition of the adsorbates to the surface was reversed, superimposed spectra were obtained. Superimposed cation-anion spectra was also obtained when perylene and 1,4-dinitrobenzene were adsorbed on alumina without precautions to exclude oxygen.

Enhancing Effect of Co-adsorbate on Radical-Ion Formation

Because of the relatively greater spread of the TNB radical-anion spectrum compared with that of the perylene cation and because the *g* values of the two radicals are not greatly different, overlap of the two spectra is virtually confined to the central feature of the anion spectrum [Fig. 1(b)]. Observation of the intensity of one of the outer features therefore permitted separate assessment of the *radical-anion* concentration even when both radicals were present. A quantitative study of the enhancement of the radical-ion spectrum in the presence of the co-adsorbate was therefore possible using a calibration curve in which the intensity of the outer line of the TNB spectrum was plotted against the doubly integrated area of the whole of the TNB spectrum in a separate series of experiments. Known amounts of perylene were added to an alumina + TNB + benzene system at room temperature without precautions to exclude oxygen and the re-

TABLE I
EFFECT OF ORDER OF ADDITION OF ADSORBATES TO THE ALUMINA SURFACE ON TYPE OF SPECTRUM OBSERVED

1	2	3	Observed spectrum
Perylene	Oxygen	TNB	Superimposed
Oxygen	Perylene	TNB	Superimposed
TNB	Oxygen	Perylene	Superimposed
Oxygen	TNB	Perylene	Superimposed
Perylene	TNB	Oxygen	Radical-anion
TNB	Perylene	Oxygen	Radical-anion

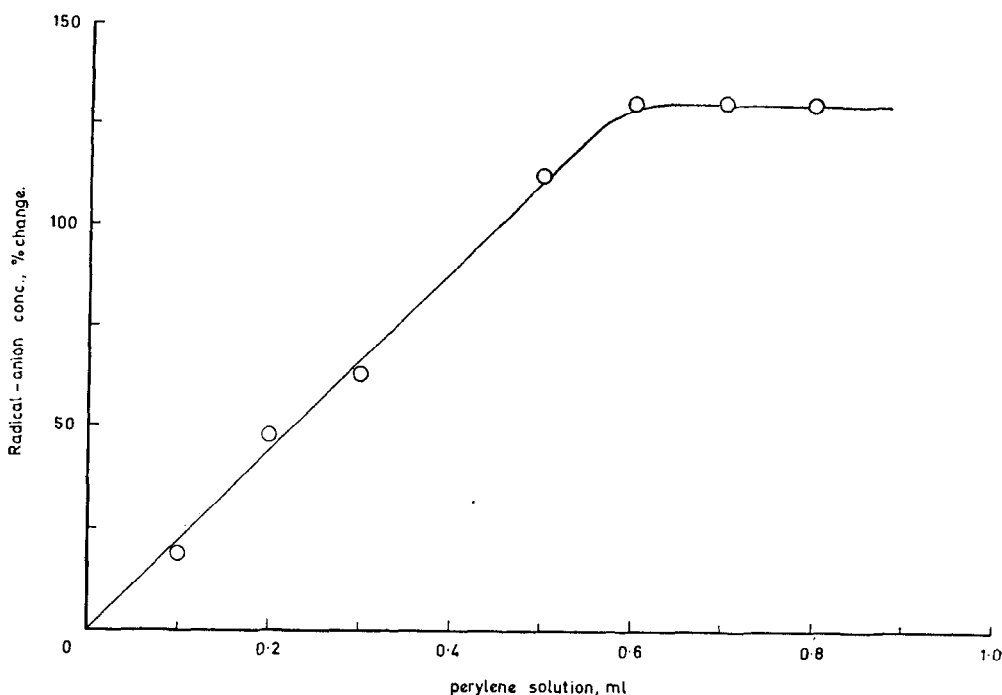


FIG. 2. Effect of perylene concentration on TNB radical-anion concentration.

sultant changes in the radical-anion concentration followed by observation of the outer unperturbed feature of the radical-anion spectrum. Figure 2 shows the results of these experiments. Addition of perylene resulted in a more than twofold increase in the concentration of the TNB radical-anion, saturation occurring when the radical-anion concentration had reached $\sim 2.7 \times 10^{17}$ spins/g. The effect of added TNB on the surface concentration of perylene radical-cations was followed by a double integration of the superimposed derivative spectra combined with separate observation of the intensity of the outer feature of the radical-anion spectrum. A 70% enhancement of the radical-cation concentration was observed in the presence of TNB, the maximum concentration being 1.4×10^{17} radical-cations/g.

DISCUSSION

The fact that perylene radical-cations are readily formed on a surface which has previously been saturated with TNB and, conversely, that TNB radical-anions are

formed on a surface saturated with perylene provides convincing evidence that the electron-transfer processes involved occur at different sites on the alumina surface. Direct electron transfer between donor and acceptor species can be disregarded because no ESR signals were observed in the absence of the catalyst. When the mixed solution containing donor and acceptor molecules is brought into contact with the alumina surface, in the absence of molecular oxygen, only the radical-anion is formed, although both radicals are formed if oxygen is present. This is further evidence for the specific nature of the role of oxygen in the electron-transfer process by which the radical-cation is formed (3), since clearly TNB, although a ready electron acceptor, is not a substitute for molecular oxygen.

These observations can be interpreted using the Peri model (6) for the surface of partially dehydrated catalytic aluminas. In the later stages of the dehydration process in which γ -alumina is formed, surface defects of different kinds are produced.

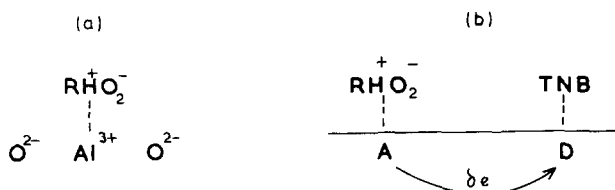


FIG. 3. (a) Abnormally exposed aluminum ion acting as an electron acceptor in the presence of oxygen. (b) Reinforcement of electron-donor site D by adsorption of donor molecule at site A.

One of these, an "overexposed" aluminum ion, in the presence of an oxygen molecule, converts suitable donor molecules such as perylene or anthracene to the radical-cation form, the O_2^- species occupying the defect site on the surface [Fig. 3(a)]. The resultant surface complex is chemically unstable and undergoes rapid degradation by the reactions



It has previously been shown that even after brief residence on the surface little of the original hydrocarbon can be recovered (3). Another defect center, which is associated with the first and which contains an excess of oxide ions, is a powerful electron-donor site, converting suitable acceptor molecules such as nitrobenzene, TNB, or tetracyanoethylene to the radical-anion form. In this electron-transfer process molecular oxygen is not required.

Significantly, the perylene cation is only formed on the alumina surface by adsorption from mixed solutions of donor and acceptor molecules when oxygen is present initially. This implies that, although TNB and oxygen must compete for the perylene in solution, oxygen is unable to displace TNB from the adsorbed TNB-perylene complex. The results in Table 1 support this view. The fact that radical-cations are not formed on an alumina surface previously saturated with nitrobenzene, even when oxygen is present initially, may be attributed to the more polar nature of this acceptor compared to TNB. Polar molecules are known to interact with the oxidizing centres on the catalyst surface (3).

The finding that a marked enhancement of the radical-anion signal results when perylene or anthracene is adsorbed on the

surface and similarly that the perylene radical signal is reinforced by subsequent adsorption of TNB can be explained if it is assumed that there is a range of sites of varying electron-donor or electron-acceptor strength on the surface, at least some of which are capable of mutual interaction. Site D, the electron-donor center in Fig. 3(b), may consist of two or more oxide ions occupying immediately adjoining lattice sites on the alumina surface. If the strength of this particular electron-donor center is marginally insufficient to convert TNB to the radical-anion, adsorption of perylene on site A may reinforce site D to the point at which electron transfer can occur. A similar explanation can be given for the reinforcement of the donor signal by the co-adsorption of an acceptor. It should be noted that the marked enhancement of the radical-anion signal occurs whether or not oxygen is present during the adsorption of perylene or anthracene. The adsorption of an electron-rich molecule on an abnormally exposed aluminum ion will result in the formation of a charge-transfer complex in the absence of oxygen, as evidenced by the yellow coloration on adding perylene to a degassed alumina sample (3). Even though the adsorbed species remains spin-paired, a reinforcement of the electron-donating power of a neighboring reducing center may still be expected.

Although the connection between redox activity and catalytic activity remains obscure, this synergetic action of the sites on the dipolar alumina surface may be significant in catalysis. The fact that powerful electron-donor and electron-acceptor sites can be stabilized in close proximity on the surface is explained by the low mobility of the multiply charged ions in

the alumina lattice at temperatures as high as 800°C. At 1100°C the ion mobility is much increased and the electron-transfer properties of the surface are rapidly and irreversibly destroyed.

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