JOURNAL OF CATALYSIS **61**, 291–292 (1980)

LETTERS TO THE EDITORS

Comments on "On the Electron Donor and Electron Acceptor Properties of the γ-Alumina Surface"

Polycondensed aromatic hydrocarbons act as electron donors in reaction with sulfuric acid or aluminium chloride, but behave as electron acceptors toward sodium. Perylene (ionization potential, 6.83 eV; electron affinity, 1.12 eV) on an oxide surface might therefore be expected to function either as a donor or as an acceptor according to the nature and strength of the surface sites.

The conversion of perylene into a free radical form by electron transfer at the surface of activated silica–alumina was first reported in 1961 (*1*, *2*). Since then, numerous studies (*3*) have been made of the formation of ion-radicals from perylene and other polycyclic aromatic hydrocarbons adsorbed on the surfaces of amorphous and crystalline aluminosilicates and alumina catalysts. In all of these papers the findings have been interpreted in terms of *cation*-radical formation. Professor Muha (*4*), while agreeing with this explanation for the perylene + silica–alumina system, suggests that it is the *anion*-radical of perylene that is generated on a γ-alumina surface. We remain unconvinced by this claim for several reasons:

i. Muha has relied heavily, in his argument, on the differences in hyperfine splitting in the spectra obtained in solution for the perylene cation and the perylene anion. We have never believed that solution hyperfine coupling constants could be safely used to distinguish between these species on a surface, where there is every reason to believe that the wavefunction involved and the related electron spin densities will be modified.

ii. The absence of anisotropy in the ESR spectrum clearly indicates that the perylene ion-radical is undergoing motion on the surface. We have always visualized this as molecular tumbling at a particular site. Muha's idea of an ion possessing the size and shape of the perylenium ion tumbling across the surface of an alumina at room temperature is one that we find difficult to accept.

iii. Muha believes that the anion-radical of perylene is formed on the alumina surface, but the cation-radical on silica–aluminas. Yet we observed a similar increase in the intensity of the trinitrobenzene spectrum in the presence of perylene on both alumina and zeolites (*5*, *6*). Incidentally, one point in Muha's own argument seems difficult to account for, namely, the absence of competition for donor sites if both radicals, formed on the alumina surface, are anions.

iv. A study has been made of the oxidation of aromatic amines on the alumina surface and on silica–alumina surfaces (*7*). Here there seems to be no question that with both types of catalyst electron transfer from the adsorbate to the surface is involved. The density and strength of the *acceptor* sites on the alumina surface are not therefore as low as Muha suggests.

v. When perylene is chemisorbed on an aluminium-exchanged silica (0.8 wt% Al), the ESR spectrum of the system consists of the perylenium ion signal and a superimposed six-line spectrum with a splitting of 16 G (*8*). The sextet must arise from the hyperfine interaction of a trapped electron with a $^{27}Al^{3+}$ ion in the surface, the electron presumably being transferred from the organic substrate. ESR signals from trapped electrons on the alumina surface have also

0021-9517/80/010291-02$02.00/0

been reported. As an example, the spectra of fluoranil, duroquinone, methylnaphthoquinone, and anthraquinone and its monochloroderivatives adsorbed on alumina have approximately the same intensity and the same hyperfine structure (*9*). The latter consists of six components with a splitting of 8.7 G (anthraquinone, 7.6 G). These results have been interpreted in terms of a donor–acceptor complex, the electron acceptor being a three-coordinate aluminium atom in the alumina surface.

Until more convincing evidence is available, we see no reason to change our view that polycyclic aromatic hydrocarbon molecules adsorbed onto a γ-alumina surface are held at electron-deficient sites as *cation*-radicals.

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Received January 18, 1979