Nature of the Radical formed from Perylene on the Alumina Surface

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Summary An examination of the effect of fluoride ion on the radical-forming power of catalytic aluminas demonstrates, beyond reasonable doubt, that the radical formed from perylene adsorbed on the alumina surface is positively charged.

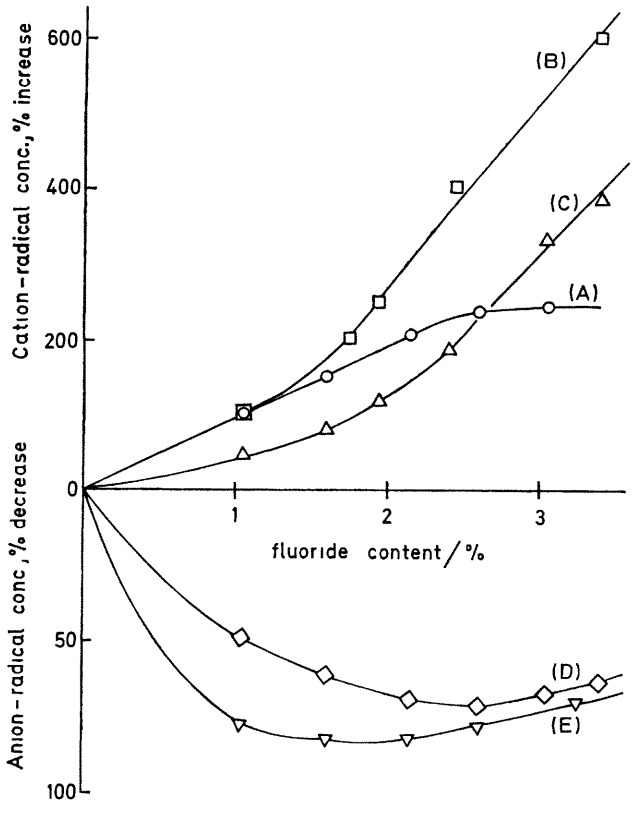

FIGURE Ion-radical concentration on the surface of 700 °C-activated fluorided alumina as a function of the fluoride content with (A) perylene, (B) 9,10 dimethylanthracene, (C) triphenylamine, (D) TCNE, and (E) TNB as the adsorbate (The ordinate has two scales)

THE present authors, with their coworkers, demonstrated, many years ago, that suitably prepared alumina catalysts possess, simultaneously, electron-donor and electron-acceptor properties [1] Since then, many of the phenomena observed in these systems have been interpreted on the basis of their redox activity [2] In recent papers,[3] however, Muha has challenged the entire basis of this work by claiming, largely on spectroscopic evidence, that the radical formed from perylene on the alumina surface is not the cation but the corresponding anion species We have already provided arguments against this contention[4] and also experimental evidence [5] We here record an additional experimental finding which in our opinion furnishes incontrovertible evidence that the original view is correct

The catalytic properties of alumina are profoundly affected by the incorporation of small amounts of fluoride ion [6] We now find that this ion has also a marked effect on the radical-forming power of the catalyst The results are shown in the Figure Small additions of fluoride (<2%) decrease the electron-donor properties of the alumina as shown by radical formation with 1,3,5-trinitrobenzene (TNB) or tetracyanoethylene (TCNE) With perylene, 9,10-dimethylanthracene, or triphenylamine, the effect is exactly the reverse and a dramatic increase in the radical-forming power of the adsorbent is observed Since there can be no doubt that the radical formed from TNB or TCNE is the anion, or indeed that the radical formed from triphenylamine is the cation, these results demonstrate, beyond reasonable doubt, that the radical generated when perylene is adsorbed on an active alumina surface is the cation-radical and not the anion, as contended by Muha [3]

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