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Effect of a Coadsorbate on Ion-Radical Formation on Alumina Surfaces

The surface of a suitably activated alumina catalyst possesses well-marked redox properties. Superimposed ESR spectra of the anion radical of an aromatic nitrocompound and the cation radical of a polycyclic aromatic hydrocarbon are readily obtained from the same alumina sample (*1*). Since overlap of the spectra of a nitrobenzene anion radical and the perylene cation radical is virtually confined to the central feature of the anion triplet, observation of the peak amplitude of one of the outer features permits separate assessment of the anion-radical concentration even when both species are present on the catalyst surface. Double integration of the superimposed derivative spectrum combined with a measurement of the peak-to-peak height of the outer line of the triplet signal yields the cation-radical concentration. The results of such a quantitative study of the 1,3,5-trinitrobenzene (TNB) + perylene + alumina system were reported in a previous paper (*1*). Addition of perylene resulted in an increase in the TNB anion-radical concentration, saturation only appearing after the surface concentration had more than doubled (ca. 130% increase). Simultaneously, a 70% enhancement of the adsorbed perylene cation-radical concentration occurred.

A recent study of the TNB + perylene + alumina system by Muha (*2*) has confirmed the enhancing influence of a suitable coadsorbate on ion-radical formation on the alumina surface. According to this investigator, however, the total integrated intensity of the spectrum obtained when TNB and perylene were both present on the surface was only ~10% greater than the sum of the integrated intensities when TNB and perylene were each present alone on the adsorbent. Clearly, the discrepancy between Muha's quantitative result and our factor-of-two value for the TNB + perylene intensity enhancement demanded further inquiry.

Since assessment of the separate radical concentrations required the measurement of peak amplitudes in addition to integrated intensities, it seemed advisable to reinvestigate the enhancement effect using integrated intensities only, the method used by Muha. The results of this study are presented in Table 1. The aluminium oxide–hydroxide (boehmite) was supplied by Akzo Chemie Ltd., the principal contaminants being Na_2O (0.0030%), Fe (0.0084%), and SO_4 (0.0033%). It was activated by heating in flowing oxygen for 30 min and subsequently in air for 4 hr at the required temperature in an electric muffle furnace, followed by cooling at 10^{-5} bar over phosphoric oxide for 30 min. The intensity enhancement factor reported in Table 1 represents the total integrated intensity of the superimposed spectra obtained when both reagents were present on the catalyst surface divided by the sum of the intensities obtained when each reagent alone was in contact with the surface and the latter was saturated in its capacity to generate radicals.

Although both the alumina sample and the method of assessment of the enhancement effect differed from those used in the earlier study, the two sets of results are in good agreement [700°C-activated sample, intensity enhancement factor for TNB + perylene, 1.7 (Table 1); 750°C sample, 2.0 (*1*)]. A 100-fold change in the supernatant concentration of perylene or of TNB had no appreciable effect on the value of the en-

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TABLE 1

Intensity Enhancement Factor as Molecular Concentration in the Supernatant Solution and Activation Temperature of the Alumina Adsorbent are Altered

Initial concn (M)	Initial concn of TNB (M)	Intensity enhancement factor		
		500°C sample	700°C sample	900°C sample
Perylene				
2.2×10^{-5}	5.0×10^{-4}	—	1.8	—
2.2×10^{-4}	5.0×10^{-3}	—	1.7	—
2.2×10^{-3}	5.0×10^{-2}	1.4	1.7	1.2
Triphenylamine				
5.0×10^{-2}	5.0×10^{-3}	1.3	1.6	1.1

hancement factor (Table 1). This finding is at variance with Muha's conclusion that "the magnitude of the enhancement depends critically and in a nonlinear fashion on the concentration of perylene and TNB in the supernatant liquid" (*2*). The intensity enhancement effect is markedly dependent on the activation temperature of the alumina, samples heated at ~700°C being the most active in this respect (Table 1). With samples calcined at 300°C, the effect was barely detectable. Since Muha's samples were activated at 482°C, comparative values for the enhancement are not those quoted in Muha's paper but the following: 1.1 (*2*); 1.4 (Table 1, 500°C sample). Although the numerical difference is still substantial, it may be due to differences in sample properties.

Muha has claimed (*2, 3*) that the radical formed from perylene on the alumina surface is not the cation but the corresponding anion species. Clearly, for this hypothesis to gain some credibility it must be shown how two anion radicals can mutually reinforce their ESR signal to give a 70% increase in total radical concentration. The view held by the present authors is that polycyclic aromatic hydrocarbon molecules adsorbed onto an active alumina surface are held at electron-deficient sites as cation radicals. On this basis the results presented in Table 1 simply demonstrate that electron-donor and electron-acceptor sites can be stabilized in close proximity on the alumina surface and that these sites are to some degree interdependent (*1*). Muha's finding that the substitution of durene or naphthalene for perylene in the supernatant liquid produced the same intensity enhancement in the TNB spectrum, yet neither of these hydrocarbons gave paramagnetic products on the alumina surface, is also easily explained qualitatively. The adsorption of an electron-rich molecule on an electron-deficient site will result in the formation of a charge-transfer complex and, even though the adsorbed species remains spin paired, a reinforcement of the electron-donating power of a neighboring reducing centre may still be expected (*1*). In an earlier paper (*1*) we reported that the addition of perylene to an alumina + TNB system produced an intensity enhancement of the anion-radical signal whether or not molecular oxygen was present during the adsorption of the hydrocarbon. We have now confirmed, using the present alumina sample activated at 700°C, that even in the absence of oxygen gas the presence of perylene still gives rise to a 45% increase in the TNB anion-radical concentration. No perylene radicals are formed on the alumina surface in the absence of oxygen.

A study of the oxidation of aromatic amines on the alumina surface and on silica–alumina surfaces provided strong evidence that with both types of catalyst electron transfer from the adsorbate to the surface was involved (*4*). Table 1 shows that values of the intensity enhancement factor for the triphenylamine + TNB + alumina system closely parallel those for the perylene + TNB + alumina system. If it is accepted that the radical formed from triphenylamine is the cation, and in our opinion the evidence is convincing, then this result even on its own would firmly establish the presence of a positive rather than a negative perylene species on the alumina surface.

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REFERENCES

1. Flockhart, B. D., Leith, I. R., and Pink, R. C., *J. Catal.* **9**, 45 (1967).
2. Muha, G. M., *J. Catal.* **58**, 470 (1979).
3. Muha, G. M., *J. Catal.* **61**, 293 (1980).
4. Flockhart, B. D., Mollan, P. A. F., and Pink, R. C., *J. Chem. Soc. Faraday Trans. 1* **71**, 1192 (1975).

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