Trapped Electrons in Aluminosilicates

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FORMATION of cation-radicals from aromatic compounds of low ionisation potential by electron transfer to the surfaces of activated silica–aluminas,[1,2] aluminas,[3] and zeolites[4,5] is now well established from e.s.r. studies. There is also evidence that some form of chemisorbed oxygen, under the influence of electrostatic fields at the surfaces of the oxides, is the electron acceptor,[6] but so far no one has obtained e.s.r. signals from the above systems which could be attributed to the transferred electrons.

We now report that detection of these electrons by the e.s.r. method at room temperature is possible using silica–aluminas where some of the Al^{3+} ions in the surface are widely dispersed or isolated from each other. One method of preparing such materials is cation exchange of controlled amounts of Al^{3+} ions into the surface of pure silica.[7] When the exchanged silica is dried in air to 550°, cooled in a desiccator, and added to a 10^{-3}M-solution of perylene in purified benzene, an e.s.r.† spectrum of the system at room temperature contains a signal due to transferred electrons, in addition to that arising from the perylenium ions. Figure 1 shows a typical spectrum for an exchanged silica containing 0·8% aluminium. The new signal has a *g*-value, 2·0026, very close to that of the perylenium ion, so the two signals are superimposed; but four lines of equal intensity two on each side of the perylenium ion signal, with a splitting of 16 ± 2 gauss, are clearly apparent. By using this value it is easily shown that the new signal is a sextet which arises from the hyperfine interaction of a trapped electron with a $^{27}Al^{3+}$ ($I = \frac{5}{2}$) ion in the surface. While the concentration of perylenium ions is as high on these materials as on amorphous silica–aluminas or zeolites, the highest concentrations of trapped electrons we have observed so far, at room

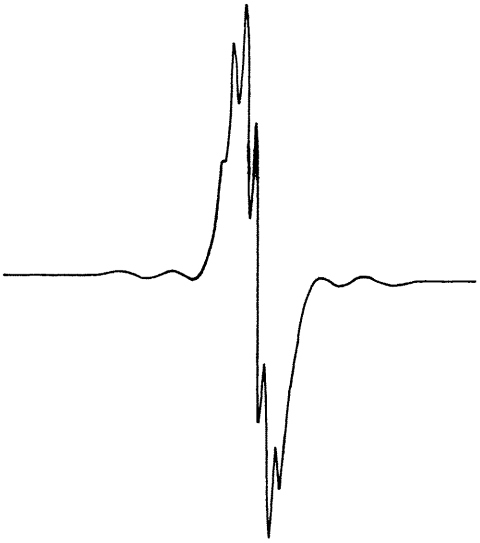

FIGURE 1. *E.s.r. spectrum of system containing chemisorbed perylene on* Al-*exchanged silica* (0·8 *wt.* % Al) *in benzene at room temperature.*

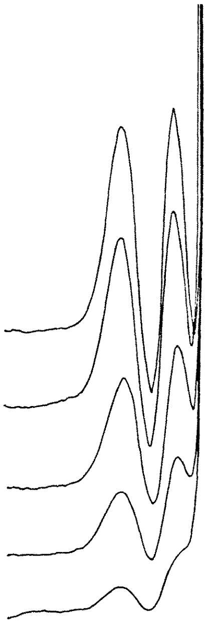

FIGURE 2. *Influence of addition of TCNE solution on system described for Figure* 1. *Only one side of the total spectrum at high amplification is shown with deliberate shift of base line for clarity of presentation.*

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† E.s.r. spectra were obtained using a Decca X-1 spectrometer operating at 9270 MHz. with a magnetic field modulation of 100 kHz.

temperature, is only 5% of the total electrons transferred. We have also found that trapping of the electrons is very sensitive to the conditions of exchange of silica, the amount of Al^{3+} ions in the surface, and the pretreatment of the resulting material. Thus, when exchanged silica was dried out *in vacuo* to 500° and cooled to room temperature, electron transfer on addition of perylene in degassed benzene did not occur in the sealed-off system unless oxygen was added. After both signals had grown to maximum intensity, removal of solvent and oxygen caused a rapid decrease of the perylenium ion signal of ~65%, but completely eliminated the signal due to the trapped electrons.

The following experiment confirms that the new signal is indeed due to trapped electrons. Portions of a 10^{-2}M-solution of tetracyanoethylene (TCNE), which is a good electron-acceptor, were added to the system responsible for the spectrum in Figure 1. After each addition there was a substantial diminution in the intensity of the signal arising from the electrons in the surface (Figure 2) without altering the intensity of the perylenium ion signal.

Isolation of Al^{3+} ions in the surface of conventional silica–aluminas can also be accomplished by treating activated catalyst with tetramethylsilane in a vacuum system. At 200°, or above, reaction with surface hydroxy-groups is rapid with liberation of methane as the only gaseous product, and chemical incorporation of silicon. Samples of catalyst containing 13% and 25% alumina were treated in this way at 205° until reaction had virtually stopped and $\sim 2{\cdot}0 \times 10^{14}$ hydroxy-groups per cm.^{2} reacted. When these modified silica–aluminas were cooled to room temperature and quickly transferred in air to sample tubes containing a solution of perylene in benzene, e.s.r. analysis gave signals such as those shown in Figures 1 and 2.

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