Photochemical Formation of $[HFe_3(CO)_{11}]^-$ and $[HFe(CO)_4]^-$ from $Fe(CO)_5$ adsorbed on Hydrated Alumina

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Photolysis of $Fe(CO)_5$ adsorbed on hydrated alumina produced simultaneously hydride species, $[HFe_3(CO)_{11}]^-$ and $[HFe(CO)_4]^-$, and an intermediate species, $Fe(CO)_4$ adsorbed on the basic sites of alumina.

The photolysis products of organometallic complexes adsorbed on solid surfaces are sometimes quite different from those produced in the gas phase or in fluid solution owing to catalytic effects as well as to adsorbed species. For example, Jackson and Trusheim[1,2] have reported that the photolysis of silica-adsorbed $Fe(CO)_5$ gives $Fe_3(CO)_{12}$ rather than $Fe_2(CO)_9$ which is the photolysis product in the gas or liquid phase. A similar result has been obtained on porous Vycor glass by Darsillo *et al.*[3] We report here that the photolysis of $Fe(CO)_5$ adsorbed on hydrated alumina leads to formation of hydride species, $[HFe_3(CO)_{11}]^-$ and $[HFe(CO)_4]^-$, and a surface-trapped intermediate, $Fe(CO)_4(ads)$.

The $Fe(CO)_5$ used was obtained from Aldrich and alumina (Brunauer–Emmett–Teller, BET, surface area, *ca.* $100 m^2 g^{-1}$) from Nihon Aerosil. Adsorbed species were monitored by FTIR spectroscopy (Horiba FT-300) with a resolution of 1 cm^{-1}. The alumina was pressed into a self-supporting disc and outgassed at room temperature for 1 h in an IR cell with CaF_2 windows. $Fe(CO)_5$ was introduced into the cell at *ca.* 0.05 Torr, and then the alumina disc was illuminated for 10 min with light from an Hg lamp which was filtered through a band-pass filter centred at 366 nm. A small amount of CO was evolved, and the colour of the alumina changed to rose-pink during illumination. The gas-phase products as well as unreacted $Fe(CO)_5$ were removed by evacuation for 1 h, and concentrated HCl vapour was admitted into the cell to characterize adsorbed species.

Figure 1 shows the IR spectra after each experiment, and Figure 2 the difference spectra calculated from the spectra in Figure 1. The band at 2003 cm^{-1} in spectrum (a) of Figures 1 and 2 is assigned to alumina-physisorbed $Fe(CO)_5$ which can be removed by brief pumping. Under dynamic vacuum, the rose-pink colour of the alumina disc gradually faded, followed by a change in the IR spectrum from (b) to (c) in Figure 1. The species giving rise to the change in the spectrum [Figure 2(b)] is designated as species I. Hugues *et al.*[4,5] have reported that the pink species $[HFe_3(CO)_{11}]^-$ is formed in the dark by interaction of $Fe_3(CO)_{12}$ with hydrated alumina in hexane solution. The IR spectrum of the $[HFe_3(CO)_{11}]^-$ thus obtained is analogous to spectrum (b) in Figure 2. Species I is, therefore, assigned to $[HFe_3(CO)_{11}]^-$. Although it was reported[4,5] that $[HFe_3(CO)_{11}]^-$ is also produced slowly from $Fe(CO)_5$ on hydrated alumina, we could not reproduce this process at the gas–solid interface, probably because $[HFe_3(CO)_{11}]^-$ is unstable under low pressures owing to its reversion to $Fe(CO)_5$. We have also found that $[HFe_3(CO)_{11}]^-$ is formed by the photolysis of $Fe_3(CO)_{12}$ adsorbed on silica, the surface of which exhibits acidic properties in the presence of gas-phase water, though no hydride species was produced on hydrated silica in the absence of gas-phase water.[6] Since the formation of $[HFe_3(CO)_{11}]^-$

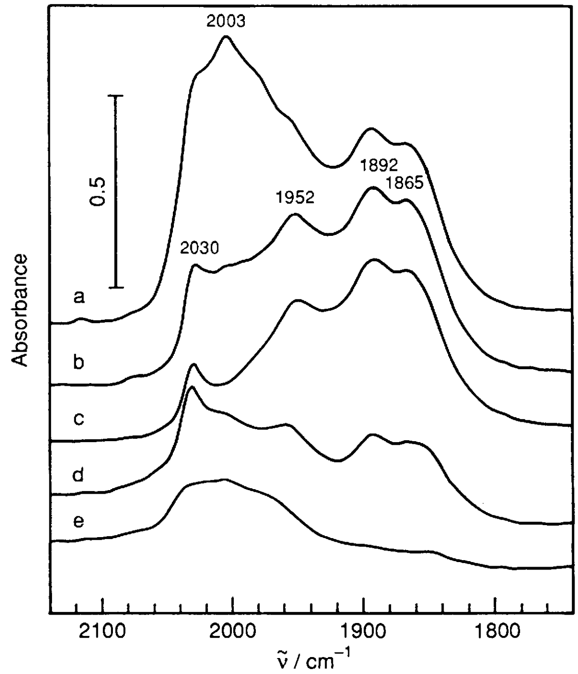

Figure 1. IR spectra of (a) $Fe(CO)_5$ adsorbed on hydrated alumina after illumination, (b) species remaining after 15 min evacuation, (c) after 60 min evacuation, (d) 5 min after the introduction of HCl gas, and (e) 70 min after (d). The background spectrum has been subtracted.

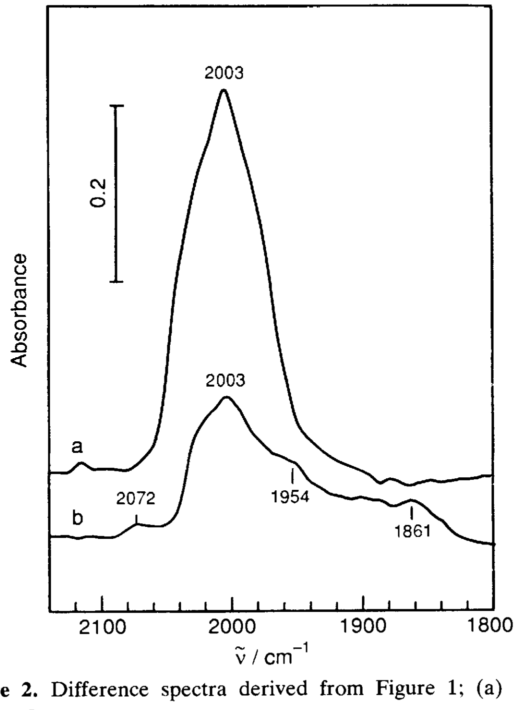

Figure 2. Difference spectra derived from Figure 1; (a) a − b, (b) b − c.

from iron carbonyls occurs on basic surface sites,[4,5] which can donate electrons to the adsorbed species, the ligand-to-metal charge transfer caused in $Fe(CO)_5$ by absorption of light could give the same effect as strong basic catalysts on adsorbed $Fe(CO)_5$.

The IR spectrum of the species remaining after prolonged evacuation shows bands at 2030, 1952, 1892, and 1865 cm^{-1} [Figure 1(c)], and the latter two bands rapidly decreased after introducing HCl gas as seen in spectrum (d). Deuterium exchange of the surface hydroxy groups and adsorbed water led to a slight shift of the latter two peaks to lower frequency, whereas the former two peaks remained unchanged. The latter two bands were not observed when the alumina sample was outgassed at temperatures above 300 °C. These results suggest that two different species are involved and that the species giving rise to the bands at 1892 and 1865 cm^{-1} (species II) is a hydride while the other (species III) is not. When pyridine was adsorbed on the alumina outgassed at 300 °C, on the other hand, a species with bands at 2030w, 1942sh, and 1914s cm^{-1} appeared after the adsorption of $Fe(CO)_5$ in the dark. Edgell *et al.*[7] have studied the reaction of $Fe(CO)_5$ with piperidine and determined the structure of the products by IR spectroscopy. They assigned a species with bands at 1995w, 1909m, and 1880s cm^{-1} to $[HFe(CO)_4]^-$, and a species with bands at 2038w, 1945m, and 1916s cm^{-1} to $Fe(CO)_4(NHC_5H_{10})$. Therefore, it is concluded from these results that species II is $[HFe(CO)_4]^-$ and species III is assigned to $Fe(CO)_4$ adsorbed on the basic sites of alumina. Species III could be an intermediate in the formation of $Fe_3(CO)_{12}$.

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