F.T.I.R. Spectra of Carbon Monoxide Adsorbed on Platinum Sols

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Infrared spectra of adsorbed carbon monoxide on platinum colloid particles dispersed on aqueous media exhibit a band in the region 2070—2040 cm^{-1}.

Infrared spectra of carbon monoxide on platinum surfaces have been reported for a variety of interfacial types: finely divided metal catalysts,[1] single crystal metal surfaces,[1] and metal electrode surfaces.[2] In this study, the spectra of carbon monoxide sorbed at the platinum sol/aqueous interface are reported and the relationship between this interface and the platinum electrode/aqueous interface is considered.

Platinum sols were prepared either by citrate[3] or borohydride[4] reduction of hexachloroplatinic acid. The resulting sols have been characterised by transmission electron microscopy
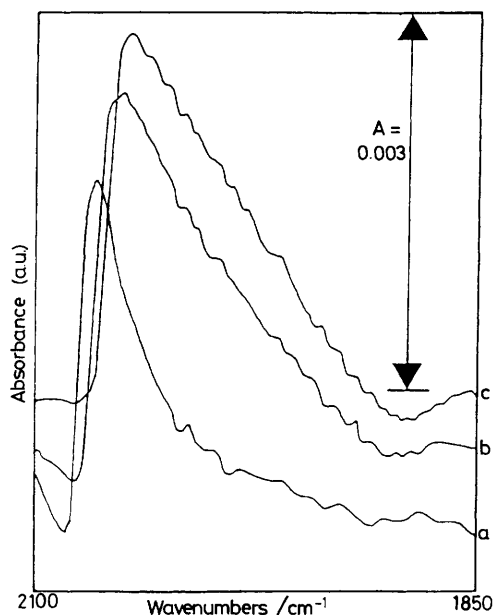
Figure 1. Infrared spectra of carbon monoxide adsorbed on a borohydride-generated platinum sol as a function of time after preparation of the sample: (a) spectrum after *ca.* 2 min [$v(CO)_{ads}$ = 2066 cm^{-1}], (b) after 35 min [$v(CO)_{ads}$ = 2052 cm^{-1}], and (c) after 229 min [$v(CO)_{ads}$ = 2045 cm^{-1}].

Figure 2. Graph of $v(CO)_{ads}$ against time after preparation of the sample for carbon monoxide adsorbed on a borohydride-generated platinum sol.

and X-ray photoelectron spectroscopy. The average particle size for the citrate preparation was *ca.* 3.0 nm and for the borohydride preparation was *ca.* 6.0 nm. In both cases, the resulting colloid exhibited a range of particle sizes. Also in both cases, the dry-deposited sol which was the subject of microscopic examination exhibited different patterns of aggregation. In the case of citrate-generated sols, the aggregation usually assumed the form of irregularly shaped bundles of particles (*i.e.*, clusters), and for borohydride-generated sols, the aggregation was generally in the form of linked chains of particles (*i.e.*, necklaces). A different form of platinum particle was generated by carbon monoxide reduction of platinum dioxide (PtO$_2$·xH$_2$O, Adam's Catalyst). Infrared transmission spectra were recorded of the aqueous sols held as a thin-layer (5 to 10 μm) between calcium fluoride windows, using the spectrum of the windows as a background. The spectrum of water was then subtracted from the spectrum of each sol until the very broad band (*ca.* 2137 cm^{-1}) in the spectrum of water was effectively eliminated.

Saturation of the aqueous platinum colloid samples, from both citrate and borohydride reductions, with carbon monoxide resulted initially in the appearance of $v(CO)_{ads}$ at 2065—2070 cm^{-1} (Figure 1). This band shifted with time to 2040—2050 cm^{-1} (Figure 2). The stretching frequency of adsorbed carbon monoxide at zero time (Figure 2) corresponds to the frequency observed in the infrared spectrum recorded immediately after preparing the sample. The near coincidence of $v(CO)_{ads}$ for platinum particles of different average dimensions (3.0 nm: 2065—2070 cm^{-1}; 6.0 nm: 2065—2070 cm^{-1}) appears to indicate that particle size, *per se*, does not strongly influence the position of $v(CO)_{ads}$. Aggregation occurs spontaneously with time and is probably promoted by the progressive evaporation of the aqueous solvent in the thin layer. The band at 2065—2070 cm^{-1} broadens with time selectively on the low wavenumber side. This broadening and the displacement of the absorption maximum may arise from any one (or more) of the following factors: a redistribution of surface sites associated with flocculation, changes in charge at
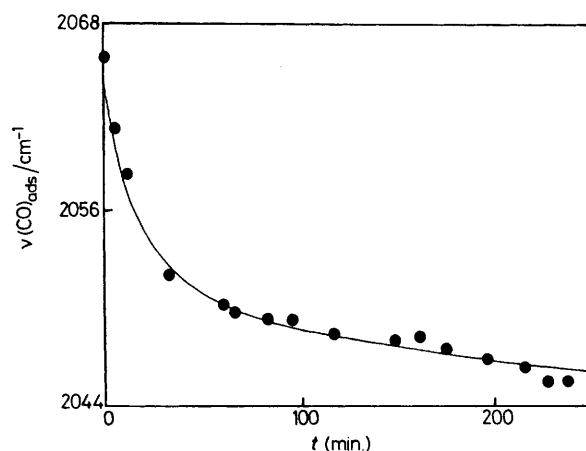
the metal surface which will perturb the π-acceptor bonding, the formation of new, more highly energetic surface sites from the reduction of residual platinum (II or IV) surface phases, reconstruction of the metal surface associated with CO chemisorption, and contributions from anomalous refractive index change. It is clear that carbon monoxide prior to, and even after, colloid aggregation is predominantly present in the linear adsorption mode (*i.e.*, there is very little absorption below 1900 cm^{-1} which could be ascribed to carbon monoxide bridging metal surface sites[1]).

For platinum particles formed by the partial reduction of platinum dioxide in aqueous media, a broader $v(CO)_{ads}$ is observed at 2040—2050 cm^{-1} which generally does not vary with time. As expected, enhanced levels of aqueous carbon dioxide (2343 cm^{-1}), resulting from the reduction of platinum dioxide by carbon monoxide, are apparent in the spectrum.

The position of $v(CO)_{ads}$ (2065—2070 cm^{-1}) for the platinum sols coincides with its position for platinum electrode surfaces in an acidic medium at −100 mV (*vs.* standard hydrogen electrode).[2] This result suggests that the colloidal platinum particles resemble a platinum electrode in a relatively reduced (cathodic) condition. X-ray photoelectron spectra of the dry-deposited platinum sols exposed to CO also indicate that the surface layers of the colloidal particles are predominantly (but not exclusively) platinum metal. A detailed report of this work including complete surface analysis data will be published in the near future in which the issues raised in this paper will be explored and tested further.

References

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