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FTIR STUDIES OF SURFACE ADSORPTION
ON NOBLE METAL HYDROSOLS

A thesis submitted to the
University of Auckland for
the degree of
Doctor of Philosophy

by
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Carbon monoxide adsorption, surface speciation and particle size distributions have been studied in platinum, palladium, and rhodium hydrosol systems using Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy and transmission electron microscopy. In transmission electron micrographs of unprotected platinum and palladium hydrosols, particle necklacing believed to arise from sintering during preparation, is apparent. The average particle sizes of all hydrosols studied were in the range of 2 to 12 nm. X-ray photoelectron spectra of the metal hydrosols revealed evidence for (Pt-O)_{ads}, Pt(II) and Pt(IV) oxides on platinum hydrosol particles whereas Pd(II) and Pd(IV) oxides were detected on the surfaces of palladium hydrosol particles. These surface oxides are found to be important in influencing hydrosol surface processes such as CO adsorption as a function of pH, inhibition of CO adsorption by alcohols and surface corrosion products resulting from the addition of iodide and cyanide.

Fourier transform infrared spectra of CO-treated metal hydrosols revealed bands due to CO linearly adsorbed on the metal particles at ca. 2070 cm^{-1} (Pt), 2067 cm^{-1} (Pd) and 2045 cm^{-1} (Rh) whereas bands due to bridge-adsorbed (B_{ads}) CO were detected at ca. 1950 cm^{-1} (Pd) and 1890 cm^{-1} (Rh). The use of CO as a spectroscopic probe molecule enabled the study of changes in the surface properties of the metal hydrosols which were induced by changes in the dispersion medium. For example, \nu(CO)_{ads} was observed to decrease in infrared spectra of CO-treated platinum and rhodium hydrosols as pH was increased by KOH or other dissolved salts yielding
alkaline solutions. This suggested a reduction in CO coverage resulting from hydroxyl adsorption and consequent increased oxide growth on the particles. In contrast, CO adsorption on platinum and rhodium hydrosols was enhanced in acidic media possibly as a result of the neutralisation of surface hydroxyls. The spectroscopic behaviour of adsorbed CO on platinum and rhodium hydrosols was only comparable to that of CO adsorbed at an electrode surface in acidic media when protecting agent was present which prevented aggregation of the hydrosol in such media. Inhibition of CO adsorption on platinum hydrosols was induced by the addition of aliphatic alcohols, poly(vinyl alcohol) and poisoning anions such as CN⁻ and SH⁻. Correlations of ν(CO)ads with CO coverage suggested that island formation of adsorbed CO was occurring for CO adsorption on unprotected palladium hydrosols and protected platinum and rhodium hydrosols as a function of pH.

In allied investigations, an infrared spectroelectrochemical study of corrosion of a nickel electrode in aqueous cyanide media has revealed that [Ni(CN)₄]²⁻ is detected at potentials more cathodic than 200 mV vs. SCE. Cyanide was oxidised to cyanate (OCN⁻) and then successively to carbon dioxide at potentials more anodic than 200 mV vs. SCE. The appearance of features at 2094 cm⁻¹ (HCN) and 2256 cm⁻¹ (HNCO) were attributed to pH changes associated with the oxidation of cyanide to cyanate. The appearance of a band at ca. 2218 cm⁻¹ in infrared spectra of the thin layer at very high potentials (> 1000 mV vs. SCE) was believed to arise from an unstable nickel(II) isocyanate complex.
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LIST OF ABBREVIATIONS AND SYMBOLS

FTIR = Fourier transform infrared spectroscopy
ATR = Attenuated total reflectance
SNIFTIRS = Subtractively normalised interfacial Fourier transform infrared spectroscopy.
PM-FTIRRAS = Polarisation modulated Fourier transform infrared reflection-absorption spectroscopy.
TEM = Transmission electron microscopy
XPS = X-ray photoelectron spectroscopy
NMR = Nuclear magnetic resonance
EXAFS = Extended X-Ray absorption fine structure
HREM = High resolution electron microscopy
SERS = Surface enhanced Raman scattering
CTAB = Cetyl trimethyl ammonium bromide
PVA = Poly(vinyl alcohol)
B_2 = The two-fold bridging mode of CO adsorbed on metal surfaces
I = Current in amperes (A)
i_A = Current density in μA cm^{-2}
A'((CO)) = Normalised absorbance of the \nu(CO)_{ads} Band
θ((CO))_{ads} = Fractional CO coverage on the metal hydrosol particles
Θ((CO))_{ads} = Metal-face-averaged CO coverage on the metal hydrosol particles
λ_n = Mean free path of electrons in XPS (in nm)
FWHM(i) = Full width at half maximum of the ith curve-fitted peak (XPS)

$A_i/M = \text{Peak area ratios (in XPS)}$

$A_{ox}/A_M = \text{Total metal oxide to metal peak area in curve-fitted X-ray photoelectron spectra.}$

$\sum(A_{CO}) = \text{The sum of the sub-band absorbances in curve-fitted } \nu(\text{CO})_{ads} \text{ bands}$

$A_{450} = \text{Turbidity at 450 nm in metal hydrosols as measured by ultra-violet/visible spectroscopy}$

$A_{2137} = \text{Absorbance of the association band of water in the infrared spectra of hydrosols at 2137 cm}^{-1}$

$ICV = \text{Irradiated cell volume}$

$V = \text{Volume of irradiated cell volume}$

$R = \text{Radius of the infrared beam}$

$L = \text{Sample pathlength in infrared spectroscopy}$

$S_M = \text{Total surface area of colloidal metal particles}$

$S_{CO} = \text{Surface area occupied by CO molecules on the metal hydrosol surface.}$

$S_{M,\text{atom}} = \text{Average surface area per metal atom (M=Pd, Pt)}$

$a = \text{Lattice vector lengths}$

$[M] = \text{Concentration of colloidal metal particles in metal hydrosols}$

$r = \text{Average particle radius of metal hydrosol particles.}$

$\rho = \text{Density of metal comprising metal particles.}$

$N_{\text{surf}} = \text{Total number of surface metal atoms available for CO adsorption in the irradiated cell volume.}$

$N_{CO} = \text{Total number of adsorbed CO molecules in the irradiated cell volume.}$

$S_{\text{Internal}}/A_{\text{External}} = \text{Ratio of internal CO molecules to external CO molecules in island}$
films of adsorbed CO.

dv/dpH = Slope of the v(CO)_{ads} vs. pH curves in metal sol/CO adjusted pH studies.

dv/d\psi_o = The rate of change of frequency (v) with surface potential (\psi_o) as applied to metal hydrosol/CO systems

dv/dE = The rate of change of frequency (v) with surface potential (E) as applied to metal electrode/CO systems.