

The Characterization of Adsorbed Carbon Monoxide on Colloidal Palladium by Infrared and High Resolution ^{13}C Nuclear Magnetic Resonance Spectroscopy

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Carbon monoxide adsorbed on a stabilized 20 Å palladium colloid in methylcyclohexane has been characterised by solution IR and high resolution NMR spectroscopy.

It is of interest to investigate the co-ordination chemistry of surface metal atoms in transition metal colloids with a view to making comparisons with both heterogeneous supported metals and molecular organometallic clusters. To this end we have begun to investigate the surface chemistry of colloidal metals in terms of the concepts of molecular cluster chemistry, with a view to the development of the surface organometallic chemistry of colloidal metals. In this paper we report the application of standard spectroscopic techniques of molecular organometallic chemistry (high resolution NMR and IR spectroscopy) to the characterization of carbon monoxide, the most common ligand in organometallic cluster chemistry, adsorbed onto colloidal palladium in non-polar solvents.

The metal colloid solutions were prepared by the method we previously reported¹ for the preparation of stable colloidal transition metals in non-polar organic solvents, by the condensation of the metal vapour into methylcyclohexane solutions of isobutylaluminumoxane, $[\text{Bu}^i\text{AlO}]_n$, at -120°C in a rotary metal vapour synthesis reactor. Aluminumoxane to metal ratios of *ca.* 10 were used. The aluminumoxane, which is a low molecular weight oligomer,² fulfills the typical role of a polymer stabilizer in colloid chemistry, associating with the surface of the metal particles and preventing aggregation. The colloidal palladium prepared in this manner is highly dispersed ($20 \pm 3 \text{ \AA}$)¹ placing these metal particles in a size range approaching that of the core sizes of some of the larger molecular carbonyl clusters, and making them promising candidates for the application of molecular spectroscopic techniques.

Carbon monoxide was passed through the solution for several minutes. The rapid adsorption of CO was revealed by IR spectroscopy (Figure 1). Bands at 2062s and 1941m cm^{-1} correspond to the expected absorptions for terminal (linear) and bridging carbonyls. The profile of the bands resembles

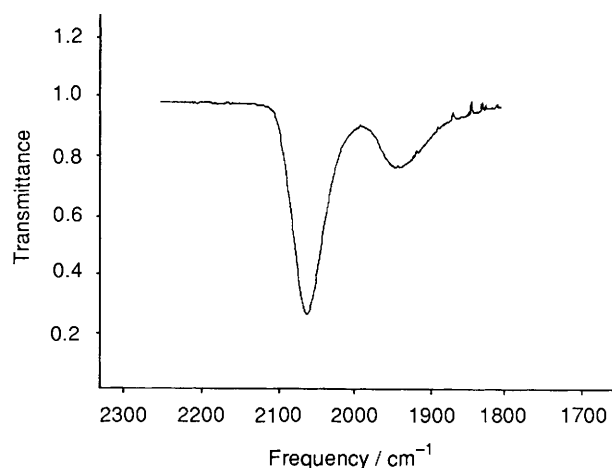


Figure 1. IR spectrum of CO on isobutylaluminumoxane stabilized colloidal palladium in methylcyclohexane (see text).

that found for CO on metal surfaces and crystallites,³ and contrasts with the relatively sharp bands characteristic of molecular cluster carbonyls. The frequencies, especially that of the linear CO, are lower than the range often reported for CO on palladium, but it is not possible to draw any precise conclusions on the nature of the carbonylated colloidal metal particles from simple comparisons with the IR spectrum of CO on palladium since the stretching frequency for surface adsorbed CO is markedly affected by coverage, particle size, and the presence of impurities.⁴

The small size of the colloidal palladium clusters raised the prospect that the adsorbed CO might be amenable to ^{13}C NMR spectroscopy in solution. Samples of a palladium colloid were prepared by concentrating the original organosols to a concentration of $\sim 1\text{--}2\%$ metal (a factor of 5–10), filtering as before, and exposing the concentrated solution to 99% ^{13}C CO for several minutes.

^{13}C NMR spectra (75 MHz)⁵ of CO on colloidal palladium at room temperature show a broad (19 ppm) inhomogeneously broadened line (T_2 12 ms) centred at δ 190 [Figure 2(b)]. Although this lineshape is essentially unchanged at 333 K [Figure 2(c)], cooling the sample to 220 K results in a broadened line with a shoulder becoming apparent to lower field [Figure 2(a)]. Solutions of ^{13}C CO in methylcyclohexane containing poly(isobutylaluminumoxane) show a sharp singlet of low intensity at δ 184 due to dissolved ^{13}C CO, which is absent in the palladium containing sample.

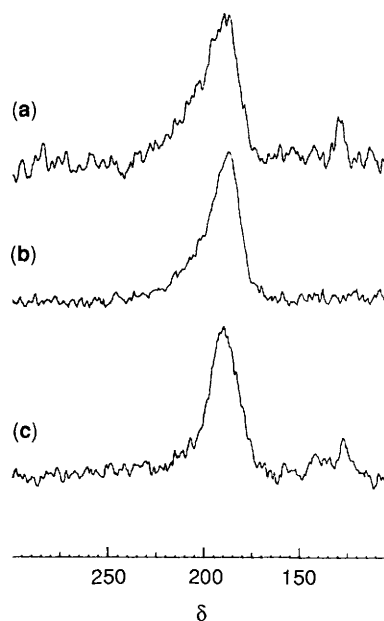


Figure 2. Variable temperature 75 MHz ^{13}C NMR spectra of CO adsorbed on colloidal palladium (*ca.* 1% in methylcyclohexane, see text) at (a) 220 K (364 transients); (b) 298 K (8000 transients); (c) 333 K (50 000 transients). Spectra (proton decoupled) were acquired on a commercial spectrometer using a conventional high resolution probe.

At 220 K the resonance becomes markedly asymmetric, with an apparent shoulder at δ ca. 210 [Figure 2(a)]. Bridging carbonyls in supported metals and carbonyl clusters typically have chemical shifts to low field of terminal carbonyl resonances, and we conclude that the lineshape we observe reflects the presence of both types of carbonyls, consistent with the IR spectrum. Neither the observed lineshapes nor room temperature relaxation measurements allow an unambiguous assignment of the relative populations, and it is possible that in the inhomogeneous surface environment provided by the polymer stabilized colloid particles the terminal and bridging carbonyls have overlapping chemical shift ranges. At 333 K the low-field shoulder is not observed, and we ascribe this to the effect of an increase in the rate of exchange of CO molecules between the two sites. The relatively large linewidth of the CO resonance in what we take to be the high temperature limiting spectrum is attributed to the polydispersity of the colloid particles. An alternative explanation, incomplete averaging of the CO chemical shift tensor by the non-isotropic tumbling of the colloid particles, can be ruled out on the basis of the observation that a hole burned in the CO resonance⁶ does not broaden with time and recovers with T_1 [T_1 (298 K) = 160 ms].

We note that the ¹³C resonance is quite far from the isotropic terminal carbonyl shifts obtained by solid state NMR spectroscopy for CO on palladium/ η -alumina (δ 675)⁷ or palladium/ γ -alumina (δ 750),⁸ but within the range reported both for terminal carbonyls in transition metal cluster carbonyls^{9,10} and for CO adsorbed on supported rhodium and ruthenium^{11–14} catalysts. The metallic particles in those studies, however, were larger and presumably more metallic than those studied here, and the large shifts are attributed to a Knight shift interaction with the electrons in the conduction band, a phenomenon associated with the onset of metallic properties.¹⁵ Palladium *metal* has a Knight shift of -3.05%, much larger than that for rhodium (0.41%), and so the expected shift of co-ordinated CO on a metallic palladium particle would be expected to be much greater than that for CO on a similar rhodium particle (see above).

Details of the NMR experiment, and analogous experiments with platinum colloids and with other small adsorbed molecules such as ethylene will be reported in a subsequent paper.

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