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NOTES

Evidence for Reversible Formation of Rhodium Tricarbonyl Species in Surface Supported Rhodium Catalysts

The formation of an apparent tricarbonyl of rhodium was observed when $[Rh(CO)_2Cl]_2$ deposited on SiO_2 was exposed to 600 Torr of CO at 300 K. The $\nu(CO)$ bands assigned to the tricarbonyl species were at 2072 and 2107 cm^{-1}, quite close in frequency to the two bands reported when $[Rh(CO)_2Cl]_2$ in solution was converted to a tricarbonyl complex of Rh by exposure to high pressures (13 atm) of CO. On SiO_2 and in solution the conversion to the tricarbonyl was only partial with the bands of the initial dimer always remaining. The ability to add a third CO per Rh was observed subsequently for mildly reduced $RhCl_3/SiO_2$ or $Rh(NO_3)_3/SiO_2$, but with these materials it was possible to prepare samples in which the conversion to the tricarbonyl was nearly complete at 600 Torr; a third band associated with the tricarbonyl emerged near 2030 cm^{-1} as the 2040-cm^{-1} band of the surface dicarbonyl disappeared. The spectral behavior observed in this study was quite similar to that reported for $Rh^I(CO)_2$ on Al_2O_3 when exposed to higher pressures of CO. The presence of three bands for the tricarbonyl eliminates a strict C_{3v} symmetry for the tricarbonyl and suggests a square planar C_{2v} or a distorted C_{3v} structure. The increased ability to add a third CO is briefly discussed in terms of the effect of the surface on the geometry and electronic structure about Rh atoms.

The ability of a metal center to expand its coordination sphere by reversible addition of a ligand reactant is a critical element in most metal-catalyzed processes—including heterogeneous processes. Extensive studies of CO as a ligand in homogeneous systems have delineated many mechanisms clearly demonstrating such reversible addition of this ligand. It is however, more difficult to precisely establish the critical steps and active sites leading to an overall catalytic process in heterogenous systems. One reason is that key reversible addition and activation steps for a reactant might occur at sites in very low concentration at the surface and might, therefore, not be observable by techniques employed. The ability to create or stabilize larger concentrations of the reactive species is essential to their identification and understanding. One way to achieve this is to produce a proposed reactive surface intermediate via an alternate approach that might create the intermediate at higher concentrations and/or with a longer lifetime. An aim of studies using metal carbonyls as the source of supported metal catalysts is the stabilization of reactive intermediates that might not be detected with catalysts prepared from the conventional starting materials.

We report here the results of depositing a molecular metal carbonyl, $[Rh(CO)_2Cl]_2$, onto silica, and compare these results with our observations when $RhCl_3$ or $Rh(NO_3)_3$ is the precursor to a supported Rh catalyst. Although $[Rh(CO)_2Cl]_2$ maintains its molecular integrity as it adsorbs on SiO_2, it exhibits much enhanced ability (as compared with the same compound in solution) to reversibly coordinate a third CO ligand at the silica-bound rhodium atoms. This ability to add CO was subsequently found for mildly reduced silica supported $RhCl_3$ and $Rh(NO_3)_3$, suggesting this may be a more common property of supported Rh than previously suspected. The formation of a $Rh^I(CO)_2$ surface species upon reduction of $RhCl_3/SiO_2$ and $Rh(NO_3)_3/SiO_2$ systems is well documented (*1–4*), but the ability of this silica bound Rh(I) to coordinate a third CO ligand under ambient conditions has not been reported, although the detection of a

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rhodium tricarbonyl was observed recently with $RhCl_3$ on alumina at low temperatures (*5*).

A description of the infrared cells and equipment used appears elsewhere (*6*). $[Rh(CO)_2Cl]_2$ adsorption onto silica (Cab-O-Sil) pellets suitable for infrared measurements was achieved via sublimation after pretreating the silica by evacuating at 400°C for 1 h.

Table 1 lists the $\nu(CO)$ frequencies obtained after 35 min exposure of SiO_2 to $[Rh(CO)_2Cl]_2$ vapor, while Fig. 1B shows the carbonyl spectrum obtained. The relative intensities for bands in the $[Rh(CO)_2Cl]_2/SiO_2$ sample closely match those of $[Rh(CO)_2Cl]_2$ in heptane, but the frequency of each band is shifted upward by 5–10 cm^{-1}. This close correspondence with the solution spectrum, coupled with the observation that no gas was detected above the sample after deposition, has been interpreted to mean $[Rh(CO)_2Cl]_2$ adsorbs without decomposition or ligand dissociation, and binding to the surface only slightly perturbs the bonding and structure of the complex. In the $\nu(OH)$ IR region, diminution of the band at 3747 cm^{-1}, assigned to isolated SiO_2 surface hydroxyl groups, and emergence of a broad band at 3650 cm^{-1}, assigned to H-bonded surface hydroxyls, were observed for the $[Rh(CO)_2Cl]_2/SiO_2$ sample. As with $Co_2(CO)_8/SiO_2$ (*6*), this indicates H-bonding of the complex to surface hydroxyl groups, probably through the chloride bridging ligands in this case.

TABLE 1

Rhodium Dicarbonyl Frequencies

Sample	$(CO)^a$ cm^{-1}
$[Rh(CO)_2Cl]_2$ in heptane	2035(s), 2090(s), 2106(sh)
$[Rh(CO)_2Cl]_2/SiO_2$	2043(s), 2097(s), 2112(sh)
$RhCl_3/SiO_2$^{b}	2043(s), 2100(s), 2111(sh)
$Rh(NO_3)_3/SiO_2$^{b}	2039(s), 2098(s), 2109(sh)

[a] The observed ^{13}CO bands are omitted.

[b] Rh(I) samples formed from listed starting material after mild reduction in 600 Torr at 50°C followed by evacuation.

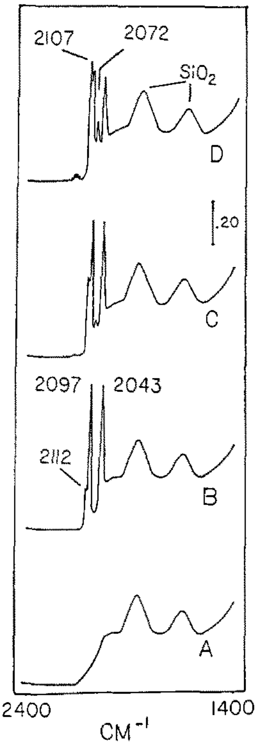

FIG. 1. Behavior of $\nu(CO)$ region of $[Rh(CO)_2Cl]_2/SiO_2$. (A) silica background after heating to 400°C for 1 h while evacuating; (B) after 35 min exposure to the vapor of $[Rh(CO)_2Cl]_2$ and under vacuum; (C) 100 Torr CO; (D) 600 Torr CO. The diminution of the bands in (B) is apparent in (C) and (D) by comparing their intensities to the intensities of the silica bands marked.

Under subambient pressures (~600 Torr) of CO, samples of $[Rh(CO)_2Cl]_2/SiO_2$ displayed two additional $\nu(CO)$ bands (2072 and 2107 cm^{-1}) with concommitant decrease of the bands initially present. These results are displayed in Figs. 1C and D. The process was totally reversible with the spectrum reverting to that in Fig. 1B upon evacuation of the CO.

$[Rh(CO)_2Cl]_2$ has been reported to add CO in solution to form a tricarbonyl species, although high pressures of CO (13 atm) were required at room temperature (*7*). The product, which was reasonably assigned as $Rh(CO)_3Cl$, reformed $[Rh(CO)_2$

Cl]$_2$ when the CO pressure was reduced. Due to the close correspondence between the ν(CO) bands assigned to Rh(CO)$_3$Cl in solution and the new bands obtained in this study upon exposure of the silica bound complex to CO (Table 2), the formation of the Rh(CO)$_3$Cl species on the SiO$_2$ surface is concluded.

It has been widely reported that mild reduction of RhCl$_3$/SiO$_2$ or Rh(NO$_3$)$_3$/SiO$_2$ to form Rh(I) ions followed by adsorption of CO produces a ν(CO) spectrum quite similar to that observed for [Rh(CO)$_2$Cl]$_2$ (*1–3*). These rhodium species generally show two ν(CO) bands, one in the range 2030–2040 cm^{-1} and the other at 2090–2100 cm^{-1}, depending upon details of treatment. The rhodium carbonyl species responsible for this spectrum generally have been described as dicarbonyls of Rh(I). The only feature found with [Rh(CO)$_2$Cl]$_2$ but not reported in many of the studies of the purported Rh(CO)$_2$ species is the weak shoulder near 2110 cm^{-1} which arises from vibrational coupling between carbonyl groups across the Rh–Rh bond of the dimer. The presence of a ν(CO) high-frequency shoulder after mild reduction and exposure for these RhCl$_3$/SiO$_2$ and Rh(NO$_3$)$_3$/SiO$_2$ samples would suggest a dimeric structure similar to [Rh(CO)$_2$Cl]$_2$.

TABLE 2

Rhodium Tricarbonyl Frequencies

Sample	(CO) cm^{-1}	Ref.
[Rh(CO)$_2$Cl]$_2$ in 1,2-dichloroethane (13 atm)[a]	2052, 2098	*7*
[Rh(CO)$_2$Cl]$_2$ in hexane (13 atm)[a]	2060, 2100	*7*
[Rh(CO)$_2$Cl]$_2$/SiO$_2$ (600 Torr)	2072, 2107	This work
RhCl$_3$/SiO$_2$[b] (600 Torr)	2030, 2074, 2109	This work
Rh(NO$_3$)$_3$/SiO$_2$[b] (600 Torr)	2030,[c] 2076, 2111	This work
Rh^{I}(CO)$_2$/Al$_2$O$_3$[d]	2026, 2078, 2120	*5*

[a] Pressures listed in parentheses are those at which the listed sample was partially converted to the tricarbonyl.

[b] Supported Rh(I) samples formed from the listed starting material by mild reduction in 600 Torr CO at 50°C.

[c] Appeared as a small shoulder on the 2039-cm^{-1} dicarbonyl band.

[d] Tricarbonyl formed with this sample at 423 Torr CO and 241 K and at 65 Torr CO and 90 K.

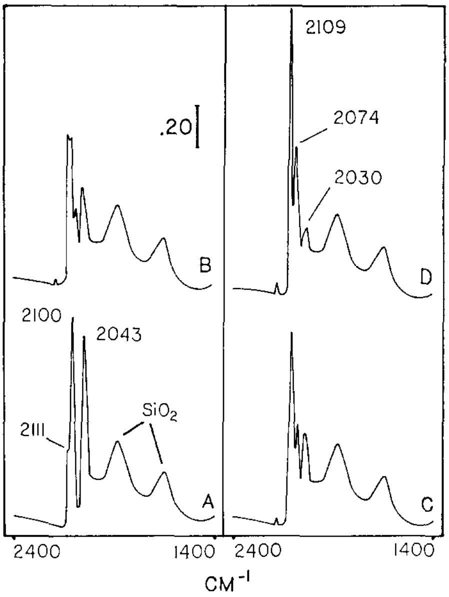

FIG. 2. Behavior of ν(CO) region of RhCl$_3$/SiO$_2$. After deposition of RhCl$_3$ onto silica, the sample was reduced in 600 Torr CO at 50° for 0.5 h. (A) sample following evacuation: (B) 100 Torr CO, (C) 200 Torr CO, (D) 600 Torr CO.

These observations, coupled with the recent report that RhCl$_3$/Al$_2$O$_3$ could be reduced and exposed to CO at low temperatures to produce what appeared be the tricarbonyl species (*5*), suggested expanding this study to include silica-supported RhCl$_3$ and Rh(NO$_3$)$_3$. Samples of RhCl$_3$/SiO$_2$ and Rh(NO$_3$)$_3$/SiO$_2$ were prepared by incipient wetness (1% loading) and pressed into wafers suitable for infrared measurements. The spectra of samples placed in IR cells described previously (*6*) and exposed to 600 Torr CO at 50°C for 0.5 h were very similar, after evacuation (Fig. 2A), to those in Fig. 1B and to spectra reported in the literature for similarly prepared Rh/SiO$_2$ samples (*2, 3*). The presence of a ν(CO) band pattern very much like [Rh(CO)$_2$Cl]$_2$ indicates a dimeric structure for the Rh(CO)$_2$ surface species. Presumably, a dimeric surface species could be produced with bridging surface oxides instead of chlorides to explain the close agreement of the ν(CO) spectrum of samples derived from $RhCl_3$ or $Rh(NO_3)_3/SiO_2$ with that of the supported rhodium dimer.

Under a pressure of CO (~100 Torr) both the $RhCl_3/SiO_2$ and $Rh(NO_3)_3/SiO_2$ samples displayed three new ν(CO) bands (Table 2 and Fig. 2). Two of these bands, at about 2075 and 2110 cm^{-1}, closely match the bands assigned to $Rh(CO)_3Cl$ formed by addition of CO to $[Rh(CO)_2Cl]_2$ in solution or on SiO_2. The third band, at 2030 cm^{-1}, has not been reported for $Rh(CO)_3Cl$. It is, however, very close to the strong lower frequency band (near 2040 cm^{-1}) for $[Rh(CO)_2Cl]_2$ or surface $Rh(CO)_2$ species. The new 2030-cm^{-1} feature may have been obscured in previous studies by the 2040-cm^{-1} band of dicarbonyl species also present. Figure 2 shows a $RhCl_3/SiO_2$ sample for which the CO pressure (600 Torr) was sufficient to effect nearly complete conversion to the tricarbonyl compound leaving only a shoulder near 2040 cm^{-1}.

In a previous study (*5*), the presence of just two ν(CO) bands led to an assumption of C_{3v} symmetry for the surface bound $Rh(CO)_3Cl$, although a metal d^8 center such as Rh(I) would be expected to have square planar geometry in $Rh(CO)_3Cl$ and be of C_{2v} symmetry with three IR active ν(CO) fundamentals ($A_1 + 2B_1$). The three ν(CO) bands for the tricarbonyl species generated from $RhCl_3$ or $Rh(NO_3)_3$ prepared in the present work by incipient wetness methods can best be explained in terms of a square planar $Rh(CO)_3X$ where X is a surface oxide for samples generated from $Rh(NO_3)_3SiO_2$ and either a surface oxide or chloride for those from $RhCl_3/SiO_2$. It may be inferred that the tricarbonyl generated from $[Rh(CO)_2Cl]_2$ on SiO_2 is the same square planar species.

Recent studies of CO reactions with supported metal atoms have included increasing interest in the effects of the support upon the ability of the transition metal center to coordinate CO. Such studies include the impact of the support upon the carbonyl chemistry of an adsorbed metal carbonyl species as well as the profound effects on catalytic reactions involving CO in systems displaying strong metal–support interactions (see (*8*) for recently published SMSI models).

Metal carbonyls generally become more labile toward loss of CO ligands upon interaction with an oxide support surface (*9*). This appears to be the first report of a transition metal carbonyl complex increasing its ability to *add* CO as a result of *in tact* deposition on an oxide support. The reason for the increased ability of $[Rh(CO)_2Cl]_2$ on SiO_2 to reversibly add CO is unclear at this time. Calculations suggest, though, that the ground state energies of planar and bent configurations of this compound differ by only about 4 kcal/mol (*10*). Conversion from one to the other configuration, effected by adsorption on a surface, might lower the energy of orbitals involved in coordination of a third CO. The lack of complete characterization of the tricarbonyl product and the uncertainty about the actual solution structure of $[Rh(CO)_2Cl]_2$ render further speculation pointless at this time.

It is significant that the Rh(I) dicarbonyl formed by mild reduction of deposited Rh(III) showed behavior similar to that of supported $[Rh(CO)_2Cl]_2$. Catalyst promoter effects, studied for Rh/SiO_2 samples used as catalysts for CO hydrogenation, suggest the increased activity due to promoters such as manganese or molybdenum oxide is due to the ability of the promoter oxide to stabilize Rh(I) relative to its complete reduction to Rh metal (*11*). The resulting $Rh(I)(CO)_2$, formed in the presence of CO, is assumed to be more active toward reversible CO coordination than is a Rh(0) surface carbonyl species. Our observation of reversibly formed tricarbonyl species of supported Rh(I) suggests one reason why stabilization of this oxidation state might be catalytically significant.

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