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Generation and Characterization of Rhodium Carbonyls Formed on Silica and Alumina under Mild Conditions

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The effect of the metal precursor on the surface structure of rhodium supported on SiO_2 and Al_2O_3 and treated under very mild conditions was examined. For both SiO_2 and Al_2O_3 supports, the mild conditions used produced samples with properties different from those that have heretofore been reported. Rh(I) on SiO_2 was obtained by sublimation of $[Rh(CO)_2Cl]_2$ and by mild reduction under CO of $RhCl_3/SiO_2$ and of $Rh(NO_3)_3/SiO_2$. In each case, three ν(CO) IR bands (two strong and one weak) were obtained with frequency and intensity patterns that closely matched those for molecular dirhodium complexes such as $[Rh(CO)_2Cl]_2$ and $[Rh(CO)_2OSiMe_3]_2$, indicating a dinuclear structure on the SiO_2 surface. Solvent extraction results led to the conclusion that if a dicarbonyl species was generated with $Rh(NO_3)_3/SiO_2$ it was in the form $[Rh(CO_2O_s]_2$ (where O_s is a surface oxide), while direct sublimation of $[Rh(CO)_2Cl]_2$ onto SiO_2 and reduction of $RhCl_3/SiO_2$ both formed physisorbed $[Rh(CO)_2Cl]_2$ that could be extracted readily from the surface into pentane. The $[Rh(CO)_2Cl]_2$ absorbed on pretreated Al_2O_3 behaved differently. Three ν(CO) IR bands initially evident (two strong and one weak) displayed a pattern different from that for the parent dirhodium complex. The weak band vanished within an hour while the two strong bands remained. The remaining bands were indistinguishable from the ν(CO) bands reported for monomeric surface $Rh^I(CO)_2$ species derived from $RhCl_3/Al_2O_3$ and $Rh(NO_3)_3/Al_2O_3$, while the short-lived species identified with the weak band is proposed to be a monocarbonyl of Rh(I). Pretreatment of the Al_2O_3 at 800°C produced a sample with shifted ν(CO) bands and color much different from that for other samples studied. The formation of the proposed monocarbonyl and the different behavior after 800°C pretreatment are discussed in terms of the role of Cl and Lewis acid sites.

INTRODUCTION

Precise control of the factors influencing reaction rates and selectivities in heterogeneous catalytic reactions is an important goal in the field of surface science. For heterogeneous catalysts consisting of transition metal species supported on oxide surfaces, observed reactivities and selectivities frequently depend on the form in which the transition metal is deposited. The catalytic properties sometimes differ for catalyst samples prepared from metal salts as compared with those from organometallic complexes. A recent example is the significantly lower rate of CO_2 hydrogenation for Al_2O_3-supported $RuCl_3$ than that with ruthenium carbonyl complexes on Al_2O_3 (*1*). Chloride incorporation into the metal–surface interactions for the catalyst prepared with $RuCl_3$ was thought to play an important role in determining the properties of that catalyst.

Many organometallic and metal carbonyl precursors of supported transition metal catalysts can be added to a support from the vapor phase. This allows for pretreatment of a support surface prior to addition of the catalyst precursor metal complex, with the pretreated surface remaining unaffected by exposure to solvent and/or atmosphere during addition of the metal. The complex itself then can be treated under

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very mild conditions after its addition to the surface in order to develop the desired catalyst. A significant question is the extent to which supported metal catalysts formed in this manner differ chemically or catalytically from those formed by mild reduction of a deposited metal salt.

Differences in catalyst samples prepared from different salts of the same metal also have been observed. $RhCl_3$ and $Rh(NO_3)_3$ were found to produce different relative amounts of Rh(0) and Rh(I) after reduction on Al_2O_3 (*2*) and displayed considerably different activities and selectivities in the hydrogenation of CO when supported on SiO_2 (*3*). In both of these studies with supported rhodium, the presence of chloride in the sample prepared with $RhCl_3$ was proposed as the source of the observed differences.

Recent work with SiO_2-supported rhodium has shown that dinuclear surface structures result from the direct vapor deposition of $[Rh(CO)_2Cl]_2$, as well as from reduction of rhodium derived from supported $RhCl_3$ or $Rh(NO_3)_3$ (*4*). When the metal precursor was $[Rh(CO)_2Cl]_2$, simple physisorption of the molecular complex on SiO_2 appeared to occur. The dinuclear surface species generated from $Rh(NO_3)_3/SiO_2$ was assigned to an oxide-bridged structure, $[Rh(CO)_2O_s]_2$ (O_s is a surface oxide with net minus one charge), while the nature of the dinuclear species derived from $RhCl_3/SiO_2$ was ambiguous, possibly being $[Rh(CO)_2Cl]_2$ and/or $[Rh(CO)_2O_s]_2$.

The structure of the $Rh^I(CO)_2$ surface species is well characterized and has been established to exist as isolated mononuclear $Rh^I(CO)_2$ units (*5–7*) at low-to-moderate Rh loading in Rh/Al_2O_3 samples generated from the carbonylation of rhodium salts and from $[Rh(CO)_2Cl]_2$. Recent EXAFS studies on $RhCl_3/Al_2O_3$ samples indicate that the $Rh^I(CO)_2$ fragment formed upon carbonylation is bound to the surface by three oxides resulting in a five-coordinate metal center (*6*). $Rh^I(CO)_2$ bound to two surface oxides and resulting in a four-coordinate square planar geometry about the metal center also has been discussed with respect to samples derived from $[Rh(CO)_2Cl]_2/Al_2O_3$ (*7*). No Rh–Cl interactions have been proposed for $Rh^I(CO)_2$ species generated from either $RhCl_3/Al_2O_3$ or $[Rh(CO)_2Cl]_2/Al_2O_3$.

Infrared spectroscopy and solvent extraction techniques were used in the present study to gain a more complete understanding of the importance of metal precursor and of chloride incorporation to the nature of the supported rhodium catalysts formed from the rhodium carbonyl dimer and rhodium salts treated under very mild conditions on SiO_2 and Al_2O_3 surfaces.

EXPERIMENTAL

$[Rh(CO)_2Cl]_2$ was prepared according to the method of McCleverty and Wilkinson with the use of a specially designed reactor (*8*). The silica was grade EH-5 from Cabot Corp., commonly known as Cab-O-Sil. The alumina was CK-300 γ-Al_2O_3 from Akzo Chemie.

Samples of $RhCl_3/SiO_2$ and $Rh(NO_3)_3/SiO_2$ were prepared by incipient wetness. Silica powder sufficient to yield 1% Rh loadings was added to $RhCl_3$ and $Rh(NO_3)_3$ aqueous solutions and the slurries were stirred overnight to dryness.

Wafers suitably thin to record transmission IR spectra were pressed with a stainless-steel die. Pressures of 1500 and 30,000 psi were used for the silica and alumina samples, respectively. The wafers were cut into suitable sizes for use in cells described elsewhere (*9*). $[Rh(CO)_2Cl]_2$ was deposited by sublimation onto pure SiO_2 or Al_2O_3 wafers that had been heated to varying temperatures under 10^{-5} Torr. Such samples are designated as $[Rh(CO)_2Cl]_2/SiO_2(Al_2O_3)$ hereinafter. Wafers of $RhCl_3/SiO_2$ and $Rh(NO_3)_3/SiO_2$ were heated to 50°C in 600 Torr CO in the IR cells. These samples are designated $RhCl_3/SiO_2$ or $Rh(NO_3)_3/SiO_2$ even after carbonylation.

Metal carbonyl complexes were extracted from the oxide supports within the special cells by mechanically raising the sample to the top of the cell, replacing the cell bottom with a Schlenk solution well (*10*) containing the extraction solvent, and submerging the sample in the solvent for a minimum of 10 min. The cell was continuously purged with dry N_2 during this procedure. A syringe was used to extract solution from the bottom of the cell to record the infrared solution spectrum. To obtain concentrations sufficient for an IR spectrum, minimal amounts of solvent were used in the Schlenk solution well and additional wafers, present in an auxiliary carriage, were dipped in the solution. The wafers were raised to the top of the cell following the extraction procedure, the Schlenk solution well was replaced by the original cell bottom containing IR windows, and the IR spectrum of the wafer again recorded.

A Nicolet 10-MX Fourier transform infrared spectrometer was used. The typical resolution of IR spectra was 2 cm^{-1}. A scan time of 2 min resulting in a maximum of 54 interferograms was commonly used.

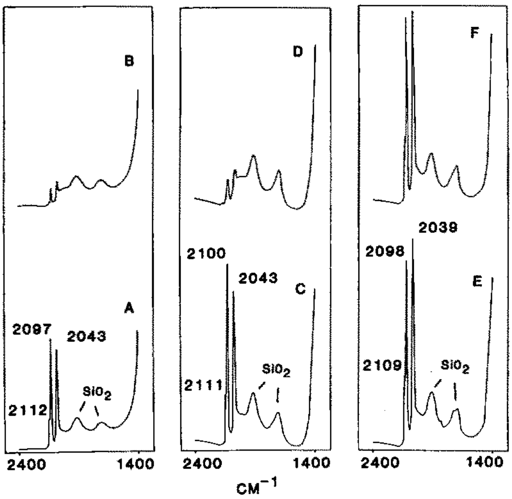

FIG. 1. Behavior of ν(CO) IR region of SiO_2-supported rhodium upon solvent extraction. The $[Rh(CO)_2Cl]_2/SiO_2$ sample was prepared as described in the text. Shown are surface IR spectra of $[Rh(CO)_2Cl]_2/SiO_2$ (A) before and (B) after solvent extraction with pentane. Surface $Rh^I(CO)_2$ species were also generated from samples of $RhCl_3/SiO_2$ and $Rh(NO_3)_3/SiO_2$ as described in the text. Spectra of $RhCl_3/SiO_2$ sample (C) following treatment with CO and (D) after extraction with pentane. Spectra of $Rh(NO_3)_3/SiO_2$ sample (E) following treatment with CO and (F) after extraction with pentane.

RESULTS

Rh/SiO$_2$. $[Rh(CO)_2Cl]_2$ was loaded via sublimation onto SiO_2 wafers that had been pressed for transmission infrared measurements and heated at 400°C under vacuum for over 1 h. The silica wafers, while positioned between the IR windows of the cell, were exposed to the $[Rh(CO)_2Cl]_2$ vapor for 35 min. This procedure provided for monitoring of the ν(OH) IR region during loading, the results of which have been presented elsewhere (*4*). The amount of rhodium on the surface was estimated to be <1% on the basis of elemental analyses in previous studies and of IR intensities. A typical ν(CO) IR spectrum that results from this preparation is shown in Fig. 1A. (SiO_2 samples prepared at other pretreatment temperatures, 100–800°C, gave results identical to those for the sample pretreated at 400°C.)

Samples of $RhCl_3/SiO_2$ and $Rh(NO_3)_3/SiO_2$ were prepared by incipient wetness. (1% Rh loading) without prior pretreatment of the support. Pretreatment of the SiO_2 before metal loading, as with the $[Rh(CO)_2Cl]_2/SiO_2$ samples, would be pointless since the water from the aqueous solutions of the rhodium salts would reverse the effects of the procedure. Wafers were pressed and placed in IR cells where they were exposed to 600 Torr CO at 50°C for ½ h and then evacuated. This temperature was sufficient for the reduction of Rh^{3+} ions to Rh(I). Higher temperatures facilitate conversion of rhodium to the zero-valent state. Typical IR spectra obtained in the ν(CO) region are shown in Figs. 1C and 1E.

The spectra obtained for each of the three different preparation methods display one weak and two strong ν(CO) bands. The three-band pattern in each case is strikingly similar to that obtained in the IR spectra of molecular $[Rh(CO)_2Cl]_2$ (*4*),

$[Rh(CO)_2OSiMe_3]_2$, and $[Rh(CO)_2OSiPh_3]_2$ (*11*), suggesting that these three preparations lead to surface dinuclear structures analogous to the structures of the molecular complexes. The similarity of spectra for the $[Rh(CO)_2Cl]_2/SiO_2$ sample and molecular $[Rh(CO)_2Cl]_2$, the absence of any gas phase CO, and the previously reported behavior (*4*) of the ν(OH) IR region during adsorption of the dinuclear complex strongly suggest that the rhodium complex physisorbs on the oxide surface and, therefore, could be extracted from the surface with an appropriate solvent. On the other hand, a surface species of the type $[Rh(CO)_2O_s]_2$, analogous to the silanato-bridged complexes mentioned above, should not be easily extracted from the surface.

Extractions of the surface carbonyl species obtained with each of the three preparations were attempted, using pentane as the solvent. Spectra of the oxide wafers after the extraction procedure are shown in Figs. 1B, 1D, and 1F. Most of the surface rhodium carbonyl was removed from the silica for both the $[Rh(CO)_2Cl]_2/SiO_2$ and the $RhCl_3/SiO_2$ samples, while the extraction process did not appear to remove metal carbonyl from the surface of samples generated from the $Rh(NO_3)_3/SiO_2$. Solution IR spectra of the pentane after the extraction procedure for the $[Rh(CO)_2Cl]_2/SiO_2$ and the $RhCl_3/SiO_2$ gave a ν(CO) spectrum identical with that of molecular $[Rh(CO)_2Cl]_2$ dissolved in pentane, while no ν(CO) bands were present in the pentane after the attempted extraction from $Rh(NO_3)_3/SiO_2$ wafers, nor was any coloration of the pentane evident in the latter case.

Rh/Al_2O_3. The Al_2O_3 was pressed into wafers suitable for transmission infrared measurements and pretreated by heating to 400°C while being evacuated for 1 h. Exposure of pretreated Al_2O_3 to the vapor of $[Rh(CO)_2Cl]_2$ for 10 min resulted in an IR spectrum with two strong ν(CO) bands (2025 and 2104 cm^{-1}) and a weak shoulder (~2095 cm^{-1}) as shown in Fig. 2B. The two strong bands are indistinguishable from those reported for $Rh^I(CO)_2$ species on Al_2O_3 prepared by other means (*5–7*); the weak shoulder has not been reported previously. The two strong ν(CO) bands were significantly broader than the ν(CO) bands recorded for $[Rh(CO)_2Cl]_2/SiO_2$ and $[Rh(CO)_2Cl]_2$/zeolites even though the percentage loading was approximately the same for all the samples (*4*). IR spectra were recorded at time intervals after the loading process. The sample remained in the IR beam and was not moved between scans, assuring that the spectra were recorded for the same part of the wafer. The frequencies and intensities of the two strong ν(CO) bands, presumably due to surface $Rh^I(CO)_2$ species, were unchanged, while the ν(CO) band initially evident as a shoulder weakened and vanished within a short period of time. Typical spectra are shown in Figs. 2B and 2C where the shoulder disappeared within 1 h. The initial three-band pattern in the ν(CO) region also was observed when Al_2O_3 was pretreated at 100, 200, or 800°C,

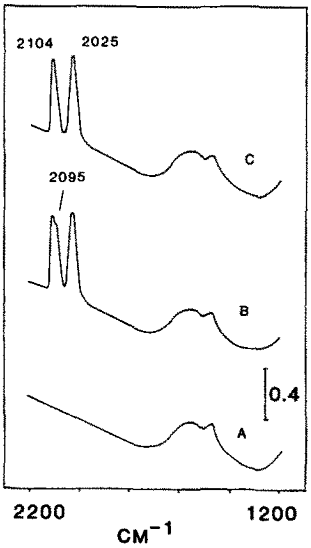

FIG. 2. Behavior of ν(CO) IR region of $[Rh(CO)_2Cl]_2/Al_2O_3$. (A) Spectrum of Al_2O_3 background after heating to 400°C for 1 h while evacuating; (B) spectrum immediately after 10 min exposure to $[Rh(CO)_2Cl]_2$ vapor in a closed cell; (C) spectrum 1 h after exposure to $[Rh(CO)_2Cl]_2$ vapor in a closed cell.

although the frequencies for the latter sample were shifted upward by 5–8 cm^{-1} and the sample was blood red in color while all others were gold.

An elemental analysis of a sample pretreated at 200°C showed 0.8% Rh loading and the mole ratio of Rh : Cl was 1 : 1. Longer exposure times of the pretreated Al_2O_3 to the $[Rh(CO)_2Cl]_2$ vapor facilitated higher loadings. However, the weak shoulder was no longer observed, possibly due to the breadth of the two intense $\nu(CO)$ bands.

DISCUSSION

Rh/SiO_2. Extraction experiments established definite differences between the silica-supported Rh samples derived from $[Rh(CO)_2Cl]_2$ or $RhCl_3$ on the one hand and $Rh(NO_3)_3$ on the other, even though $\nu(CO)$ spectra for all three samples are quite similar. The fact that the extract from the $[Rh(CO)_2Cl]_2$ and $RhCl_3$-derived samples is $[Rh(CO)_2Cl]_2$ suggests (but does not prove) that this is the species on the surface in those cases. This result is expected for $[Rh(CO)_2Cl]_2$ sublimed onto SiO_2 because the chemically passive nature of this surface, as reported in many metal carbonyl/oxide surface studies, usually results in simple physisorption of a metal carbonyl at room temperature. The conversion of $RhCl_3/SiO_2$ to $[Rh(CO)_2Cl]_2/SiO_2$ also is not surprising because the conditions used (50°C and 600 Torr CO) are similar to those used to synthesize the dimer directly from crystalline $RhCl_3 \cdot nH_2O$ (*8*).

The nature of CO-reduced $Rh(NO_3)_3/SiO_2$ is less clear. Obviously, there is no Cl present to facilitate conversion to $[Rh(CO)_2Cl]_2$, but by analogy with oxy-bridged dimers like $[Rh(CO)_2OSiPh_3]_2$ it is reasonable to conclude that surface oxides have formed bridges between directly interacting $Rh^I(CO)_2$ species to form $[Rh(CO)_2O_s]_2$. Table 1 presents solution IR $\nu(CO)$ frequencies of the various bridged rhodium carbonyl dimers for comparison with the spectra of the surface species.

TABLE I

Carbonyl Frequencies for Oxy-Bridged Rhodium Species

Sample	$\nu(CO)^a$ (cm^{-1})	Ref.
$[Rh(CO)_2O_s]_2/SiO_2^b$	2039 s, 2098 s, 2109 sh	This work
$[Rh(CO)_2OSiPh_3]_2$	2014 s, 2076 s, 2090 m	*11*
$[Rh(CO)_2OSiMe_3]_2$	2009 s, 2072 s, 2088 m	*11*

[a] ^{13}CO frequencies are not included.

[b] O_s, surface oxide.

The oxide-bridged surface species has been proposed previously for the product of carbonylation of $RhCl_3/SiO_2$ (*12*) and for a sample derived from an allylic carbonyl rhodium complex on SiO_2 (*13*). The $\nu(CO)$ band pattern in this study establishes the dinuclear surface structure, but the experimental results suggest a chloride rather than an oxide-bridged structure for the sample derived from $RhCl_3/SiO_2$.

Rh/Al_2O_3. The $\nu(CO)$ bands obtained for $[Rh(CO)_2Cl]_2/Al_2O_3$ do not match those of the parent carbonyl. Indeed, the two strong $\nu(CO)$ IR bands that remain after the weak shoulder (2095 cm^{-1}) disappears are indistinguishable from those recorded for $Rh^I(CO)_2$ on Al_2O_3 generated by a variety of other means in numerous studies (*5, 7, 13*) and which have been assigned to the symmetric and asymmetric carbonyl stretches of $Rh^I(CO)_2$ fragments on isolated sites on an Al_2O_3 surface. There are two possible interpretations for the initial three $\nu(CO)$-band pattern.

One possibility—that the three initial $\nu(CO)$ bands arise from one surface complex that converts over time to $Rh^I(CO)_2$—is dismissed because the intensities and frequencies of the two intense bands (2025 and 2104 cm^{-1}) remain essentially unchanged as the 2095 cm^{-1} shoulder disappears. This leaves the interpretation in which the two intense bands are due to $Rh^I(CO)_2$ formed immediately after depositing $[Rh(CO)_2Cl]_2$, while the shoulder is a second species, perhaps a rhodium monocarbonyl.

The transient monocarbonyl could form on a different Rh oxidation state—perhaps a higher oxidation state not yet reduced to

Rh(I). Indeed, bands near 2090 cm^{-1} have been assigned by Scurrell (*14*) to magnesia-supported $[Rh(CO)Cl_5]^{2-}$. Their frequency is much lower, though, than those reported by Mattera *et al.*, at 2125–2178 cm^{-1} for monocarbonyls of Rh(III) in ionomers (*15*) or even the 2120 cm^{-1} frequency observed for CO on Rh(II) ions on surfaces (*5*). On the other hand the frequency for the transient species is well above the 2060–2075 cm^{-1} range usually found for monocarbonyls on Rh(0). It is tempting, therefore, to assign the 2095 cm^{-1} band to a monocarbonyl of Rh(I) since this frequency is intermediate between those commonly reported for single CO oscillators on Rh metal and on Rh(II) or Rh(III).

The formation of the monocarbonyl may be due to a small undetected loss of some CO during the original sublimations of the dimer onto the Al_2O_3. The monocarbonyls also may occur at sterically crowded sites on the highly porous surface or at locations where Cl occupies one ligand site normally occupied by a CO. At any rate, the monocarbonyl is less stable on the surface than is the dicarbonyl species, as expected from the results of many previous studies of Rh(I) on aluminas.

Previous studies have reported little or no Rh–Cl interactions for Al_2O_3-supported $Rh^I(CO)_2$ species (*6, 7*), but the procedure used in the present study to prepare the $[Rh(CO)_2Cl]_2/Al_2O_3$ samples may favor such interactions. (Sample analyses showed that all the Cl was retained in these samples.) The 800°C pretreatment of the Al_2O_3 in the present study creates Lewis acid sites at coordinately unsaturated aluminum atoms. Because $[Rh(CO)_2Cl]_2$ was loaded by sublimation, no solvent was present to interfere with possible interactions between the molecular complex and such surface Lewis acid sites. Some of the $[Rh(CO)_2Cl]_2$ could adsorb by the formation of Lewis acid/base adducts between the bridging chlorides of the parent complex and the coordinatively unsaturated aluminum atoms. The result would be $Rh^I(CO)_2$ bound to the surface through Rh–Cl–Al as well as Rh–O–Al interactions. Indeed, the striking color difference when the Al_2O_3 was pretreated at 800°C and the shift in $\nu(CO)$ frequencies for that sample, as compared with samples prepared with Al_2O_3 pretreated at lower temperatures, are consistent with the hypothesis that it consisted primarily of $[Rh(CO)_2Cl_2]^-$ ions coordinated to the high concentration of Lewis acid surface sites present.

CONCLUSIONS

Under the mild conditions used to treat Rh on SiO_2 in this study, formation of Rh(I) predominates and carbonylation leads primarily to dimeric surface species identical or closely analogous to the chloride-bridged dimer, independent of whether the starting material is $[Rh(CO)_2Cl]_2$ or one of the Rh(III) salts. Apparently, the difference between the wet SiO_2 surface, formed by addition of the salts from water solution, and the fully dehydrated and partially dehydroxylated surfaces, upon which the $[Rh(CO)_2Cl]_2$ sublimed, was largely irrelevant in determining the nature of the final species formed.

It is significant, though, that when $Rh(NO_3)_3$ was the precursor to supported rhodium, it produced a distinctly different sample, as evidenced by extraction results, even though the $\nu(CO)$ spectra for all three samples were very similar.

The two different species that are obtained, postulated as $[Rh(CO)_2O_s]_2$ and physisorbed $[Rh(CO)_2Cl]_2$, might be expected to display different catalytic properties. First, the different bridging ligands, O_s and Cl, would be expected to have slightly different electronic and steric effects on the metal centers. More importantly, maximum metal dispersion would be expected for $[Rh(CO)_2O_s]_2$ because the bridging ligands between the metal centers are inherent to the surface, while the chloride-bridged $[Rh(CO)_2Cl]_2$ might more readily form three-dimensional aggregates.

Although $[Rh(CO)_2Cl]_2$ produced Rh^I

$(CO)_2$ when added to Al_2O_3, consistent with observations of other workers, a second species, possibly a monocarbonyl, appeared immediately after adding the carbonyl complex. An alumina surface pretreated at 800°C also exhibited behavior toward the dimer that differed from that for all other pretreatments. The fact that the surface is not contaminated by solvent when using this method of catalyst formation and that Cl might be intimately involved at the Rh(I) center on the Al_2O_3 surface may explain these novel observations.

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