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A New Interpretation of the IR Bands of Supported Rh(I) Monocarbonyl Complexes

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Abstract: The characteristic CO vibrational frequency of supported monocarbonyl complexes Rh^{I}CO, at 2014 and 1984 cm^{-1} on dealuminated Y zeolite and alumina, respectively, is lower than the frequencies of both the symmetric and the antisymmetric CO normal modes of the corresponding stable supported Rh(I) dicarbonyls. The CO mode with a measured frequency between those of the symmetric and antisymmetric CO frequencies of the dicarbonyls, previously assigned to rhodium monocarbonyl, is reassigned to mixed carbonyl dihydrogen complexes Rh(H$_2$)(CO) or Rh(H)$_2$(CO). This reassignment is based on a critical analysis of reported experimental data, supplemented by quantum chemical calculations.

Introduction

Supported rhodium carbonyl complexes form an important class of catalysts and precursors for the preparation of different supported rhodium species.[1] Recently, Zhou and Andrews reported vibrational frequencies of rhodium carbonyl complexes in a neon matrix and hypothesized that these isolated complexes can be used as models for supported rhodium carbonyl species.[2] Based on a linear relationship between the charge of the Rh center of the monocarbonyl complex Rh^{q}CO ($q = -1, 0, 1$) in a neon matrix and the measured carbonyl stretching frequency of such supported species, these authors estimated the charge of mononuclear rhodium species supported on zeolite, alumina, and silica,[2] using literature data. This interpretation recalls a preceding discussion concerning the assignment of IR bands of CO in supported rhodium monocarbonyls.[3,4] Since the coordination shell of the rhodium center in these species is unsaturated, an additional ligand of low reactivity may coordinate. For this reason, these complexes are considered to be important intermediates in the activation of N$_2$[4] and of the C−H bonds of alkanes.[5]

Supported Rh(I) monocarbonyls are unstable and thus their identification and characterization is complicated.[3,4] With a critical analysis of reported experimental data corroborated by theoretical modeling, we suggest a new assignment of the IR frequency that corresponds to the C−O mode of supported monocarbonyl complexes Rh^{I}CO. We will show that their characteristic CO vibrational frequency is smaller than the frequencies of both the symmetric and the antisymmetric CO normal modes of the corresponding stable supported Rh(I) dicarbonyls. The CO mode with a frequency between those of the symmetric and antisymmetric CO frequencies of the dicarbonyls, previously assigned to rhodium monocarbonyls,[3,4] actually arises from mixed complexes containing an additional intact or dissociated hydrogen molecule, Rh^{I}(H$_2$)(CO) and Rh^{I}(H)$_2$(CO), respectively. Such complexes with molecular or atomic hydrogen are well-known in transition metal cation chemistry.[6]

Results

Our quantum chemical models of supported Rh(I) monocarbonyl are based on the recent determination of the location and structure of stable complexes Rh^{I}(CO)$_2$ in dealuminated Y (DAY) zeolite.[7] Combining experimental IR and EXAFS studies with density functional (DF) calculations, it was found that the dicarbonyl complex exhibits a planar pseudo-square structure with the Rh cation bonded to two oxygen centers that are connected to an Al center in a four-ring of the zeolite framework.[7] Here, we model the complexes Rh^{I}CO, Rh^{I}H$_2$(CO), and Rh^{I}(H)$_2$(CO) located in the same position of a DAY zeolite structure since all these intermediate species are produced from the dicarbonyl complex. All calculations have been carried out at the gradient-corrected density functional level with the program ParaGauss[8,9] for parallel computers (see the Methods section).

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Table 1. Experimental and Calculated Vibrational Frequencies (in cm^{-1}) of CO in Different Rh(I) Carbonyl Complexes on Support or in Solution: Symmetric (ν_{sym}) and Antisymmetric (ν_{asym}) Vibrations of $Rh^I(CO)_2$; ν_{mono} of Rh^ICO; ν_{mix} of $Rh^IH_2(CO)$ or $Rh^I(H)_2(CO)$ Species[j]

system	ν_{sym}	ν_{asym}	ν_{mono}	$\nu_{sym} - \nu_{mono}$	$\nu_{asym} - \nu_{mono}$	ν_{mix}	$\nu_{asym} - \nu_{mix}$
supported							
DAY[a]	2118	2053	2093	25	−25		
DAY − *new*[b]			*2014*	*104*	*39*	*2093*	*−40*
Al_2O_3[c]	2099	2028	2061	38	−33		
Al_2O_3 − *new*[d]			*1984*	*115*	*44*	*2061*	*−33*
TiO_2[e]	2104	2028				2078	−50
in solution[f]							
n-hexane[f]	2084	2015	2001	83	14		
cyclohexane[f]	2082	2013	1996	86	17		
THF[f]	2081	2010	1970	111	40		
calculated							
$Rh^I(CO)_2$/zeo	2114[g]	2060[g]	2046	68	14	2076[h]	−16
						2096[i]	−36

[a] Data and assignment according to ref 3. [b] Assignment suggested in this work based on the experimental frequencies of ref 3. [c] Data and assignment according to ref 4. [d] Assignment suggested in this work based on the experimental frequencies of ref 4. [e] Data and assignment according to ref 12a. [f] Experimental data for the acetylacetonate dicarbonyl complex of Rh(I), $[Rh(CO)_2(acac)]$, in the corresponding solvent, according to ref 11. [g] Reference 7. [h] Mixed complex $Rh^IH_2(CO)$/zeo with H_2 ligand undissociated. [i] Mixed complex $Rh^I(H)_2(CO)$/zeo with H_2 ligand dissociated. [j] Numbers in italics represent the new assignment of measured frequencies ν_{mono} and ν_{mix} suggested in this work.

In the following, we shall focus on the interpretation of the bands assigned to Rh(I) monocarbonyls supported on DAY zeolite since this system corresponds to our model cluster and the structure and location of the initial $Rh^I(CO)_2$ complex are well-known.[3,7] We will also discuss the IR bands corresponding to rhodium monocarbonyls on alumina due to the similarity in the experimental IR spectra for the transformation of $Rh^I(CO)_2$ species on both supports.

On DAY zeolite and alumina, Rh(I) cations form well-defined and stable supported $Rh^I(CO)_2$ species[3,4,7,10] with vibrational frequencies $\nu_{sym} = 2118-2115$ cm^{-1} and $\nu_{asym} = 2053-2049$ cm^{-1} on DAY[3,7] and $\nu_{sym} = 2099$ and $\nu_{asym} = 2028$ cm^{-1} on alumina[4] (Table 1). The IR frequencies ν_{mono} assigned to the rhodium monocarbonyl species on these supports are 2093 and 2061 cm^{-1} on DAY and alumina,[3,4] respectively. These frequency values lie *between* those of the symmetric and antisymmetric modes of the corresponding dicarbonyl species. The calculated carbonyl IR frequencies[7] of the complex $Rh^I(CO)_2$ supported on a cluster model, representative for DAY zeolite, are $\nu_{sym} = 2114$ cm^{-1} and $\nu_{asym} = 2060$ cm^{-1}, very close to the experimental values.[3]

Using the same zeolite cluster model, we optimized the structure of the supported monocarbonyl species Rh^ICO and we calculated the vibrational frequency of CO at 2046 cm^{-1}. This value is *smaller* than the frequencies of either the symmetric or the antisymmetric modes of the corresponding dicarbonyl complex. This difference in position of the monocarbonyl frequency (with respect to the dicarbonyl modes) between the experimental assignment and the computational modeling leads us to reconsider the reported assignment of the CO stretching frequency.

In this context we consider the relative position of the monocarbonyl band of molecular analogues of supported Rh(I) carbonyls. The CO vibrational band of the complex $Rh(CO)_2$(acac) in various solvents[11] is also split into symmetric and antisymmetric parts, $\nu_{sym} = 2084-2081$ cm^{-1} and $\nu_{asym} = 2015-2010$ cm^{-1} (Table 1). In these solvents, the CO vibrational frequency of the corresponding monocarbonyl species, ν_{mono}, is smaller than either one of the frequencies ν_{sym} and ν_{asym} of the dicarbonyls.[11] Monocarbonyls are produced by UV-initiated partial decarbonylation of the corresponding dicarbonyl complexes and, to account for their short lifetime, observed by ultrafast transient IR spectroscopy.[11] As can be seen in Table 1, ν_{mono} is by 14−40 cm^{-1} *smaller* than ν_{asym}; this difference is similar to the value $\nu_{asym} - \nu_{mono} = 14$ cm^{-1}, derived from our quantum chemical model calculations. According to the assignment of supported rhodium monocarbonyls in refs 3 and 4, the ν_{mono} values are by 40 (DAY) and 32 cm^{-1} (alumina) *higher* than the corresponding frequency ν_{asym}. This comparison of molecular and supported rhodium carbonyl complexes suggests that previous assignments of the bands to supported rhodium monocarbonyl species are questionable. Indeed, if one considers the original measurements[3] it becomes apparent that the assignment of these bands is not straightforward since the species are unstable. In both reported cases[3,4] of supported monocarbonyls, the corresponding band appeared during the conversion of the initial species $Rh^I(CO)_2$ under UV irradiation or heating.

The band in question with a frequency of 2093 cm^{-1} was observed when $Rh^I(CO)_2$ species in DAY zeolite were heated at 250 °C in diluted H_2 flow.[3] Under heating in a vacuum such species were not observed. When H_2 is removed from the flow, this band is partially transformed into a new one at 2014 cm^{-1}. Based on this observation, together with the comparison with molecular rhodium carbonyl complexes,[11] we suggest that the band at 2093 cm^{-1} may be associated with mixed species Rh^IH_2(CO), while the band at 2014 cm^{-1} can be assigned to the monocarbonyl Rh^ICO. Also on the (110) surface of TiO_2, mixed surface complexes containing both hydrogen and CO ligands have been suggested[12] to form after heating of rhodium dicarbonyls in hydrogen atmosphere. The CO frequency of this species is 2078 cm^{-1} (Table 1), similar the mixed complex in zeolites, 2093 cm^{-1}. The authors hypothesized that hydrogen is included in the surface complexes because an activation of the hydrogen molecules in the presence of filament before the

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reaction substantially increases the rate of formation of the corresponding species.[12]

To check this (re-)assignment we modeled the structure of adsorbed $Rh^IH_2(CO)$ species with the same zeolite fragment used previously[7] and calculated its CO frequency. We found two stable structures, one corresponding to an undissociated and the other to a dissociated hydrogen molecule in the Rh(I) complexes, $Rh^IH_2(CO)$ and $Rh^I(H)_2(CO)$, respectively. The distance between the two H atoms calculated in the former case is $R_{H-H} = 96$ pm, similar to H−H distances in molecular complexes of H_2, 79−98 pm.[13] In the complex with the dissociated ligand, the H−H distance is considerably longer, 208 pm. In general, the H−H distances between two H ligands of dihydride complexes of transition metal cations vary within a wide margin (>150 pm), depending not only on the metal but also on the relative positions of the two hydride ligands in the complex.[13] The two structures of the Rh(I) hydrogen complex are almost equally stable, with 2 kJ/mol in favor of the complex with the undissociated H_2 ligand. As anticipated, the calculated CO frequencies of both mixed complexes, $\nu_{mix} = 2076$ cm^{-1} for $Rh^IH_2(CO)$ and 2096 cm^{-1} for $Rh^I(H)_2(CO)$, fall between those of the symmetric and antisymmetric modes of the dicarbonyl species. Recall that the calculated CO vibrational frequency of the monocarbonyl species Rh^ICO, $\nu_{mono} = 2046$ cm^{-1}, is smaller than the frequencies of either the symmetric or the antisymmetric modes of the dicarbonyl, just as the measured bands at 2014 cm^{-1} on zeolite.[3]

With these computational results, it remains unclear whether the mixed species contain an undissociated or a dissociated hydrogen ligand. On one hand, the calculated CO frequency at 2096 cm^{-1} of the complex with the dissociated dihydrogen ligand is closer to the experimental value of 2093 cm^{-1}. On the other hand, the adsorption complex $Rh^IH_2(CO)$ complies better with the experimental observation that the exchange of H_2 by D_2 leaves the CO frequency of the surface species essentially unchanged.[3] We calculate this isotope exchange to shift the CO frequency at 0.3 cm^{-1} only. The calculated CO frequency of the complex with the dissociated dihydrogen ligand accidentally is close to one of the Rh−H frequencies; this results in an 18% contribution of the later mode to the vibration at 2096 cm^{-1}. When H_2 is exchanged by D_2, C−O and Rh−D modes are well separated and the characteristic CO frequency of the complex is 4 cm^{-1} higher than the complex with H_2. The shift is not large but should be experimentally observable.

During UV irradiation of $Rh^I(CO)_2$ species on alumina in N_2 atmosphere, Wovchko and Yates observed two bands at 2061 and 1984 cm^{-1} and assigned the former one to rhodium monocarbonyl species.[4] However, the latter frequency fits the trend found for molecular compounds much better since it is 44 cm^{-1} lower than ν_{asym} (Table 1). Based on the analysis of the IR spectra of Rh(I) monocarbonyls on DAY zeolite, we assign the band at 2061 cm^{-1} to the alumina supported species $Rh^IH_2(CO)$ and the band at about 1984 cm^{-1} to the supported pure rhodium monocarbonyl, Rh^ICO. The hydrogen required for the formation of $Rh^IH_2(CO)$ species during irradiation in N_2 atmosphere likely comes from surface hydroxyl groups of alumina, resulting in very low band intensities. The same bands were found also after irradiation of $Rh^I(CO)_2$ species on alumina in a vacuum.[4] Participation of hydrogen from the surface hydroxyl groups of alumina in the transformation of supported rhodium species is consistent with earlier works where isolated Al−OH groups were found to be consumed in the formation of $Rh^I(CO)_2$ species from metallic Rh.[14] Bridging OH groups were also consumed during the formation of rhodium dicarbonyls in DAY zeolite.[3] We should point out that the interpretation of experimental results is additionally complicated since the CO frequency under consideration, at 2061 cm^{-1}, is in the frequency range typical for terminal chemisorption of CO on metallic Rh particles.[14a,c]

In addition to the frequency/charge correlation for $Rh^q(CO)$ species, Zhou and Andrews[2,15] proposed a similar correlation also for dicarbonyl complexes. However, as they pointed out, the structure of the $Rh^q(CO)_2$ complexes on the surface and in a neon matrix is different. On the surface, the angle between the two CO ligands is close to 90°,[7] while the complexes with $q = 0$ and $+1$ in a neon matrix are linear.[2] To provide a frequency/charge correlation for $Rh^q(CO)_2$ complexes suitable for supported species, Zhou and Andrews combine the experimental frequencies in the neon matrix with calculated CO frequencies for isolated linear and bent $Rh^q(CO)_2$ complexes.[2] Although the construction of this correlation is somewhat complicated, the charge estimate of the $Rh^I(CO)_2$ complex supported on DAY zeolite, 0.5 e, is very close to the calculated charge of the rhodium dicarbonyl complex supported on a zeolite fragment described in ref 7, 0.53 e.

Conclusions

In conclusion, our quantum chemical modeling and the analysis of experimental data of the literature suggests the following: (a) The vibrational frequencies of the C−O mode of the monocarbonyl complex Rh^ICO supported on DAY (2014 cm^{-1}) or alumina (1984 cm^{-1}) are in each case smaller than the frequencies of either the symmetric or the antisymmetric CO modes of the corresponding stable Rh(I) dicarbonyls. (b) The CO modes with $\nu(CO) = 2093$ and 2061 cm^{-1} on DAY and alumina, respectively, with a frequency between those of the symmetric and antisymmetric CO frequencies of the corresponding Rh(I) dicarbonyls, are due to mixed complexes $Rh^IH_2(CO)$ or $Rh^I(H)_2(CO)$ containing a dissociated or an undissociated H_2 molecule as an additional ligand.

As a result of the reassignment of the CO frequencies of supported Rh(I) monocarbonyls, the charge estimates of these species on DAY and alumina by Zhou and Andrews[2,15] have to be revised.[16,17] Applying their frequency/charge correlation[15] to the correct CO frequencies of supported rhodium monocarbonyls, one finds charges of −0.05 and −0.22 e for DAY zeolite and alumina, respectively. These values do not conform to expectations for cationic complexes, but likely are due to the simplified representation of the support−complex interaction via the frequency/charge correlation.

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While the frequency/charge correlation can hold for gas-phase Rh monocarbonyls, the support likely modifies the electronic structure of these species and it is not an "innocent" ligand[18,19] that simply changes the charge of the complex. Coordinating substrate oxygen centers modify the electron distribution of Rh(I) and thus change the CO frequency in a way that is not necessarily connected with an alteration of the charge of the supported species. The direct frequency/charge correlation subsumes all such effects in the variation of the charge. Likely, this simplified representation of the support interaction results in the negative estimates of the charge of the complexes on alumina and DAY zeolite when reassigned C−O frequencies of supported monocarbonyls are used.

Methods

The program ParaGauss[9] is based on the linear combination of Gaussian-type orbitals fitting-functions density-functional method (LCGTO-FF-DF).[20] The gradient-corrected exchange-correlation functional suggested by Becke (exchange) and Perdew (correlation)[21] was used. The Kohn−Sham orbitals were represented by Gaussian-type basis sets, contracted in generalized form: (6s1p) → [3s1p] for H, (9s5p1d) → [5s4p1d] for O and C, (12s9p1d) → [6s4p1d] for Al and Si, and (19s15p10d) → [8s6p4d] for Rh.[22] The Rh^ICO, $Rh^IH_2(CO)$, and $Rh^I(H)_2$-(CO) complexes were supported on a model four-ring of a zeolite with an additional $OSiH_3$ group (denoted as T5 in ref 7). Since DAY zeolite features only isolated Al centers, only a ring with one Al center is modeled. The geometries of the complexes were optimized with the T atoms constrained to experimentally determined positions. A restricted frequency analysis was carried out where all vibrational modes of the supported complex as well as the Rh−O(zeo) modes were taken into account. Similarly to the procedure used previously,[7] we shift the calculated CO frequency by a correction of 32 cm^{-1}, which is the difference between the calculated (2111 cm^{-1}) and experimental (2143 cm^{-1}) vibrational frequency of a free CO molecule.

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Supporting Information Available: Tables of absolute energies and geometries (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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