

Metal–support interaction: A theoretical approach

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Abstract

Metal support effects in catalysis are poorly understood, but are important because they have been shown to profoundly affect catalytic rates and selectivity. Density functional calculations have been done to model the isolated single metal atom system rhodium gem-dicarbonyl on silica for which there is experiment infrared data. The systems were modeled by calculations for RhCO , Rh_4CO , $(\text{CO})\text{RhOSiH}_3$, $(\text{CO})_2\text{RhOSiH}_3$ and fragments thereof. Very good agreement was found between calculated and experimental infrared frequencies. Support effects include an upward shift of the CO frequency and charge transfer from Rh to the support. Per qualitative ideas the Rh charge, C–O frequency and π backbonding correlate. The second CO on a supported Rh(1) atom is almost as strongly bonded as the first and the binding energy of Rh to the support is not affected by the adsorption of the CO molecules. Further the adsorption of a single CO on isolated Rh(1) could contribute to an observed infrared band in the 2040 to 2070 cm^{-1} region which is normally assigned to CO on Rh clusters.

Keywords: Metal–support interaction; Rhodium gem-dicarbonyl; Density functional calculations; CO adsorption

1. Introduction

A major objective of these calculations is to move from qualitative ideas on the effect of supports on adsorption and catalysis for supported metals to a quantitative understanding of support effects.

1.1. Catalysis by supported metals

Most heterogeneously catalyzed reactions are carried out on supported metal catalysts [1]. Supports have been found to stabilize small metal particles in high dispersion to give high metal surface areas [2]. These catalysts are of great technological importance as, for example, in catalytic reforming [3–5], selective hydrogenation [6,7] and in automobile exhaust gas

cleanup [8]. A large body of work indicates that the nature of the support material can have a large effect on the activity and selectivity of heterogeneous catalytic reactions [1,9–12]. The origin of support effects is not obvious [13]. Small metal particles usually have broad particle size distributions [14]. This leads to difficulties in obtaining a fundamental understanding of the effects of particle size on catalytic properties [15]. Other factors that must be considered along with the support effect include the extent of metal loading, catalyst preparation and pretreatment and the extent of metal reduction. [16].

One of the fundamental causes of support effects is usually assumed to be an electronic effect [17]. The electronic effect is most often the focus of theoretical investigations of metal-

support interactions [18]. The division of support interactions into strong (SMSI), medium (MMSI) and weak (WMSI) has been proposed by Bond [13]. The strong effect (SMSI) has been ascribed to transition metals supported on reducible oxides like TiO_2 while the weak effect has been associated with nonreducible oxides like SiO_2 and Al_2O_3 . For example the electronic properties of the support in the Ni/ TiO_2 system has been used to explain the support effect [19]. However, there are cases where a nonreducible oxide support for a transition metal has given a SMSI effect [20,21]. A fundamental understanding of the origin of the SMSI effect remains unclear and is still a subject of current interest [22].

1.2. Theoretical treatments of metal–support interactions

The purpose of calculations is to provide information about the nature of the chemical bonding at the surface, the direction of charge flow at the metal–support interface, how the support influences the chemisorption and catalytic properties of the metal and how the support affects the bonding within adsorbed molecules. Theoretical investigations of metal–support interactions and chemisorption have been recently reviewed [18]. While this area has received some theoretical attention, most of it has not involved calculations at a very high level of sophistication. The inclusion of electron correlation effects has been found to be necessary to obtain reliable total energies and geometries for transition metal containing systems [23]. Thus calculations at a higher level than Hartree–Fock are required. While there have been many calculations for adsorbates on transition metal clusters that include correlation effects the amount of work applied to transition metal–support systems is relatively small up to the present [24,25]. DFT calculations indicate that for Ni rafts on alumina, the Ni atoms next to the surface have a positive charge while Ni atoms further from the surface are essentially

neutral [24]. This provides a range for the metal–support effect in this case.

A recent review listed about 25 transition metal–support systems for which calculations had been done [18]. However for the nonempirical methods the calculations were run with small basis sets or without electron correlation. Correlation effects were treated approximately or empirically in some cases. Referring to the listed calculations, the reviewing author stated that theoretical calculations have *not* “been performed on a level of sophistication that allows for the reliable determination of total energies in order to predict geometries at interfaces or of metal particles on a support surface” [26].

1.3. Supported rhodium catalysts

Supported rhodium catalysts have been studied often because of their importance as catalysts for a variety of reactions such as CO hydrogenation, methanol carbonylation and conversion of CO and NO in exhaust gases. The full characterization of these catalysts requires the determination of the oxidation state and dispersion of the supported rhodium and the effect of metal–support interactions on these properties. For example in the cyclotrimerization of ethylene to benzene, Rh clusters in a positive oxidation state have a greater activity than Rh metal when using Rh/ Al_2O_3 catalysts [27] whereas in zeolite catalysts some reactions are more strongly catalyzed by rhodium metal than Rh(III) [28].

The most widely used way to characterize supported rhodium has been to study the infrared spectra of adsorbed CO. From this, the structure of adsorbed species, extent of dispersion of the Rh and the oxidation state of the Rh have been inferred. From the beginning work of Yang and Garland [29], the presence of a gemdicarbonyl has been considered established by the appearance of 2 infrared bands in the 2000 to 2100 cm^{-1} region. In addition there are infrared bands usually attributed to a single adsorbed CO molecule attached to a single Rh

atom or bridging 2 Rh atoms where these sites are on a more or less large cluster of supported Rh atoms. For the rhodium gem-dicarbonyl the degree of dispersion of the Rh atoms has been a matter of some discussion. The current most widely held view is that the gem-dicarbonyl is formed on completely isolated Rh^{+1} sites [30,31].

1.4. Computational model system

Metal cluster calculational models are widely used to mimic surface phenomena [32–34]. For transition metal clusters, the cluster size is usually limited to from 1 to 12 metal atoms if HF-SCF-CI level calculations are performed [32,35,36]. This number of atoms is much smaller than the usual number of metal atoms in a metal particle that is part of an industrial supported metal catalyst so calculational results are not directly comparable to experimental data.

Density functional calculations, which include electron correlation, are presented here for isolated single metal atom systems, such as rhodium gem-dicarbonyl on silica. These provide a direct comparison of calculated quantities to experimental quantities since infrared spectra for this system are available to verify the validity of the calculations, which also provide metal–support information. This approach has the advantage of avoiding the usual imperfect comparison of small metal cluster calculations to data for extended metal surfaces or metal particles on supports.

The adsorption of CO on a bare metal surface, to which adsorption on a supported metal will be compared, is modeled by Rh_4CO with the structure shown in Fig. 1. A Rh_4 cluster was chosen because it is about as large as the workstation can handle in a reasonable length of time. A flat plane structure with the CO at a right angle to the plane was chosen because raft like structures have been proposed for Rh clusters on supports and future calculations are planned using this Rh_4CO structure bonded to a silicon oxide cluster to represent CO adsorbed

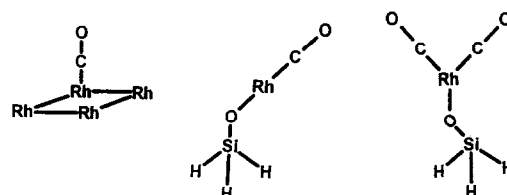


Fig. 1. Model structures.

on a supported Rh raft. To model support effects the atomically dispersed Rh system is chosen. The oxide support is modeled by a truncated silica cluster. For insulators and semiconductors dangling bonds at the truncating surface are usually saturated with pseudoatoms. For silica supports the dangling bonds of oxygen and silicon at the surface often are very successfully simply saturated with hydrogen atoms [37–39]. The specific structures for the supported Rh mon- and di-carbonyl adsorbed systems are shown in Fig. 1. The use of 3 hydrogen atoms to truncate the silica cluster is regarded as a minimal first approximation to a silica structure. Further calculations examining the effect of increasing the silica cluster size are planned.

2. Computational method

Density functional methods which do encompass electron correlation have shown good accuracy for reasonable computation times [40,41]. The calculations were done using the density functional option of Gaussian 92 [42] and were done on an IBM RISC-6000-355 using Becke's 3 parameter exchange functional with non-local correlation and local correlation provided by the Lee, Yang and Parr expression. The LANL1DZ [43–45] basis set was used to provide double-zeta valence shell functions and used the Los Alamos ECP for the inner shells. In cases where electronic convergence was initially a problem, juggling initial orbital occupancies and starting with a simplified basis set has produced convergence. Because the modest basis set in these calculations gives a free CO frequency of 2030

cm^{-1} , the frequencies of all CO complexes discussed below were normalized by multiplying by a factor of 1.05616 (i.e. 2144/2030). To be only about 5% off the exact vibrational frequency was considered reasonably good.

3. Results and discussion

3.1. Rh_4CO

The calculated properties of Rh_4CO are shown in Table 1. The scaled CO vibration frequency of 2010 cm^{-1} compares very well with the experimental frequencies. On Rh(111) CO gives frequencies from 2025 cm^{-1} for isolated adsorbed CO molecules to 2040 cm^{-1} at full coverage and for Rh(110) where CO gives frequencies from 2020 to 2040 cm^{-1} [46–48]. The calculated Rh–CO frequency at 525 cm^{-1} is close to the experimental range of 480 to 420 cm^{-1} . The calculated CO binding energy to the Rh cluster is considerably higher than the experimental values of 29 to 31 kcal/mol . These discrepancies are presumed to be due to comparing a small cluster to an extended metal.

3.2. $(\text{CO})_x\text{RhOSiH}_3$

The calculated properties for $(\text{OC})_2\text{RhOSiH}_3$, $(\text{OC})\text{RhOSiH}_3$ and RhOSiH_3 are given in Table

1. This calculation for $(\text{OC})_2\text{RhOSiH}_3$ gives CO frequencies at 2033 and 2125 cm^{-1} which may be compared to experimental frequencies for the gem-dicarbonyl rhodium structure on silica of 2038 and 2096 cm^{-1} [30](b). From estimated relative intensities of the symmetric and asymmetric carbonyl stretching frequencies of the rhodium gem-dicarbonyl species, the C–Rh–C angle has been estimated to be in the vicinity of 90 to 100° [49,50]. Our preliminary calculations give 85° which is satisfactory agreement with experiment in view of the rough nature of the experimental values. Having calculated vibrational frequencies and bond angles reasonably accurately provides confidence that other calculated quantities are correctly calculated. For the two previous calculations for $\text{Rh}(\text{CO})_2$ in which bond angles were optimized successfully, the C–Rh–C angle went to 180° [51,52]. This is in contrast to the surface gem-dicarbonyl where the C–Rh–C angle is around 90° to 100° [49,50]. There have been no previous calculations for Rh in which the effect of a support was considered.

3.3. Support effect

Comparing the CO frequency in OC-RhOSiH_3 to that of Rh_4CO in Table 1 shows that on going from Rh as part of a metal to supported Rh results in an increase of about 60

Table 1
Calculated properties of Rh_4CO , OCRhOSiH_3 , $(\text{CO})_2\text{RhOSiH}_3$ and RhOSiH_3

	Compound				
	Rh_4CO	OCRhOSiH_3	$(\text{CO})_2\text{RhOSiH}_3$	RhOSiH_3	$(\text{OC})_2\text{RhOSiH}_3$
RhOSi angle ($^\circ$)		132	175		180
$\nu(\text{C-O})$ (cm^{-1})	2010 ^a	2073 ^a	2058 ^a		2125 ^a , 2033 ^a
$R(\text{C-O})$ (A°)	1.185	1.176	1.178		1.175
$\nu(\text{Rh-C})$ (cm^{-1})	525 ^a	406 ^a	427 ^a		490 ^a , 394 ^a
$R(\text{Rh-C})$ (A°)	1.754	1.911	1.876		1.817
$Q(\text{Rh})$	-0.13	+0.26		+0.29	-0.035
$Q(\text{C})$	+0.49	+0.20			+0.32
$Q(\text{O})$	-0.14	-0.13			-0.09
BE(CO) (kcal/mol)	64	43			31,43
BE(Rh) (kcal/mol)		108		108	107

^a These frequencies have been scaled by the factor 1.056 which converts the calculated free CO frequency into its experimental value of 2144 cm^{-1} .

cm^{-1} in the CO frequency. This is attributed to electron transfer from the Rh atom to the support as the Rh atom is bonded to an oxygen atom which is more electronegative than metallic Rh atoms to which the adsorbent Rh atom is bonded in free metals. This increase in positive charge on the supported Rh atom can be seen in Table 1. Thus, in this case the effect of the support is to cause charge transfer out of the supported metal.

3.4. Frequency, charge and π -bonding correlation

The interaction of CO and transition metals has received considerable theoretical attention with a number of papers dealing specifically with rhodium. The interaction is generally described in terms of a molecular orbital model in which there is donation of electron charge from the 5σ orbital of carbon monoxide into vacant metal orbitals and back donation from the metal into empty antibonding 2π orbitals of carbon monoxide [53]. A correlation between CO frequency and metal oxidation state is generally observed. Some literature data and these calculations are compared in Table 2. Although the correlation is not exact it is seen that the ratios of the change in frequency with charge are similar for a variety of cases and also for these calculations.

The π population of CO is given in Table 3

Table 2
Rhodium charge and CO frequency correlation

	RhCO ^a	Rh(CO) ⁺ ^a	Δ	$\Delta\nu/\Delta Q$
$\nu(\text{C-O})$ (cm^{-1})	2037	2202	165	214
$Q(\text{Rh})$	+0.11	+0.88	0.77	
	OCRhOSiH ₃ ^b	Rh ₄ CO ^b	Δ	$\Delta\nu/\Delta Q$
$\nu(\text{C-O})$ (cm^{-1})	2073	2010	63	162
$Q(\text{Rh})$	+0.26	-0.13	0.39	
Average for metal carbonyls ^c				≈ 190

^a Ref. [52].

^b This calculation.

^c Ref. [57].

Table 3
Correlation of CO π population, $Q(\text{Rh})$ and $\nu(\text{C-O})$

System	CO π population	$Q(\text{Rh})$	$\nu(\text{C-O})$ (cm^{-1})
Rh ₄ CO	4.468	-0.13	2010
RhCO	4.418	-0.11	2019
OCRhOSiH ₃	4.376	+0.26	2073

for the molecules calculated here. It is seen that as the metal charge becomes more positive (due to electron transfer to the support), the CO π population decreases and consequently the CO frequency increases due to there being fewer electrons in the π antibonding orbitals. The first four π electrons occupy the π bonding orbitals.

3.5. Binding energies of CO

In Table 1 it may be seen that the binding energy of the second CO of the gem-dicarbonyl is 31 kcal/mol which is about three-fourths of the binding energy of the first CO and makes the second quite stable. Thus the experimental data commonly shows the presence of the gem-dicarbonyl when Rh(I) is present.

3.6. Rhodium atom surface migration

On many supported metal catalysts under use at high temperatures, an initially highly dispersed metal will migrate to form larger metal particles with lowered catalytic activity. This necessitates redispersion of the metal. For supported rhodium, the adsorption of CO can have a big effect on the extent of Rh dispersion. It has been suggested that CO adsorption causes considerable disruption of Rh particles to produce isolated Rh⁺ sites [54–56]. The migration of Rh(I) atoms across an oxide surface depends upon the binding energy of the Rh(I) atoms to the surface, which might be affected by CO adsorption the Rh(I). The binding energy of a Rh atom to the -OSiH₃ fragment is 108 kcal/mol, that of OCRh- to -OSiH₃ is 108 kcal/mol, while that of (OC)₂Rh- to -OSiH₃ is 107 kcal/mol. In calculating the last number

the $-\text{Rh}(\text{CO})_2$ fragment was allowed to relax to its linear lowest energy configuration. These calculated binding energies do not show that adsorption of CO has any direct effect on Rh(I) binding energies to the surface in the type of site considered. This suggests that the reason for the effect of CO on Rh dispersion must be found elsewhere.

3.7. Infrared bond assignments

These calculations strongly support the assignment of a pair of infrared bands at about 2030 and 2100 cm^{-1} to the Rh(I) gem-dicarbonyl. In the experimental infrared spectra a broad band in the 2040 to 2070 cm^{-1} region is usually assigned to linear CO adsorbed on clusters or particles of supported Rh metal. For reasons given in the literature this assignment is probably largely correct. However the calculations here, which quite accurately give the gem-dicarbonyl bands, give a band at 2073 cm^{-1} for a single linear CO on a Rh(I) site. Thus some, but likely not all, of the broad absorption intensity between the two gem-dicarbonyl peaks could be due to one CO adsorbed on Rh(I).

3.8. Rh bond angles

Calculations are given in Table 1 for the Si–O–Rh bond angle being at its equilibrium value of 132° and at 175°. The latter state is only 2.6 kcal/mol less stable than the equilibrium structure and the calculated properties are changed only slightly. Thus RhCO is relatively free to wave around on the surface which could facilitate reactivity.

4. Conclusions

These calculations lead to the following conclusions:

- Density functional calculations with non-local correlation, ECP and a moderate basis set give good results.
- Attaching a Rh atom to an oxide support rather than to a metal cluster results in an upward shift of the adsorbed CO stretching frequency of about 60 cm^{-1} .
- There is a charge shift from Rh to the support.
- Per qualitative ideas, the $Q(\text{Rh})$, $\nu(\text{C}-\text{O})$ and π backbonding correlate.
- The second CO on a supported Rh(I) atom is almost as strongly bonded as the first.
- The properties of RhCO on a support depend very little on the Si–O–Rh bond angle.
- The binding energy of Rh to the support is not affected by the adsorption of one or two CO's.
- The adsorption of a single CO on isolated Rh(I) could contribute to an observed infrared band in the 2040 to 2070 cm^{-1} region.

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