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Mobility and Clustering of Rh and Ru in Zeolite. Experiment and Theory

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Ruthenium and rhodium have been atomically dispersed on Na zeolite as shown by the infrared spectra of $\text{Rh}^{\text{I}}(\text{CO})_2$ and $\text{Ru}^{\text{I}}(\text{CO})_2$ produced upon reduction in a CO atmosphere. Formation of adsorbed CO bridging two Rh(I) surface atoms upon partial removal of adsorbed CO indicates some Rh(I) species can occupy adjacent surface sites contrary to suppositions in most current literature. While Rh(I) surface species seem to be relatively immobile below 100 °C, our data suggest that Rh^0 surface atoms are mobile to some extent. Self-consistent field density functional calculations have been performed for several surface clusters; they indicate that Rh–surface bonds are much weaker for Rh^0 species than for Rh(I) species. These calculations support the proposition that Rh^0 surface species are more mobile than Rh(I) surface species.

Introduction

Many heterogeneously catalyzed reactions are carried out on supported metal catalysts.¹ A large body of work indicates that the nature of metal–support interactions can have a large effect on the activity and selectivity of heterogeneous catalytic reactions.^{1–5} Among other effects, supports have been found to stabilize small metal particles in high dispersion to give high metal surface areas.⁶ Supported metal catalysts are of great technological importance in areas such as catalytic reforming,^{7–9} selective hydrogenation,^{10,11} and automobile exhaust gas cleanup.¹²

Supported rhodium and ruthenium catalysts have been studied most frequently because of their importance as catalysts for a variety of reactions, e.g., CO hydrogenation, methanol carbonylation, and conversion of CO and NO in automotive exhaust gases. The full characterization of these catalysts requires the determination of the oxidation state, the dispersion of the supported metal and the role of metal–support interactions in determining these properties.

The most widely used technique for characterization of supported rhodium materials has been to study the infrared spectra of CO adsorbed on the catalyst. 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 early studies of Yang and Garland,¹³ the presence of a *gem*-dicarbonyl has been considered established by the appearance of two 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, 1950 to 2070 cm^{-1} , or bridging two Rh atoms, 1800–1880 cm^{-1} , where these sites are thought to be part of larger clusters of supported Rh atoms. For the rhodium *gem*-dicarbonyl, the degree of dispersion of the Rh atom has been a matter of some discussion. The current most widely held view is that the *gem*-dicarbonyl is formed on completely isolated Rh(I) sites.^{14,15}

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 large effect on the extent of Rh dispersion. It has been concluded that CO adsorption causes considerable disruption of Rh particles to produce isolated Rh(I) sites by breaking Rh–Rh bonds.^{16–18}

In this paper some of the factors which determine surface mobility and clustering of Rh and Ru atoms on a sodium zeolite are examined both theoretically and experimentally. Theoretical calculations were carried out to determine metal–surface bond strengths for the metal in several oxidation states (to determine which states are likely to be most mobile). The experimental work focuses on using infrared spectroscopy to establish the presence of a *gem*-dicarbonyl, which is usually taken as an indication of a completely isolated metal atom, and on the presence of bridging adsorbed CO molecules, which is usually taken as indicating a metal cluster of many atoms. Neither of these indications is found to be entirely supported by the experimental data. Changing relative intensities of the *gem*-dicarbonyl and bridging CO infrared bands are interpreted in terms of the migration of surface atoms.

Sample Preparation

Ruthenium trichloride was exchanged with the sodium form of Linde LZ-Y52 zeolite (NaY, Aldrich Chemical) by dissolving 0.18 g of RuCl_3 in 30 mL of H_2O to which 0.46 g of NaY was added. This approximately neutral slurry was put into a round-bottomed flask and refluxed at 100 °C for 12 h. After refluxing, the solid was collected by vacuum filtration, washed twice with 10 mL portions of H_2O , and allowed to air-dry.

After drying, the exchanged ruthenium/zeolite mixture was made into a slurry with acetone. A thin, uniform layer was produced by placing 0.5 mL of the slurry dropwise onto a salt window. The salt window was then attached to an evacuable,

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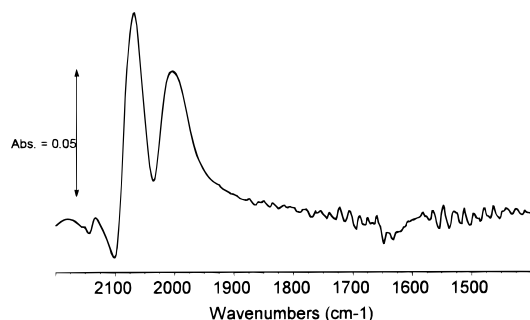


Figure 1. $\text{Ru}(\text{CO})_2/\text{Y}$ prepared by CO reduction of $\text{Ru}(\text{III})/\text{Y}$ by CO at 175 °C.

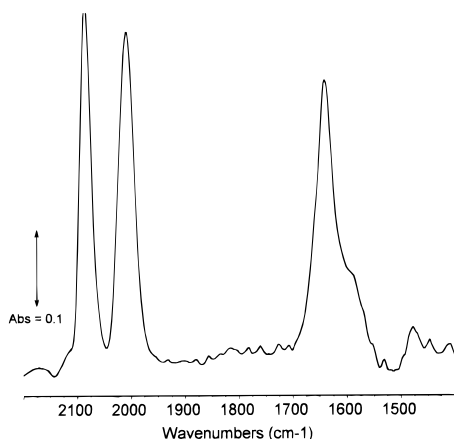


Figure 2. $\text{Rh}(\text{CO})_2/\text{Y}$ prepared by CO reduction of $\text{Rh}(\text{III})/\text{Y}$ by CO at 100 °C.

heatable cell so that transmission infrared spectra could be obtained. In a typical experiment, a $\text{Ru}(\text{III})/\text{Y}$ sample was evacuated to 10^{-5} Torr at room temperature for 24 h to remove most of the surface water. The sample was then reduced by heating at 175 °C for 6 h with 15 Torr of CO. The spectrum showed absorption bands for adsorbed water, two strong ruthenium *gem*-dicarbonyl peaks at 2064 and 2002 cm^{-1} , and little else (Figure 1). This assignment is made by analogy to the surface rhodium *gem*-dicarbonyl, to surface Ru complexes,¹⁹ and to molecular Ru dicarbonyl complexes.²⁰ The hydrogen-bonded adsorbed water is indicated by a very broad band from 3700 to 3200 cm^{-1} with a broad maximum from 3300 to 3500 cm^{-1} with a peak intensity that is 15% of the carbonyl peak intensity.

This and all subsequent spectra were taken on a Nicolet 205 FTIR spectrophotometer using 100 scans at a resolution of 4 cm^{-1} .

$\text{Rh}(\text{III})/\text{Y}$ was prepared in a similar manner by heating to 90 °C for 24 h a solution of 0.0264 g of $\text{RhCl}_3 \cdot \text{H}_2\text{O}$ and 0.510 g of NaY in 50 mL of H_2O . The filtered solid was then slurred with acetone and applied as a thin film on a salt window. This sample was evacuated at 180 °C for 24 h before reduction in 15 Torr of CO at 100 °C for 24 h. As in the ruthenium case above, the spectrum consisted of peaks for rhodium(I) *gem*-dicarbonyl at 2086 and 2010 cm^{-1} and adsorbed water (Figure 2). This assignment is indicated by a large body of work.^{14,15} The adsorbed water is indicated by a very broad band from 3700 to 3200 cm^{-1} with a broad maximum whose intensity is 1.5 times larger than the peak intensity of the carbonyl bands. Because infrared intensities of hydrogen bonded OH bands are large and variable, these bands are qualitatively but not quantitatively meaningful.

TABLE 1: SEM and XPS Analyses for Na Zeolite^a and Rh-Exchanged Zeolite

method	sample	[Na/Al] ^b	[Si/Al] ^b	[Rh/Al] ^b
SEM ^c	Na zeolite ^c	0.59	2.86	
	Rh-exchanged zeolite ^d	0.40	2.78	0.07
XPS ^c	Na zeolite ^c	1.50	3.00	
	Rh-exchanged zeolite ^d	0.75	2.84	0.40

^a Linde LZ-Y52. ^b Atom ratios. ^c No chlorine peaks observed by SEM or XPS. ^d Rh(III) indicated by XPS.

Details of these and other supported metal *gem*-dicarbonyl preparations may be found in two MS theses.^{21,22} The reduction is proposed to be described by the overall reaction, $\text{Rh}(\text{III}) + \text{H}_2\text{O} + \text{CO} \rightarrow \text{Rh}(\text{I}) + \text{CO}_2 + 2\text{H}^+$. Analyses of the rhodium-exchanged and original Na zeolite samples used were carried out by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) at the Federal Energy Technology Center, Morgantown, WV (see Table 1). Powder X-ray diffraction (XRD) indicates the sample to belong to the general class of hydrated sodium aluminosilicates without an exact match to any example in the FETC database. The analytical data for rhodium-exchanged and -unexchanged Linde LZ-Y52 zeolite samples are shown in Table 1. The SEM data which represent the “bulk” composition gives a rhodium metal incorporation of 3.0 wt %. Comparison of the SEM-based Na/Al and Rh/Al ratios for the rhodium-exchanged sample suggests a loss of three Na^+ for each rhodium incorporated. This suggests that in the bulk, at least, the rhodium species carries a 3+ charge prior to reduction. The XPS data samples primarily the external surface of the zeolite. There is agreement between the Si/Al ratios for the bulk and surface in these data as expected. The higher Na/Al ratios may be due to the requirement for additional charged species to balance unsaturated oxygen valences at the surface. The change in the XPS Na/Al ratio between Rh and Na zeolite suggests a loss of two Na for each surface rhodium. Various scenarios could account for this difference from the bulk, including the loss of Na and with protons from surface water. Thus, hydroxo-ligated rhodium(III) species, including oligated polynuclear species may be at or near the surface before reduction. The presence of polynuclear species prior to reduction could account for the relatively facile formation of a $\text{Rh}(\text{CO})\text{Rh}$ bridged species discussed later. An extension of this suggestion would infer that the IR data for bridged species has a large contribution from species at or near the external surface. Changes in the XRD powder patterns for the undoped and Rh-doped samples indicate a loss of some crystallinity for the Rh-exchanged samples.

Evidence for Rh and Ru atom Arrangements on the Surface

Evacuation of the Rh *gem*-dicarbonyl sample for 5 min at room temperature results in the disappearance of about half of the intensity of the *gem*-dicarbonyl peaks and the appearance of a strong band at 1834 cm^{-1} , which is assigned to a bridging CO structure (Figure 3). This change is reversible with the addition of 15 Torr of CO at room temperature. Several repetitions of this cycle of evacuation and CO addition resulted in only a small decrease in all peak intensities. This behavior suggests that there are Rh(I) species adjacent to each other on the surface and that dependent upon changes in coverage either *gem*-dicarbonyl or a bridging CO species can be formed on these sites. Here, adjacent means from about 2.7 Å (the Rh–Rh distance in Rh cluster carbonyls) to about 3.8 Å, which would permit reasonable bridge carbonyl bond angles.

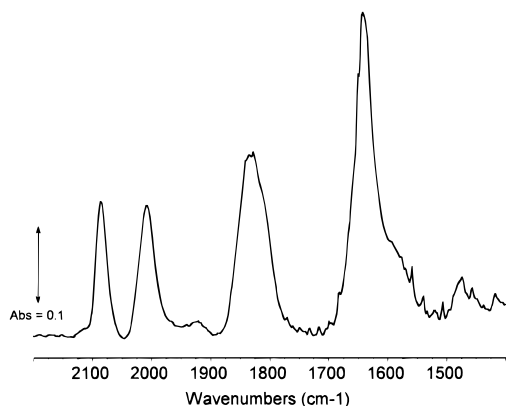


Figure 3. Bridging CO produced by evacuation of $\text{Rh}(\text{CO})_2/\text{Y}$ at 20 °C.

Continuing the evacuation of the Rh *gem*-dicarbonyl at room temperature for 1 h results in over 80% (based on peak heights) of the *gem*-dicarbonyl being converted to a bridge CO species. At both 50% and 80% conversion of the *gem*-dicarbonyl to bridge structure the gain in bridge CO peak height is directly proportional to the loss in *gem*-dicarbonyl peak height. This suggests a uniformity in over 80% of the Rh *gem*-dicarbonyl species. Evacuation with photolysis removes over 90% of the total adsorbed CO in 15 min; therefore, pore diffusion of CO is not a limiting factor in the above results.

Several other experiments were performed to give information about the stability of the surface species. When a sample was evacuated for 5 min and subsequently closed off from the vacuum system and heated to 100 °C for 1 h, no change in the intensities of the gem and bridge infrared peaks was observed. In contrast, heating this sample with simultaneous evacuation at 100 °C for 30 min removed 95% of the intensity of the gem peaks while leaving the peak for the bridge species at 1834 cm^{-1} unchanged. Further evacuation with heating at 150 °C removed the gem peaks entirely and most of the 1834 cm^{-1} bridge peak. Accompanying these losses were the appearances of a very small peak at 1970 cm^{-1} (presumably a peak for linear CO on a Rh cluster) and a small peak at 1760 cm^{-1} (0.03 absorbance), which is assigned as usual to CO bridging three Rh atoms.^{23–26} This indicates some mobility of Rh species at 150 °C. Addition of 15 Torr of CO at room temperature to this sample resulted in the gem peaks returning to 95% of their previous intensity.

In the course of attempts to replace carbonyl ligands with hydrocarbons, 760 Torr of ethylene was added to an evacuated cell containing $\text{Rh}(\text{CO})_2/\text{Y}$. At 20 °C infrared spectra showed only gas-phase ethylene peaks as well as the *gem*-dicarbonyl peaks at 2086 and 2010 cm^{-1} and the bridge CO peak at 1834 cm^{-1} . Heating this cell containing ethylene at 100 °C for 1 h resulted in a decrease in the *gem*-dicarbonyl peaks and the growth of new peaks at 1988 and 1726 cm^{-1} . These new peaks are assigned to linear and triply bridging CO on Rh clusters whose oxidation state and size are unknown. No appreciable reaction in the large excess of ethylene was evident in the spectra. Evacuation of this cell resulted in the spectrum showing peaks at only 1955, 1836, 1773 (0.06 absorbance), and 1710 cm^{-1} (0.05 absorbance). These absorbances for triply bridged CO indicate more clustering and greater mobility for Rh when heated in the reducing atmosphere produced by ethylene than when heated without ethylene in a closed cell.

While the formation of the Ru *gem*-dicarbonyl is similar to the Rh species, there are some distinct differences in behavior. Upon evacuation at 20 °C the Ru *gem*-dicarbonyl is stable and

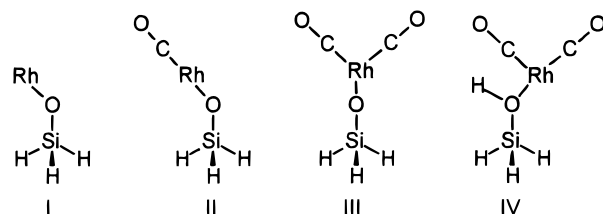


Figure 4. Calculational structures for models of Rh surface species.

TABLE 2: Bond Energies and Rh Atom Charge

	I	II	III	IV
Rh–O bond energy (kcal/mol)	102	107	121	17
Rh–CO bond energy (kcal/mol)		59	59, 55	66, 34
charge on Rh	+0.35	+0.48	+0.48	+0.16

does not form any bridge CO. This may be the result of differences in the reactivity or surface structure (e.g., absence of adjacent ruthenium centers) for Ru/Y compared to Rh/Y.

Computational Model System and Method

Surface phenomena are often examined using transition metal clusters as calculational models.^{27–29} Density functional calculations, which include electron correlation, are presented here for models of isolated single metal atom systems, in particular for rhodium *gem*-dicarbonyl on silica. 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.^{30–32} The specific model structures for the supported Rh mono- and dicarbonyl adsorbed systems are shown in Figure 4. The use of three hydrogen atoms to truncate the silica cluster is regarded as a minimal first approximation to a silica structure. Previous similar calculations³³ on these and similar model systems gave very good agreement of calculated infrared frequencies for the *gem*-dicarbonyl group with the experimental values. The calculations done here used the density functional option of Gaussian 94 and were done on an IBM RISC-6000-355 using Becke's three-parameter exchange functional with nonlocal correlation and local correlation provided by the Lee, Yang, and Parr expression. The LANL2DZ basis set was used to provide double- ζ valence shell functions and used the Los Alamos ECP for the inner shells. All calculations were done in the lowest spin state.

Calculation Results

For structures I, II, and III, all of which have Rh in a +1 oxidation state, the binding energy of Rh to surface oxygen is around 100 kcal/mol as given in Table 2. This large binding energy is seen to be independent of the presence or absence of carbonyl ligands. In structure IV the Rh is in a zero oxidation state and has a relatively low binding energy to the surface oxygen of 17 kcal/mol.

The binding energies were calculated as the difference between the total energy for a structure and the sum of the energies for the two neutral fragments produced by breaking the Rh–O bond or Rh–CO bond.

Discussion

It is suggested that the formation of a bridge carbonyl on Rh/NaY with an infrared band at 1834 cm^{-1} indicates Rh(I) species are adjacent (2.7–3.8 Å) to each other at many sites on the surface. Further, the theoretical calculations and the general

behavior of Rh and Ru *gem*-dicarbonyl species on silica, alumina, and zeolite surfaces indicate that the Rh(I) and Ru(I) species are relatively immobile on the surface at relatively low temperatures, i.e., below about 100 °C, as discussed below.

Implicit in the suggestion that the formation of bridging CO indicates Rh(I) species often occupy adjacent sites is the assumption that the Rh(I) species have low mobility at 20 °C. This is supported by the calculations which show a very strong Rh–O bond for Rh(I) species both with and without CO ligands. There is no experimental evidence that Rh(I) is mobile in the 0 to 100 °C temperature range. To redisperse Rh that has become clustered on a catalyst, oxidation, usually with air or O₂, is carried out at about 400 °C. This appears to produce dispersed rhodium oxide since partial reduction can produce dispersed Rh(I) *gem*-dicarbonyl. The most common reduction procedure of treatment with H₂ at 400 °C, followed by CO adsorption produces sintered Rh clusters and some Rh(I) *gem*-dicarbonyl.

The formation of metallic Rh clusters when strongly reducing conditions (such as H₂ treatment) are used suggests that Rh(0) is more mobile than Rh(I). The relatively low Rh–O bond strength calculated for Rh(0) supports this suggestion. This idea is further supported by our experimental data. The mild heating of the *gem*-dicarbonyl with ethylene at 100 °C provides sufficiently reducing conditions to result in some clustering even at this relatively low temperature.

The 1834 cm⁻¹ peak for bridge CO on Rh(I) is broad and has shoulders which suggest there is heterogeneity in the Rh(I)–Rh(I) distances. There is no experimental evidence either for or against the existence of Rh(I)–Rh(I) bonding. The absence of new linear CO peaks indicates that in the conversion of two adjacent *gem*-dicarbonyl species to a bridge CO species, all CO ligands except the bridge CO are lost so that no new species is formed containing a linear CO ligand attached to a Rh(I), which is part of a CO bridge.

For Rh(I), i.e., Rh in a +1 oxidation state, the actual charge on the Rh atom is not necessarily expected to be +1. The calculated charges on Rh(I) in our model compounds are from +0.35 to +0.48. As to the possibility of Rh(I)–Rh(I) bonds, based on crystallographic data, Dahl et al.³⁴ have proposed Rh(I)–Rh(I) bonding between rhodium atoms in adjacent [Rh(CO)₂Cl]₂ dimers at distances as long as 3.31 Å.

While in general CO is less tightly bound to metal oxide surfaces than to bulk metal surfaces, the situation for supported Rh *gem*-dicarbonyl species and small supported Rh clusters is less clear. For a zeolite support CO is more readily removed from Rh clusters than from Rh^I(CO)₂ species,³⁵ while for an alumina support CO desorbs more readily from Rh^I(CO)₂ species than from Rh clusters.³⁶ The calculated adsorption energies for CO on Rh(I) and Rh(0) are quite similar. The stability of M–CO interaction is enhanced by the π back-donation from the metal to CO³⁷ and destabilized by repulsions between the σ donor electron pair and other metal atom electron density.³⁸ For this reason the adsorption energies for CO on Rh(I) and Rh(0) can be very sensitive to the exact surface structure. The π back-donation favors adsorption on a Rh(0) site while reducing σ repulsion favors adsorption on a Rh(I) site. Thus the calculations here give similar adsorption energies on the two types of sites while the experimental data for zeolite and alumina supports differ as to which site is favored.

A bridge CO peak at 1834 cm⁻¹ for zeolite-supported Rh has been previously observed^{24–26,35} but a reversible change between the *gem*-dicarbonyl and bridge structures was not reported. In all of these reports the surface was a complex mixture of cluster and isolated Rh species. For Rh particles on

various supports a bond at about 1870 cm⁻¹ is usually reported as indicating a CO bridge species.^{14,36} A peak at about 1760 cm⁻¹ has been attributed to CO bridging three Rh atoms.^{23–26} Thus the 1834 cm⁻¹ band attributed to CO bridging adjacent supported Rh(I) species is at a distinctly different frequency from CO on Rh(0) clusters. Carbon monoxide adsorbed on dealuminated zeolite forms the usual *gem*-dicarbonyl but does not form a bridge species on evacuation.³⁹ For alumina-supported Rh, evacuation has not been reported to form a bridge structure by evacuation of a *gem*-dicarbonyl-containing sample. This could be due to an intrinsic difference in the alumina surface from a zeolite surface. Addition of water to zeolite shifts the Rh *gem*-dicarbonyl bands to slightly higher frequencies, presumably by the addition of a water molecule to the Rh coordination sphere.^{40,41} Evacuation of this surface does not produce the bridge structure. Additional work in our laboratory confirms this.²¹

Although Ru might be expected to occupy the same sites as Rh on our zeolite, evacuation of a sample containing Ru(I) *gem*-dicarbonyl did not produce a CO bridge species. In fact, evacuation produced very little change in intensity of the Ru(I) *gem*-dicarbonyl.

In the recent previous literature it generally has been assumed that the Rh(I) *gem*-dicarbonyl species were totally isolated from each other. On the basis of surface area and weight of Rh for a 0.92 wt % Rh on alumina, it was estimated that it was 8 Å between Rh atoms.⁴² Because the *gem*-dicarbonyl peaks do not shift in frequency as their intensity, and therefore the CO surface coverage, changes, it has been concluded that the *gem*-dicarbonyl species are isolated and not in islands.³⁵ In this paper, because of the formation of bridge CO structures and the relative immobility of supported Rh(I), it is suggested that for Rh on sodium zeolite the Rh(I) species can exist as nonbonded pairs on the surface.

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