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The Rhodium–Molybdenum Interaction in Rh/Mo/Alumina

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Rhodium and molybdenum form mixed metal particles when supported on alumina. Results of chemisorption, IR, and SIMS measurements indicate that the composition of the surface of these particles is sensitive to the environment in which the measurements are made. Molybdenum appears concentrated in the surface when the atmosphere is nonreducing, while rhodium appears concentrated in the surface when hydrogen is adsorbed. Chemisorption and infrared results indicate that molybdenum reduces the surface available for the chemisorption of carbon monoxide and hydrogen. The band for the linear carbonyl is shifted 8–11 cm^{-1} higher when molybdenum is present, which may indicate oxidation of the rhodium by the molybdenum or increased dipolar interactions between carbon monoxide molecules adsorbed on the smaller surface. Chemisorption and infrared results also suggest that adsorbed hydrogen increases electronic density at the rhodium sites. Bands for both the gem dicarbonyl and the linear carbonyl are shifted 7–10 cm^{-1} lower in either Rh/alumina or Rh/Mo/alumina when hydrogen is adsorbed.

INTRODUCTION

Rhodium and molybdenum supported on alumina have been reported to be catalysts for the synthesis of oxygenates from carbon monoxide and hydrogen (*1*, *2*). Apparently molybdenum increases the activity by a factor of 10 (*2*). Rhodium and molybdenum are also important components of the K/Co/Rh/Mo/Al_2O_3 catalysts used for making higher alcohols from syngas (*3*). Naturally it is believed that an understanding of the Rh–Mo interaction is relevant to an understanding of the catalytic activity of these types of catalysts.

Previous scanning transmission electron microscopy–energy dispersive spectroscopy results indicate that rhodium and molybdenum form mixed metal particles on alumina (*1*). The concentration of molybdenum in the particles is reported to depend on particle size (*1*). In another study, infrared results suggest that molybdenum preferentially covers the larger particles of metallic rhodium on the alumina, forming a mixed oxide surface phase that chemisorbs little carbon monoxide at room temperature (*4*). It appears from these studies that there is a chemical interaction between rhodium and molybdenum when supported on alumina, and the new phase(s) that forms has a different catalytic behavior than either rhodium or molybdenum.

In this study we consider how the composition of the rhodium–molybdenum surface phase depends on the conditions that exist when the measurements are made. It is found by SIMS that molybdenum is concentrated in the surface when the atmosphere is nonreducing, i.e., after evacuation at high temperatures. If the sample is cooled in hydrogen to room temperature and then evacuated, however, SIMS results indicate that rhodium is concentrated in the surface phase. This latter environment may be reducing because chemisorption measurements indicate that hydrogen is still adsorbed on the surface, in agreement with others (*5*).

Infrared results suggest there are rhodium–molybdenum interactions in either environment. It is also observed that adsorbed hydrogen affects the positions of the bands. It is suggested that the hydrogen "donates" electrons to the rhodium sites, as discussed previously (*6*).

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EXPERIMENTAL

Samples of 1% Rh/Al_2O_3 and 3% Mo Al_2O_3 were prepared by impregnation of Norton 6375 γ-alumina with rhodium nitrate or ammonium heptamolybdate, respectively. The Mo/Al_2O_3 was calcined at 773 K, and then impregnated with rhodium nitrate to make 1% Rh/3% Mo/Al_2O_3. The samples were reduced with flowing hydrogen at 673 K for 1 h in a glass IR cell, the SIMS treatment cell, or a conventional glass cell used for chemisorption measurements.

IR spectra were collected with a Nicolet 170SX FT–IR with a liquid nitrogen-cooled MCT detector as described previously (*4*). The glass sample cell was attached to a glass gas handling system, which was pumped with a LH TMP150V tubropump; base pressure in the gas handling system under vacuum was 10^{-5} Torr (1 Torr = 133.3 N m^{-2}). After reduction and evacuation, the samples were exposed to 100 Torr of CO at room temperature for 0.5 h, and then evacuated before the spectra were collected. To study the effect of oxygen, the samples were also slowly oxidized by exposure to 5 Torr of air for 5 min, and then repeating the procedure until a base pressure of 20 Torr was reached. After 0.5 h of exposure to the air, the samples were evacuated and reexposed to carbon monoxide before the first oxidized spectrum was collected. To study deeper oxidation, the samples were then exposed to sequences of 20 Torr of air for 5 min until a base pressure of 100 Torr was reached. After 0.5 h at this exposure, the samples were evacuated and reexposed to carbon monoxide before the second oxidized spectrum was collected.

A VG12-12S spectrometer with a high-temperature/high-pressure sample treatment cell and Ga-ion source (VG MIG 100) were used for the SIMS experiments. The sample treatment cell was pumped with a VG diffusion pump; base pressure while pumping was 10^{-6} Torr. The sample was flooded with low-energy electrons during the measurement to minimize charging. The current density was 7×10^{-4} mA/cm^2, which corresponds to an estimated erosion rate of 72 Å/h. Approximately 40 Å of the surface was eroded during these experiments. The etched area was 0.71 mm^2.

The conventional glass apparatus used to measure the amounts of hydrogen or carbon monoxide chemisorbed at room temperature has been described previously (*4*). Base pressure in this system under vacuum was also 10^{-5} Torr.

RESULTS

Figure 1 shows the ion intensities for Rh, Mo, and Al as a function of etch time in SIMS experiments. The sensitivity factors for Rh and Mo take into account differences in integration times and the relative abundance of the two elements. The Mo signal is for mass 92. The sensitivity factor for the alumina was chosen so that its intensity falls at the center of the figure. Molybdenum appears to be covering the rhodium when the sample is evacuated at 673 K (Fig. 1b) and not when the sample is cooled in hydrogen (Fig. 1a).

Figures 2 and 3 show the 1900–2200 cm^{-1} region in IR spectra for Rh/Al_2O_3 and Rh/Mo/Al_2O_3, respectively. Case (a) corresponds to the sample being cooled to room temperature in hydrogen before evacuation, case (b) to exposure of this sample to 20 Torr of air, and case (c) to the sample evacuated at 673 K and cooled to room temperature in vacuum. The envelopes have identical shapes for Rh/Al_2O_3 cooled in either vacuum or hydrogen, but not for Rh/Mo/Al_2O_3. The changes in the spectrum for Rh/Mo/Al_2O_3 in case (c) can be reversed by rereducing the sample and cooling in hydrogen.

Gaussian peaks have been fit to the envelopes as described previously (*4*). To fit the trailing edge of the envelopes, a band around 2000 cm^{-1} was inserted in cases (a) and (c), as discussed previously (*4*). Two new bands were also used in the fit of the well-known dicarbonyl shown in cases (b). One of the new bands in the oxidized sam-

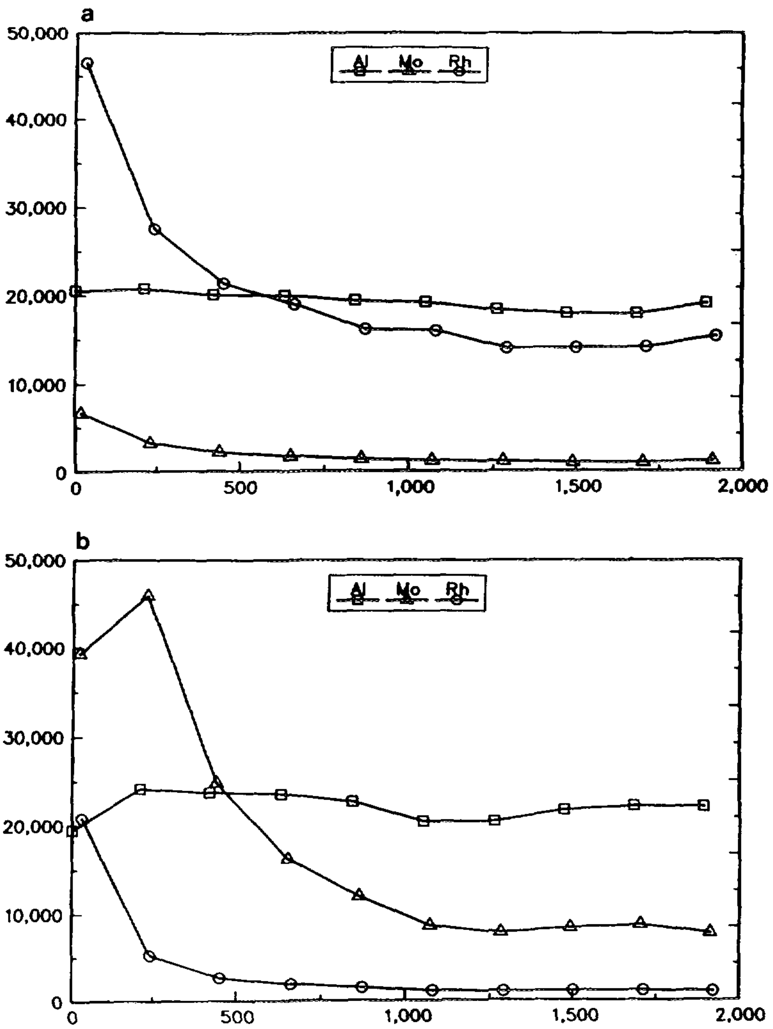

FIG. 1. SIMS intensities for 1% Rh/3% Mo/Al_2O_3: (a) sample cooled in hydrogen after reduction, (b) sample cooled in vacuum after reduction.

TABLE 1

Amounts (cm^3/g) of Hydrogen and Carbon Monoxide Chemisorbed at Room Temperature

	Rh/Al_2O_3		Rh/Mo/Al_2O_3	
Gas	Vac[a]	H_2[b]	Vac[a]	H_2[b]
H_2	0.9	0.1	0.5	0.0
CO	3.2	2.9	1.6	1.3

[a] Evacuation of the sample at 673 K.

[b] Cooling the sample in hydrogen to room temperature and then evacuation.

ple is around 2000 cm^{-1}, the position of the unidentified band in cases (a) and (b).

Table 1 shows the amounts of hydrogen and carbon monoxide adsorbed at room temperature for Rh/Al_2O_3 and Rh/Mo/Al_2O_3 after they had been either evacuated at 673 K or cooled in hydrogen before evacuation. Both samples adsorb less hydrogen when cooled in hydrogen before evacuation.

DISCUSSION

The results shown in Table 1 indicate that hydrogen remains on either sample when

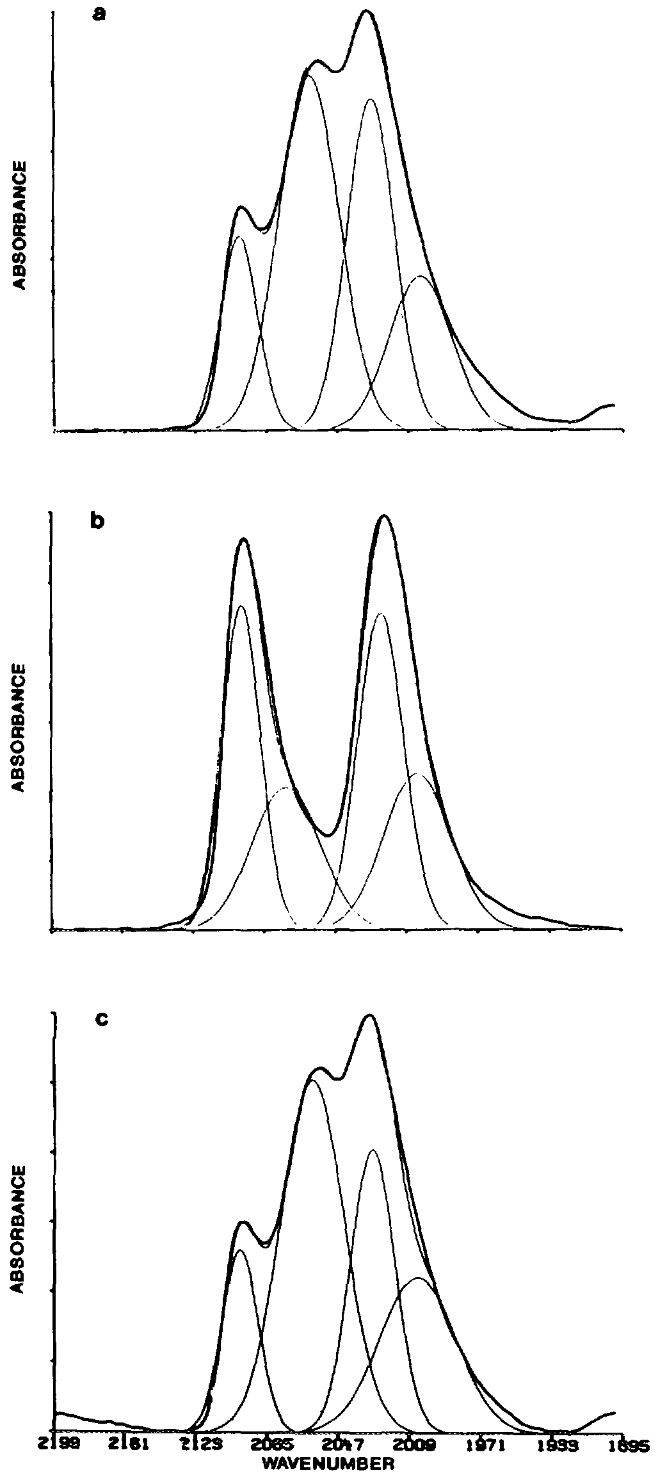

FIG. 2. Infrared spectra for carbon monoxide adsorbed on 1% Rh/Al_2O_3: (a) cooled in hydrogen before evacuation, (b) after exposure to 20 Torr of air, (c) after evacuation at 673 K.

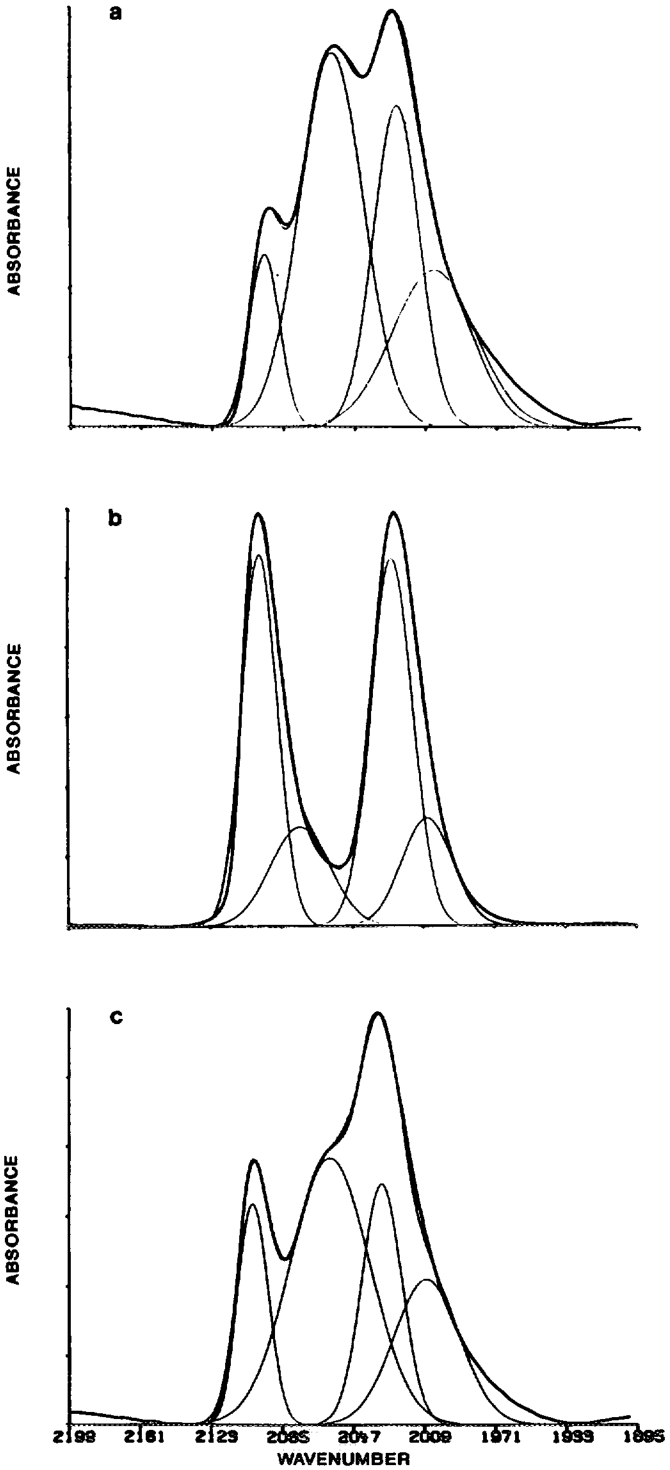

FIG. 3. Infrared spectra for carbon monoxide adsorbed on 1% Rh/3% Mo/Al$_2$O$_3$: (a) cooled in hydrogen before evacuation, (b) after exposure to 20 Torr of air, (c) after evacuation at 673 K.

the samples are cooled in hydrogen to room temperature before evacuation, in agreement with Solymosi and Pásztor (5). The addition of molybdenum suppresses the chemisorption capacity of rhodium for either hydrogen or carbon monoxide in either environment. As discussed previously, 3% Mo/Al_2O_3 is a very poor adsorber of carbon monoxide (0.05 cm^3/g), while 1% Rh/Al_2O_3 is a good adsorber (3.5 cm^3/g) (*4*). The effect of molybdenum on the chemisorption capacity is surprising since 3 wt% molybdenum is expected to cover only approximately one-third of the alumina area (*4*). This suggests that molybdenum and rhodium form a mixed surface phase, in agreement with Foley *et al.* (*1*), and this surface has a reduced tendency to chemisorb either gas at room temperature.

The SIMS results shown in Fig. 1 indicate that the average surface composition depends on the pretreatment of the surface. As deduced in the previous study (*4*), molybdenum appears to cover the rhodium surface when the sample is evacuated at 673 K. When the sample is cooled in hydrogen before evacuation, however, the SIMS results indicate that the rhodium covers the molybdenum surface.

Figures 2 and 3 show IR spectra for Rh/Al_2O_3 and $Rh/Mo/Al_2O_3$. It is clear that the shape of the envelope for Rh/Al_2O_3 is the same irrespective of whether the sample is evacuated at 673 K or cooled in hydrogen to room temperature before evacuation. This fact gives us confidence that the IR cell does not leak in the normal sense of the word.

On the other hand, there are changes in the spectra for $Rh/Mo/Al_2O_3$ depending on whether the sample was cooled in vacuum or not. The band around 2063 cm^{-1} has obviously lost intensity in the sample that had been evacuated 673 K. On the basis of previous work, the band around 2063 cm^{-1} is assigned to the linear carbonyl, and the bands around 2100 cm^{-1} and 2032 cm^{-1} are assigned to the gem dicarbonyl (*7*, *8*). It was previously suggested that the decrease in intensity of the band for the linear carbonyl indicates that molybdenum is covering the larger particles of rhodium (*4*). This supposition is consistent with the SIMS results discussed above.

Although it should be clear that the sample cells in the SIMS and IR experiments are not considered to leak in the customary sense of the word, we note that it is impossible to achieve a perfect vacuum in any experiment. In this sense we consider the evacuation at 673 to be "oxidizing." The surface is very reactive toward oxygen at this temperature, and the average oxygen concentration during the evacuation is not zero: It depends on the balance established between the oxygen being removed by the vacuum pump and that leaking past the imperfect seals of the cell. The evacuations at room temperature are not as oxidizing because the surface is less reactive, and the hydrogen adsorbed on the surface may provide a "reducing atmosphere." Therefore, the composition of the surface phase may be quite sensitive to the oxidizing or reducing nature of the environment.

The band around 2000 cm^{-1} was not assigned in the previous study (*4*). This band is required to fit the trailing edge of the band for the asymmetric stretch of the Rh(I)–dicarbonyl, as discussed previously (*4*). Because the intensities of the two bands for the Rh(I)–dicarbonyl are unequal in many studies, Rice *et al.* (*8*) suggested that there is a band around 2000 cm^{-1}, and assigned it to a Rh(I) bridging carbonyl. We also note that Wang and Yates in a study of the gem dicarbonyl on oxidized Rh/Al_2O_3 observed an increase in intensity around 2000 and 2075 cm^{-1} when the CO partial pressure in their cell was increased (*9*). On the basis of a deconvolution that takes into account a possible equilibrium between the Rh(I)–dicarbonyl and a proposed Rh(I)–tricarbonyl, they assigned this increase in intensity to a Rh(I)–tricarbonyl with bands located at 2120, 2078, and 2026 cm^{-1}. Wey *et al.* (*10*) have recently argued that the band around 2120 cm^{-1} is due to a Rh(II)-carbonyl. It is clear that the envelope between 1900 and 2100 cm^{-1} is quite complex.

We have intentionally avoided using too many peaks in fits to this region in this work. Nevertheless, there appears to be a tail on the band for the asymmetric stretch of the customary Rh(I)–dicarbonyl located around 2030 cm^{-1}, and it is this tail that requires us to include a peak around 2000 cm^{-1} in Figs. 2 and 3. We note from the spectra for the oxidized samples shown in Figs. 2b and 3b that this band also appears. In fact, we obtain a good fit of this region in the oxidized samples by adding another band around 2070 cm^{-1}. The two major bands for the Rh(I)–dicarbonyl are now symmetric, as one might expect. Since it is well known that the band for the linear carbonyl is extinguished by oxygen, we speculate that the bands around 2075 and 2000 cm^{-1} in Figs. 2b and 3b are due to the Rh(I)–tricarbonyl of Wang and Yates (*9*). The intensities of these bands increase on further oxidation with 100 Torr of air, suggesting that they are indeed bands for an oxidized rhodium species. The ratio of intensities of the two bigger bands (dicarbonyl) to the two smaller bands (tricarbonyl) remains the same on further oxidation, which is consistent with an equilibrium between these two species as proposed by Wang and Yates (*9*). Since the band around 2000 cm^{-1} appears in the spectra for the reduced samples, we speculate that the tricarbonyl is also present in reduced samples; i.e., the oxidative carbonylation that occurs to form the gem dicarbonyl (*11, 12*) also forms a tricarbonyl. If this is correct it means that the linear carbonyl thought to be around 2060 cm^{-1} is less intense than previously believed since it is overlapped with one of the bands for the tricarbonyl.

TABLE 2

IR Band Positions for CO Adsorbed On Rh/Al_2O_3 and $Rh/Mo/Al_2O_3$

Sample	Band position (cm^{-1})		
	Gem dicarbonyl		Linear carbonyl
Rh/Al_2O_3 (vac)	2100	2029	2061
Rh/Al_2O_3 (H_2)	2092	2021	2050
$Rh/Mo/Al_2O_3$ (vac)	2102	2032	2068
$Rh/Mo/Al_2O_3$ (H_2)	2095	2025	2060

Returning now to the position of the traditional linear carbonyl, Table 2 shows that its position is shifted approximately eight wave numbers higher when molybdenum is present *in either environment*. The effect of molybdenum on the linear band is the same as that of oxygen, and this analogy led us to suggest that the molybdenum oxidizes the rhodium (*4*). One could also argue that the shift is due to an increased dipolar interaction between neighboring carbon monoxide molecules adsorbed on a smaller surface (*13*). In any case, the shift suggests that a mixed rhodium–molybdenum surface phase forms.

When the samples are cooled in hydrogen, and the SIMS results indicate that rhodium is on top of the molybdenum, the same shift in position of the band for the linear carbonyl becomes more difficult to understand. We suggest that the surface phase contains both rhodium and molybdenum, and the relative concentrations of the elements in this layer depend on the environment, oxidizing or reducing. One element or the other may appear to cover the other in SIMS because the number of ions created by the ion beam is very sensitive to different matrix effects for these elements, possibly combined with oxygen, in nonstoichiometric surface phases.

A surface containing both rhodium and molybdenum would be consistent with the observed chemisorption behavior, shown in Table 1. The CO chemisorption capacity is approximately the same for either Rh/Al_2O_3 or $Rh/Mo/Al_2O_3$, irrespective of whether they are cooled in hydrogen or not. Since carbon monoxide is chemisorbed by rhodium, this indicates that the surface probably contains about the same number of rhodium adsorption sites in either environment. IR results support this assumption: The total intensity remains almost the same in the two environments, and the changes in intensities are reversible when the sample is taken through "high-temperature evacuation"-rereduction-"cooling in hydrogen" cycles. Apparently matrix effects in the SIMS experiments are very sensitive to the presence of oxygen in the mixed rhodium-molybdenum surface layer.

Finally we note that the bands for both the gem dicarbonyl and the linear carbonyl are approximately 7–10 cm^{-1} lower for both Rh/Al_2O_3 and $Rh/Mo/Al_2O_3$ when these samples have been cooled in hydrogen. We believe the downward shifts in the bands for the gem dicarbonyl and the linear carbonyl indicate that the hydrogen remaining on the surface increases the electronic density at the rhodium adsorption sites, and this increased density is donated to the antibonding orbitals of the adsorbed carbon monoxide. The adsorption site could be described as a hydridocarbonyl, if the effect is due to a local rhodium-hydrogen-carbon monoxide interaction. However the hydridocarbonyl (linear band) is believed to be at lower wave numbers (*5*, *12*). It is interesting that Yates *et al.* predicted a 10 cm^{-1} shift in the bands for the linear and dicarbonyl when hydridocarbonyls are formed in the presence of hydrogen (*6*).

CONCLUSIONS

Rhodium and molybdenum form a mixed phase when supported on alumina. The surface of this phase has a reduced capacity to chemisorb hydrogen and carbon monoxide (with respect to Rh/alumina).

The surface composition of this phase depends on whether the environment is reducing or nonreducing. SIMS experiments indicate that rhodium is concentrated on the surface when the atmosphere is reducing, and molybdenum is concentrated on the surface when the atmosphere is nonreducing.

Chemisorption and IR results indicate that the surface contains both rhodium and molybdenum in either environment. This implies that matrix effects in SIMS are significantly different in the two environments, as they would be if a mixed metal oxide surface formed in the nonreducing environment.

Molybdenum shifts the band for the linear carbonyl to higher wave numbers. The effect is similar to that of oxygen and suggests an oxidation of the rhodium by the molybdenum. Adsorbed hydrogen shifts both the bands for the gem dicarbonyl and the linear carbonyl to lower wavenumbers, which suggests a donation of electrons to the rhodium sites.

An unassigned band in Rh/alumina near 2000 cm^{-1} (*4*) is tentatively assigned to a rhodium(I)-tricarbonyl. This band occurs in spectra for both reduced and oxidized samples for both Rh/alumina and Rh/Mo/alumina.

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