

Figure 4. Remaining probability for a strong shielded Coulomb potential. $\chi = -12.00 \times 10^{-9}$, $\gamma = 7.00 \times 10^9$.

lomb and the shielded Coulomb potentials. For both potentials the agreement with the numerical result is excellent and we need to consider only up to the second order perturbation term. This approach, however, is appropriate only for weak potentials since the potential parameter(s) representing the potential strength is related to the convergence of the perturbation series. Nevertheless, this approach may be applied to relatively strong potentials if we are interested only in the short time region. This fact is well illustrated in Figure 2 for the Coulomb potential and in Figure 4 for the shielded Coulomb potential. On the other hand, for the long time region

we can use the closed form solutions given by Eqs.(49) and (50).

The numerical method proposed in Section III saves both computing time and computer memory significantly once the parameter λ is optimized and it may be helpful for the future investigation of diffusion-controlled processes in liquids.

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A Study on the Chemisorption of Carbon Monoxide on Silica-Supported Rhodium

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We have investigated the infrared absorption spectra for carbon monoxide chemisorbed on reduced and oxidized Rh/SiO₂ with and without potassium coating within the frequency range of 1800–2200 cm⁻¹ at various Rh concentrations, CO pressures, and temperatures. In case of no potassium coating, only two bands at 2070 and 1900 cm⁻¹ appeared for CO adsorbed on reduced Rh/SiO₂ while for oxidized Rh/SiO₂ four bands were found at 2100, 2070, 2040, and 1900 cm⁻¹. We have successfully tried to explain the differences between our observations and those by other investigators who used the Rh/Al₂O₃ system instead of Rh/SiO₂ on the basis of the suggestions by Yates *et al.* Accordingly, we propose that the surface OH groups are deeply involved in producing the Rh⁺¹ sites which are responsible for the gem-dicarbonyl species. On coating with potassium all the IR bands for three carbonyl species were found to suffer red shift, the magnitude of which increased with increasing Rh/CO ratio.

Introduction

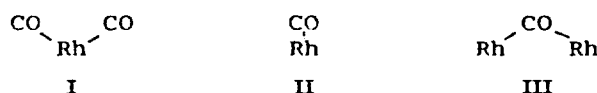
One of the current research topics of importance is the determination of the structures of molecules adsorbed on supported transition metal catalysts, and the elucidation of

the character (oxidation state, dispersed state, *etc.*) of the supported metals and the nature of support-metal interaction in such catalysts is no less important. Rhodium has been one of the more popular metals for such study, not merely because the supported rhodium catalysts are widely in use for industrial purposes but because it is relatively easy to prepare the rhodium in the Rh⁰ metallic state on a support such

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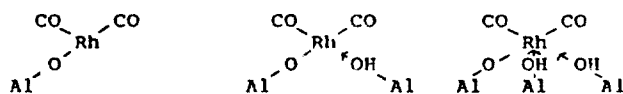
as SiO_2 and Al_2O_3 . Carbon monoxide bears a special importance as an adsorbate because it has very simple molecular structure and is also widely used in industry as an invaluable source material. Thus it is no wonder why the adsorption of carbon monoxide on the supported Rh catalysts has been the topic of so many investigations and publications.

It has long been recognized that the infrared spectra of CO chemisorbed on reduced $\text{Rh}/\text{Al}_2\text{O}_3$ typically show four absorption bands in the vicinity of 2100, 2070, 2040, and 1900 cm^{-1} , respectively, and the origins of these bands have been extensively studied by many investigators.¹⁻²⁰ It is now generally believed that the following three types of adspecies are formed when CO is chemisorbed on dispersed Rh surface:



It was not until quite a few years had elapsed that nearly all the investigators came to an agreement upon the fact that 2100 and 2040 cm^{-1} bands originate from symmetric and asymmetric stretchings of carbonyl bonds in the adspecies I (gem-dicarbonyl species) while 2070 and 1900 cm^{-1} bands are due to stretching of CO in the adspecies II (linearly-bonded species) and III (bridge-bonded species), respectively. It is found that the 2100 and 2040 cm^{-1} bands do not shift their positions with increasing CO coverage and their band intensities are almost equal to each other. Moreover, the positions of these bands closely correspond in wavenumber and character to those ($2095, 2043\text{ cm}^{-1}$) observed for the bridged dimeric compound $\text{Rh}_2(\text{CO})_4\text{Cl}_2$.^{1,17,18} In view of this absence of shift in band positions with varying CO coverage Yang and Garland¹ suggested that the gem-dicarbonyl species I could be formed only on highly dispersed sites. Recent observation by Yates and Kolasinsky⁸ has confirmed that this species is in fact nonlinear $\text{Rh}(\text{CO})_2$, C_{2v} . The bands for the species II and III at 2070 and 1900 cm^{-1} , respectively, begin to appear at lower CO coverages than do those for the species I and shift toward higher frequencies as coverage increases.^{1,2} It is notable that in the EELS (electron energy loss spectroscopy) spectra of CO chemisorbed on a Rh(111) only the bands for the species II and III are observed.²¹ It was also demonstrated that, under certain conditions, a number of other minor surface species, mostly quite labile, could also be formed.⁵

As for the character of metal sites of CO chemisorption, while investigators have easily come to agreement in that metal clusters $\text{Rh}_x(x > 2)$ are involved in the formations of linearly-bonded and bridge-bonded species, the chemical state of Rh site for the gem-dicarbonyl species has long been a subject of controversy.²⁻⁴ Due to the extensive efforts by Yates and coworkers² it seems now established that the gem-dicarbonyl species can form only on the isolated Rh sites, in which the oxidation state of Rh is +1. Robbins¹² has strongly suggested that the gem-dicarbonyl species has the following alumina-bound structures on the basis of his experimental results.



This suggestion is in accord with the proposal by Smith *et*

al.^{22,23} that surface hydroxyl groups are effective in the oxidation of Rh^0 to Rh^{+1} during the degradation of zerovalent Rh carbonyl clusters supported on Al_2O_3 . Solymosi^{13,14} has also indicated that an increase in the reduction temperature of the catalyst resulted in a decrease in intensity of the gem-dicarbonyl bands, possibly due to a depletion of surface OH groups by pretreatment at high temperatures. More interestingly, Yates *et al.*²⁴ have recently reported direct spectroscopic evidence that correlates the consumption of specific isolated OH groups to the formation of $\text{Rh}^{+1}(\text{CO})_2$ species in the presence of gaseous carbon monoxide. They have observed that the band intensities of isolated OH groups in $\text{Rh}/\text{Al}_2\text{O}_3$ and Rh/SiO_2 decrease as the intensities of $\text{Rh}^{+1}(\text{CO})_2$ bands increase in the presence of $\text{CO}(\text{g})$ and have interpreted this result as the direct evidence that the $\text{Rh}^{+1}(\text{CO})_2$ species can be formed at the expense of surface isolated OH groups. On the basis of their observation²⁴ and Robbins' suggestion¹² Yates *et al.* have proposed a possible mechanism which shows how the surface OH groups get involved in the formation of gem-dicarbonyl species on $\text{Rh}/\text{Al}_2\text{O}_3$ or Rh/SiO_2 .

So far, with a few exceptions,^{24,25} most of the experiments regarding the chemisorption of CO on dispersed Rh surface have been performed using Al_2O_3 as support. Although the general features of CO chemisorption for $\text{Rh}/\text{Al}_2\text{O}_3$ and Rh/SiO_2 are thought to be quite similar to each other, we expect a few exquisite differences between them due to their differences in chemical composition. Moreover, if it is true that the surface OH groups are deeply involved in the formation of gem-dicarbonyl species as Yates *et al.* have indicated, the elevation of sample reduction temperature may result in a distinct change in the IR spectra for CO chemisorbed on the supported rhodium. Therefore, in this paper we have investigated the chemisorption of carbon monoxide on a silica-supported Rh to gain more insight into the nature of gem-dicarbonyl species using the catalyst sample prepared at an elevated temperature (573K). Besides, we have also investigated the chemisorption of CO on an unreduced $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}/\text{SiO}_2$ and an oxidized Rh/SiO_2 in the hope that it may provide additional informations.

Rh catalysts are known to be sensitive to the presence of species such as alkali metal and early transition metal ions or oxides. Many studies of alkali promotion in single crystals²⁶⁻²⁹ and supported metals,³⁰⁻³² as well as theoretical investigations,^{33,34} have suggested that alkali species may have significant electronic and/or electrostatic interactions with transition metals which result in modifications in the nature of adsorption of molecules such as CO. In this paper we have also observed the changes in the IR spectra of CO chemisorbed on Rh/SiO_2 coated with potassium film as a function of CO pressure and temperature for better understanding of the effect of alkali promoters.

Experimental

To prepare the adsorbent an adequate amount of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (Aldrich Chem. Co., reagent grade) was dissolved in distilled water and silica gel (HDK Wacker N20, BET surface area $200\text{ m}^2/\text{g}$) was added to it so that a thin slurry was formed. The resulting slurry was stirred until a homogeneous mixture was obtained. This then was dried at $80-90^\circ\text{C}$ for 72 hours and was ground to fine powder using an agate mortar and pestle. After grinding, a portion of the powder

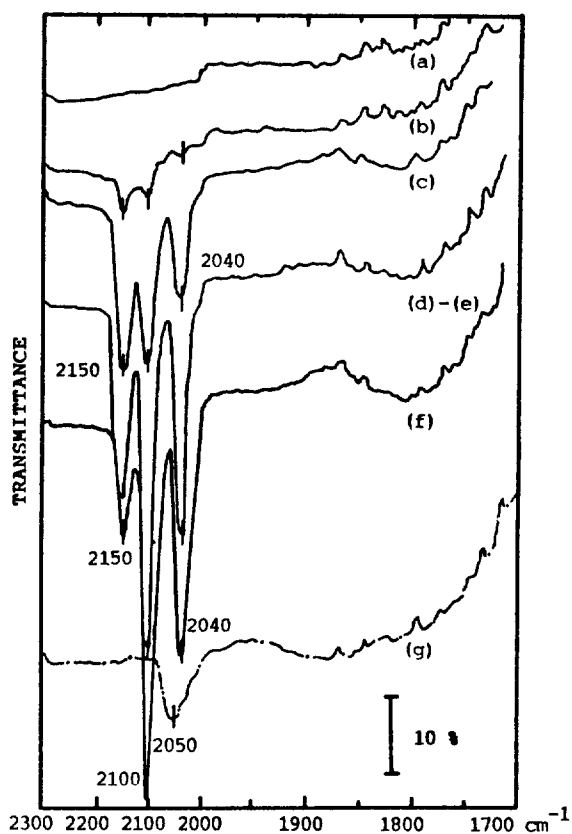


Figure 1. IR spectra for CO adsorbed on 4.0% RhCl₃·3H₂O/SiO₂ sample at 1.0 torr as a function of temperature. (a) base line (b) 25°C, (c) 50°C, (d) 100°C, (e) 150°C, (f) 200°C, (g) after reduction with H₂ (CO pressure: 1 torr).

was taken and pressed into a pellet, 2 cm in diameter, using a pressure of 400 kg/cm², which was then used for the adsorption experiment shown in Figure 1. Another portion of the powder was reduced at 300°C for 24 hours under the stream of H₂ and then 30–40 mg of the powder were also pressed into a similar pellet. This pellet was placed in a cell connected to the vacuum system and was reduced at 300°C for 50 minutes in the H₂ atmosphere. This then was evacuated for 10 minutes twice. Finally the system was cooled down to room temperature for the final evacuation and the adsorption experiment shown in Figure 2 was carried out. The oxidized form of the catalyst was prepared by exposing the pellet to oxygen under various conditions (pressure, temperature, and exposure times).

All the IR spectra were recorded on a Perkin-Elmer Model 782 double beam infrared spectrophotometer and the infrared cell used in our experiment was described elsewhere in detail.³⁵ The method of coating and annealing the sample with thin film of potassium was identical with that described by Park³⁶ and the amount of potassium contained in the catalyst was analyzed, as before,³⁸ by measuring the electrode potential for the solution obtained by dissolving the sample in a known amount of water.

Hydrogen gas used for prereduction was a domestic product of 99.99% in purity while that used for reduction inside the cell was the product of 99.9999% in purity which was obtained from the N. V. Philips Eindhoven Co. The CO and O₂ gases were purchased from the Matheson Gas Products Co.,

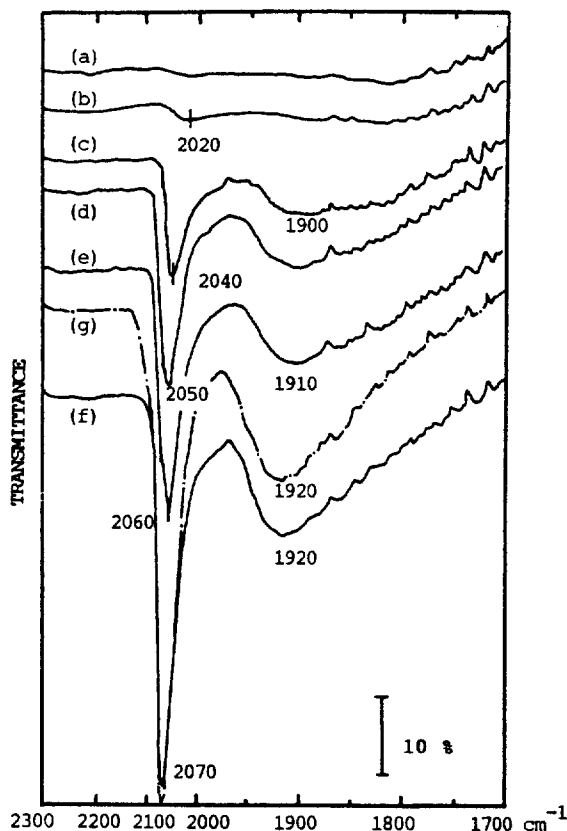


Figure 2. IR spectra for CO adsorbed on 4.0% reduced Rh/SiO₂ sample at 20°C as a function of CO pressure. (a) base line, (b) 1 × 10⁻³ torr, (c) 3 × 10⁻³ torr, (d) 8 × 10⁻³ torr, (e) 3 × 10⁻² torr, (f) 0.156 torr, (g) 1 torr.

both of 99.99% in purity. These gases were used without further purification.

Results and Discussion

(A) Adsorption of CO on silica-supported Rh without potassium coating. Shown in Figure 1 are the IR spectra for CO chemisorbed on an unreduced 4.0% (Rh content) RhCl₃·3H₂O/SiO₂ sample at 1.0 torr of CO pressure and various temperatures. From this we see that in case of unreduced RhCl₃·3H₂O/SiO₂ three bands appear at 2150, 2100, and 2040 cm⁻¹, respectively, and the latter two bands rapidly grow in intensity with increasing temperature. Smith and collaborators²² have attributed the 2150 cm⁻¹ band to the CO species bonded to Rh⁺³ in the unreduced RhCl₃·3H₂O/SiO₂. As the temperature goes up, more and more Rh⁺³s seem to be reduced to Rh⁺¹ in the presence of gaseous CO, which in turn intensifies the bands at 2100 and 2040 cm⁻¹. On reducing with H₂ gas Rh⁺¹ is further reduced to Rh⁰ and, as is shown by the spectra (g) in Figure 1, the 2050 and broad 1900 cm⁻¹ bands due to the linearly-bonded Rh-CO and bridge-bonded (Rh)₂CO, respectively, show up while the bands at 2150, 2100, and 2040 cm⁻¹ all disappear. Displayed in Figure 2 are the IR spectra for CO chemisorbed on a reduced 4.0% Rh/SiO₂ sample at 20°C plotted as a function of CO pressure. It is noteworthy that the linearly-bonded species band gradually shift toward shorter wavelength side as the CO pressure increases and it is nowadays well known that this

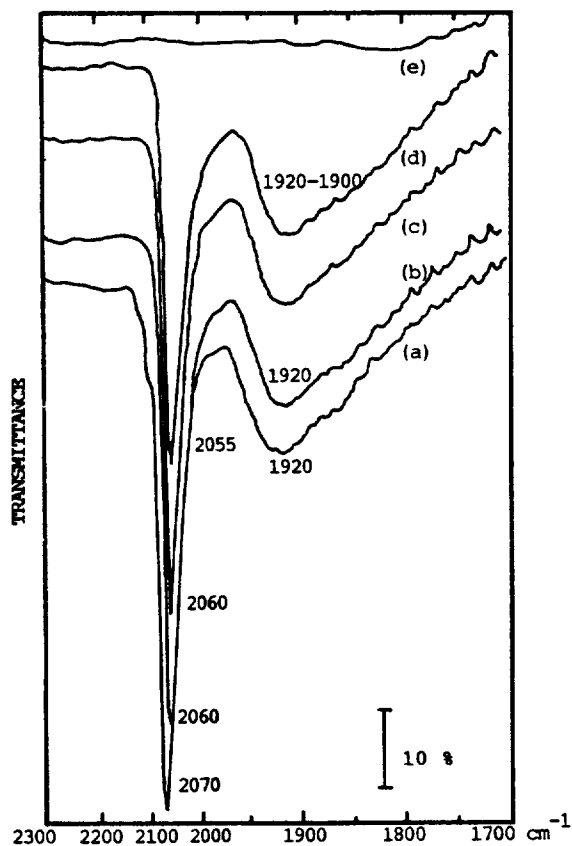


Figure 3. IR spectra for CO adsorbed on 4.0% reduced Rh/SiO₂ sample at 20°C as a function of pumping time. (a) CO pressure of 1 torr, (b) 5 min, (c) 30 min, (d) 12 hrs, (e) base line.

shift is caused by dipolar couplings among the adsorbed CO molecules.³⁷ In Figure 2 we can recognize only the bands at 2070 and 1900 cm⁻¹. No evidence can be found in these spectra that even a trace of gem-dicarbonyl species has formed on the Rh surface. This observation is in contrast to the case of reduced Rh/Al₂O₃ which have been reported by a few investigators.^{1,2} In the case of reduced Rh/Al₂O₃ it was found that all of the four bands at 2100, 2070, 2040, and 1900 cm⁻¹ appeared at any CO pressure. It may at first seem puzzling to explain why there can exist such differences. It appears that the answer to this question can be derived from the Solyosi's suggestion^{13,14} that a depletion of surface hydroxyl groups due to the increase in the reduction temperature may prevent the formation of Rh⁺¹ sites responsible for gem-dicarbonyl species. In fact, while our sample Rh/SiO₂ was reduced at 300°C, other investigators^{1,2} all prepared their Rh/Al₂O₃ samples below 150°C. Such Rh/Al₂O₃ samples prepared at lower temperatures are expected to abound in surface OH groups much more than our Rh/SiO₂ sample. Absence of 2100 and 2040 cm⁻¹ bands in Figure 2 may actually indicate that our reduced Rh/SiO₂ sample does not contain the concentration of surface OH groups high enough to produce the gem-dicarbonyl species *via* the mechanism proposed by Yates *et al.*²⁴ At this stage, therefore, the explanation of our observations on the basis of the mechanism due to Yates *et al.* seems to be in order.

As shown below, carbon monoxide molecules are first chemisorbed on the Rh_x⁰ surface to yield the linearly-bonded

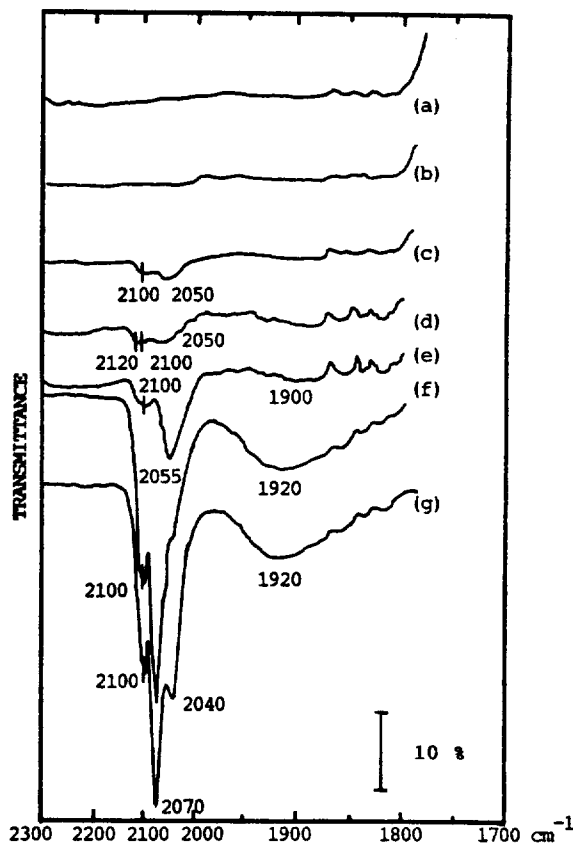
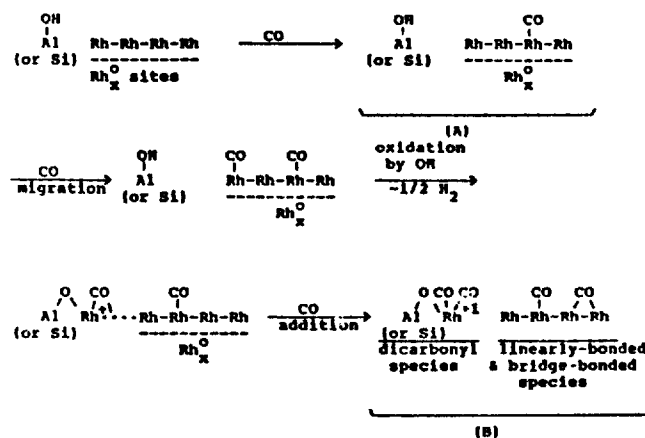


Figure 4. IR spectra for CO adsorbed on oxidized 4.0% Rh/SiO₂ sample at 20°C as a function of CO pressure. (Oxygen pressure; 10 torr, oxidation temperature; 100°C, exposure time; 5 min). (a) base line, (b) 5 × 10⁻³ torr, (c) 5 × 10⁻² torr, (d) 5 × 10⁻² torr, (after 5 min), (e) 0.115 torr, (f) 1.0 torr, (g) 1.0 torr, (after 60 min).



and the bridge-bonded species and the CO molecules in these species are supposed to migrate over the Rh_x⁰ surface until they become combined to the edge or corner metal atoms in the Rh crystallites. The Rh-CO species formed on the edge or corner Rh atoms can readily be approached by nearby OH groups on the surface of support materials (Al₂O₃ or SiO₂) to undergo oxidation to produce the gem-dicarbonyl species. Thus, in this mechanism the rate determining step seems to be the oxidation of Rh-CO by the surface hydroxyl groups. Therefore, unless the concentrations of both Rh-CO and OH are high enough, the desired oxidation is not likely to

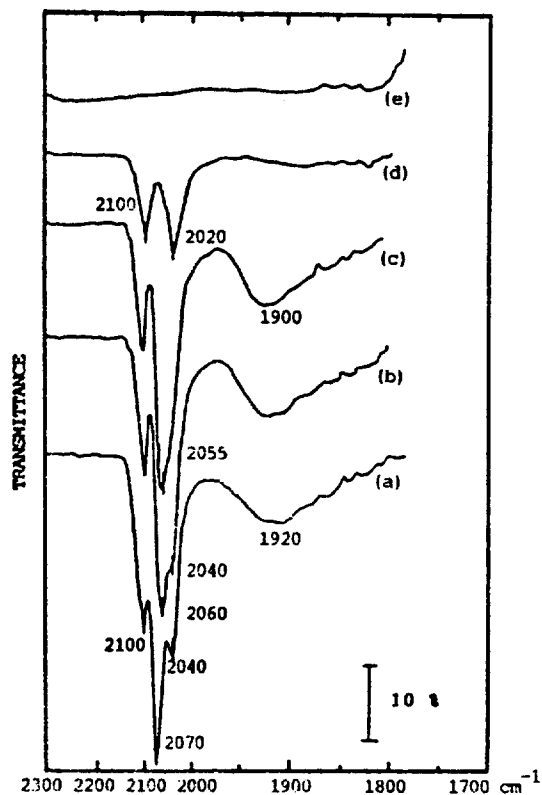


Figure 5. IR spectra for CO adsorbed on oxidized 4.0% Rh/SiO₂ sample at 20 °C as a function of pumping time. (a) CO pressure of 1.0 torr, (b) 5 min, (c) 30 min, (d) 12 hrs, (e) base line.

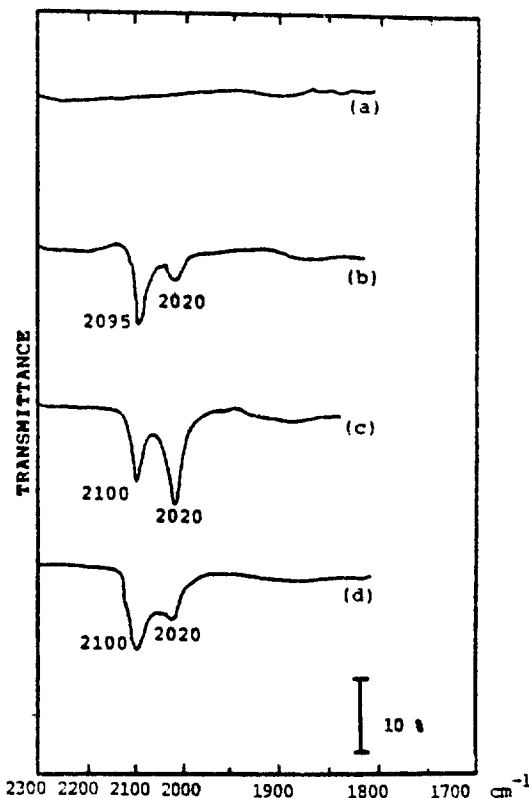


Figure 7. Desorption IR spectra for CO adsorbed on oxidized Rh/SiO₂ sample after 12 hours of pumping as a function of metal contents. (a) base line, (b) 1%, (c) 4%, (d) 10%.

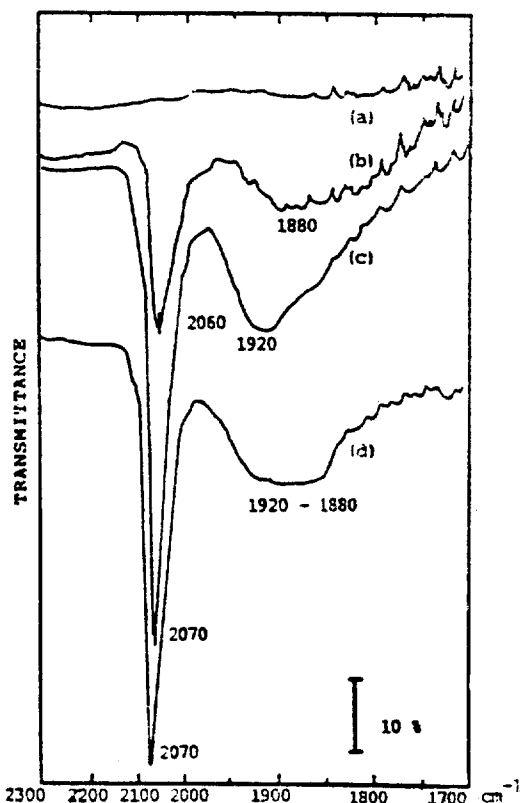


Figure 6. IR spectra for CO adsorbed on Rh/SiO₂ sample at CO pressure of 1.0 torr as a function of metal contents. (a) base line, (b) 1%, (c) 4%, (d) 10%.

happen. This mechanism is also consistent with the observation that addition of H₂ converts the dicarbonyl species to the linearly-bonded and the bridge-bonded species.^{24,25}

Figure 4 shows that the gem-dicarbonyl species can be formed on the oxidized Rh/SiO₂ sample, too. In order to obtain the spectra shown in Figure 4 we placed the reduced Rh/SiO₂ pellet in the infrared cell connected to the vacuum line and had it reduced for 50 minutes at 300 °C twice under the stream of H₂ gas and then evacuated the cell down to 10⁻⁵ torr. After the temperature was cooled down to about 100 °C, the sample was oxidized by exposing it to the oxygen gas of 10 torr for 5 minutes while maintaining the constant temperature, and then the sample chamber was again evacuated to perform the adsorption experiment. As can be clearly seen from Figure 4 the 2100 and 2040 cm⁻¹ bands representing the gem-dicarbonyl species appear with increasing intensities as the CO pressure increases. The 2070 and 1900 cm⁻¹ bands also gradually intensify with increasing CO pressure. No other investigators have ever reported such observations for oxidized Rh/SiO₂ sample except Gonzalez *et al.*²⁵ who tried to investigate the effect of coadsorption of CO and O₂ on the reduced Rh/SiO₂. Observations displayed in Figure 4 indicate that on exposure to O₂ the Rh_x⁰ surface in the reduced Rh/SiO₂ can partially be oxidized to produce the Rh⁺¹ sites, although the mechanism for such oxidation is not clear. In Figure 5 and 7 are shown the desorption spectra for CO on an oxidized Rh/SiO₂ sample which demonstrate that the gem-dicarbonyl species are more tightly bound than the linearly-bonded and the bridge-bonded species.

In Figure 6 are shown the IR spectra for CO chemisorbed

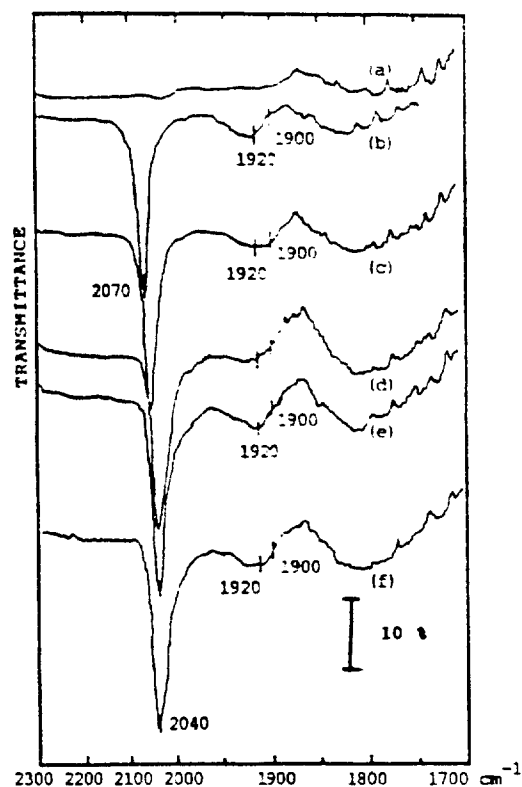


Figure 8. IR spectra for CO adsorbed on reduced 4.0% Rh/SiO₂ sample at 1.0 torr as a function of temperature. (a) base line, (b) 25 °C, (c) 50 °C, (d) 100 °C, (e) 150 °C, (f) 200 °C.

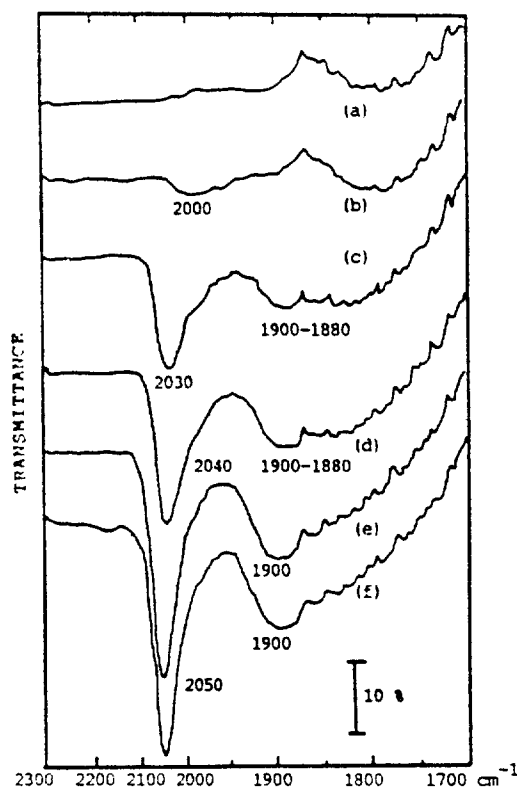


Figure 10. IR spectra for CO adsorbed on K-promoted 4.0% Rh/SiO₂ sample at 25 °C as a function of CO pressure. (a) base line, (b) 9×10^{-3} torr, (c) 8×10^{-2} torr, (d) 0.294 torr, (e) 1.0 torr, (f) 10 torr.

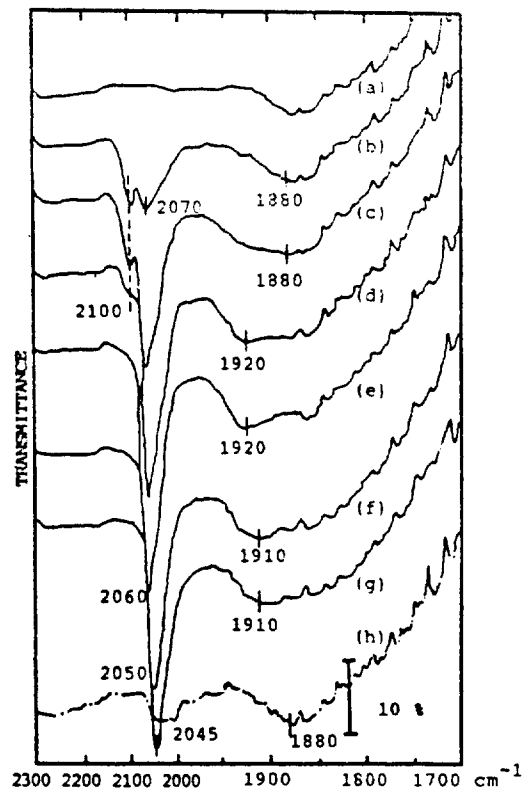


Figure 9. IR spectra for CO adsorbed on oxidized 4.0% Rh/SiO₂ sample at 1.0 torr as a function of temperature. (a) base line, (b) 25 °C, (c) 50 °C, (d) 75 °C, (e) 100 °C, (f) 150 °C, (g) 200 °C, (h) 12 hrs of degassing.

on a reduced Rh/SiO₂ sample at the CO pressure of 1.0 torr plotted as a function of metal contents. We obtained these spectra to examine the hypothesis by several investigators^{2,3} that for the gem-dicarbonyl species to be formed the isolated Rh sites are indispensable. From Figure 6 we see that even for 1% Rh content (well dispersed sample) the 2100 and 2040 cm⁻¹ bands do not appear, which means that the well-dispersed Rh sites alone do not necessarily produce the gem-dicarbonyl species. The idea that the surface OH groups are deeply involved can explain the situation very well. As the size of Rh crystallites becomes smaller, or the metal particles are better dispersed, the number of edge or corner atoms increases. And these atoms can be more readily approached by the surface OH groups to yield the Rh⁺ sites. Even if a large number of edge and/or corner atoms are present, lack of enough number of OH groups can lead to the failure of formation of dicarbonyl species. This seems to be exactly the case for our observation shown in Figure 6.

We have also observed the effect of temperature on the chemisorption of CO on reduced and oxidized Rh/SiO₂, as shown in Figures 8 and 9. As the temperature goes up, the 2070 cm⁻¹ band tends to shift toward longer wavelength side. The reason for this is that rising temperature accelerates the exchange of CO molecules between the gas phase and the adsorbed phase and also causes more vigorous migration of the adsorbed molecules over the Rh surface, so that the effect of dipolar couplings among the adsorbed CO molecules will be attenuated.

(B) Adsorption of CO on silica-supported Rh with potassium coating. When the Rh surfaces in reduced and oxidized Rh/SiO₂ pellets were coated with potassium film as

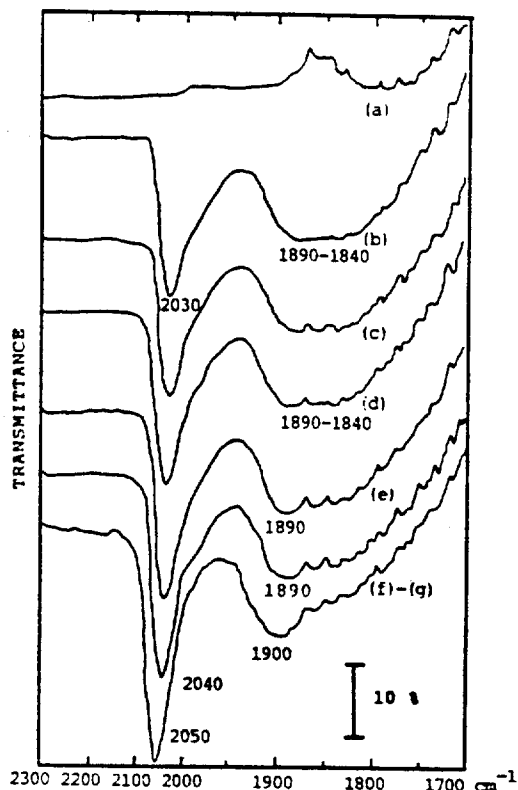


Figure 11. Desorption IR spectra for CO adsorbed on K-promoted 4.0% Rh/SiO₂ sample at 25°C as a function of time. (a) base line, (b) 12 hrs, (c) 2 hrs, (d) 1 hr, (e) 30 min, (f) 5 min, (g) CO pressure of 10 torr.

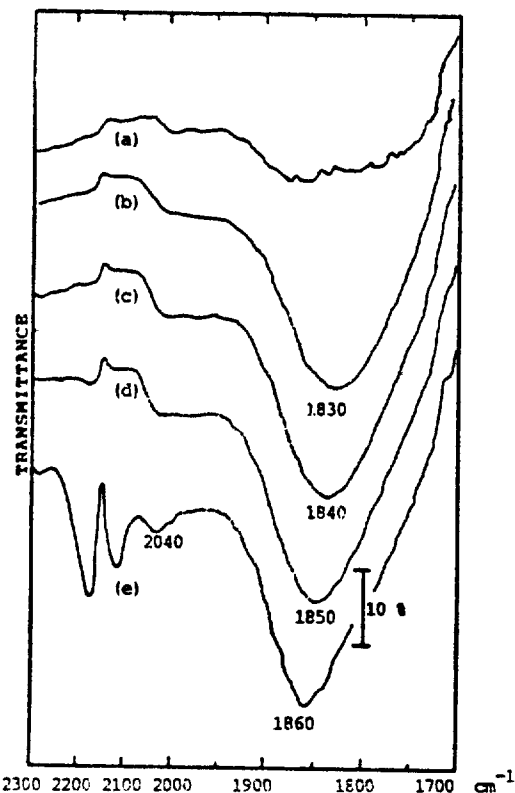


Figure 12. IR spectra for CO adsorbed on K-promoted 4.0% Rh/SiO₂ sample at 25°C as a function of pressure. (a) base line (b) 0.1 torr, (c) 1.0 torr, (d) 10 torr, (e) 50 torr.

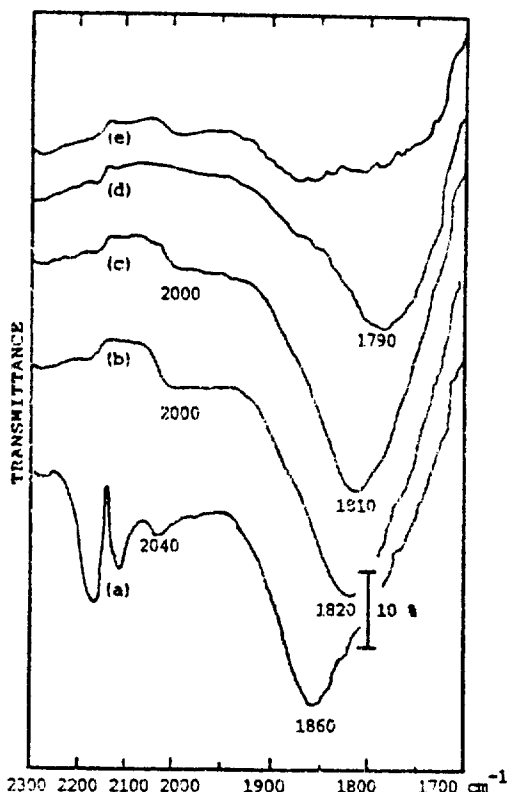


Figure 13. IR spectra for CO adsorbed on K-promoted 4.0% Rh/SiO₂ sample at 25°C as a function of pumping time. (a) CO pressure of 50 torr, (b) 5 min, (c) 30 min, (d) 12 hrs, (e) base line.

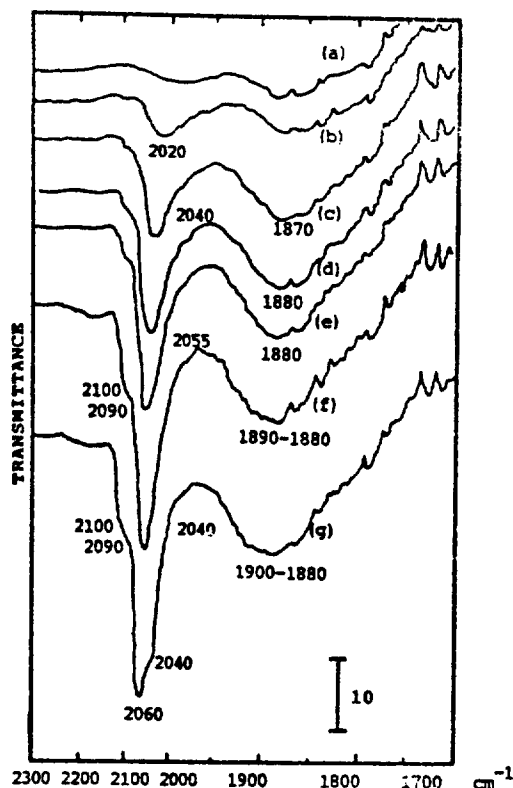


Figure 14. IR spectra for CO adsorbed on K-promoted oxidized 4.0% Rh/SiO₂ sample at 25°C as a function of pressure. (a) base line, (b) 1×10^{-2} torr, (c) 8×10^{-2} torr, (d) 0.5 torr, (e) 1.0 torr, (f) 3.0 torr, (g) 5.0 torr.

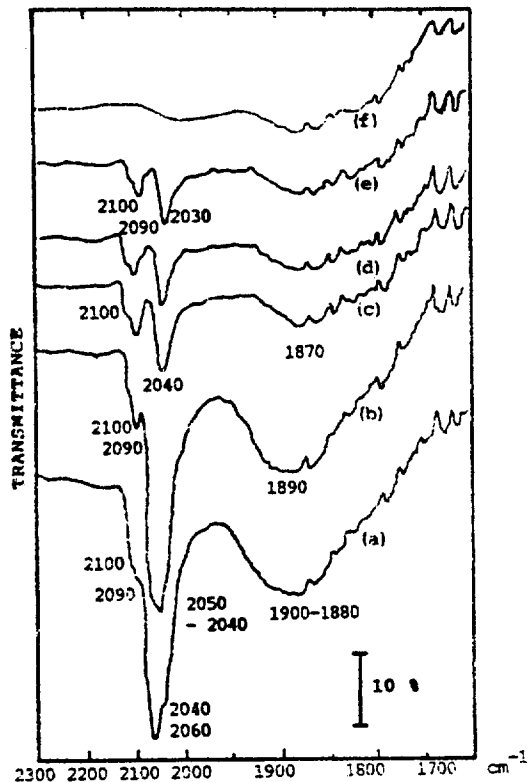


Figure 15. IR spectra for CO adsorbed on K-promoted oxidized 4.0% Rh/SiO₂ sample at 25°C as a function of pumping time. (a) CO pressure of 5 torr, (b) 5 min, (c) 30 min, (d) 1 hr, (e) 2 hrs, (f) base line.

in our previous work for Ru,³⁸ a few drastic changes in the IR band profiles occurred. Shown in Figures 10 and 11 are the adsorption and desorption spectra of CO on K-promoted 4.0% reduced Rh/SiO₂ sample plotted as a function of CO pressure and pumping time, respectively. From these spectra we see that the IR bands for the Rh-CO and Rh₂CO species all undergo the bathochromic shifts—by as much as 20–30 cm⁻¹ for 2070 cm⁻¹ band and 20–90 cm⁻¹ for 1900 cm⁻¹ band compared to the case of no potassium coating. When the amount of potassium coated on the Rh/SiO₂ pellet was increased, the 2070 cm⁻¹ band became barely recognizable, as shown in Figures 12 and 13, leaving the broad 1900 cm⁻¹ band alone to dominate the spectra. As is shown by Figures 14 and 15, in the case of oxidized pellet the 2100 cm⁻¹ band also suffer red shift by as much as 10 cm⁻¹ compared to its counterpart of no potassium coating. We have already pointed out in our previous works^{35,36} that such bathochromic shifts are brought forth by enhancement in the electron-donation capability of metal atoms due to the presence of potassium. The magnitude of this red shift seems to increase for three carbonyl species in the order of Rh(CO)₂ < Rh-CO < Rh₂CO, which indicates that on coating with potassium the species with higher Rh/CO ratio suffers more red shift.

Conclusions

The following important conclusions may be drawn from the present study:

(1) The surface hydroxyl groups seem to play a critical

role in yielding the gem-dicarbonyl species when CO molecules are chemisorbed on Rh/SiO₂ and Rh/Al₂O₃. Reduction temperature seems to be a very important factor that determines the concentration of surface OH groups in supporting materials. In order to obtain more concrete evidences for this idea we are planning to prepare several Rh/SiO₂ samples each of which will be reduced at different temperature under the stream of H₂ and observe the behaviors of OH and CO bands.

(2) It is found that oxidation of the reduced Rh/SiO₂ by exposing to O₂ gas can also give rise to the gem-dicarbonyl species. The mechanism for this oxidation, however, remains to be studied.

(3) On coating the reduced and oxidized Rh/SiO₂ pellets with potassium film all the IR bands for three carbonyl species were found to undergo red shift by about 10 cm⁻¹ for 2100 cm⁻¹, 20–30 cm⁻¹ for 2070 cm⁻¹ band and 20–90 cm⁻¹ for 1900 cm⁻¹ band. The magnitude of this red shift was found to increase with increasing Rh/CO ratio as is expected from the fact that the presence of potassium enhances the metals' ability of back-donating electrons to antibonding π* orbitals of CO molecules. If such back-donation occurs, it will naturally weaken the bond strength in CO which in turn facilitates the reaction of CO with other molecules.

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The C₄ Photocycloadduct Formation of Khellin with Some Olefins

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The photocycloaddition reaction of khellin with several olefins has been investigated. The photocycloadducts are formed regioselectively on furanyl 4',5'-double bond of khellin probably due to the localization of excitation energy on the furanyl 4',5'-double bond in the reactive excited state. The photocycloaddition reaction proceeds through the excited triplet state and the same product was formed when khellin is irradiated with dimethylfumarate or dimethylmaleate indicating the formation of common intermediate. The quantum yields of photocycloadduct formation, fluorescence, and intersystem crossing are very sensitive to proton-donating ability of solvents.

Introduction

The furochromones, khellin and visnagin, two photobiologically active compounds isolated from *Ammi visnaga*¹, closely resemble psoralen in structure and khellin has been used to sensitize λ -phages by 360nm UV light². Recent observations^{3,4} indicate that oral administration of khellin and subsequent exposure to sunlight or long wavelength UV (UVA) light induces repigmentation in vitiligo. Compared with the usual psoralen photochemotherapy recommended for vitiligo, khellin and UVA treatment appears to be equally effective and has the major advantage that khellin produces neither substantial side effects nor phototoxic erythema reactions.

One psoralen molecule intercalated in DNA duplex absorbs photons to form [2+2]-cycloadducts, both monoadducts and biadducts which result in interstrand crosslinks of DNA duplex.^{5,6} The photobiological activities of psoralen have been correlated with this photoreactivity toward pyrimidine bases, especially thymine.^{7,8}

A [2+2]-photocycloadduct on furan ring of khellin has been isolated from the irradiated frozen solution of khellin and thymine and *cis-syn* stereochemistry of cyclobutane ring has been determined.⁹ However, the mechanism of the reaction and action of khellin in vitiligo treatment has not been clearly established.

In this study, photoreaction of khellin with various olefins was investigated to give some insight into the reactive ex-