Infrared Study of Rhodium Clusters Entrapped within Zeolites

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A study of $Rh_6(CO)_{16}$ supported on zeolite has shown that the carbonyl cluster may be decarbonylated by O_2 or *in vacuo* at 373 K without substantial loss of its molecular structure. On alumina $Rh_6(CO)_{16}$ was easily fragmented, zero-valent rhodium being oxidized by O_2 and water to form $Rh(I)$ which upon carbonylation gave $Rh(I)(CO)_2$ complexes. The infrared spectra of zeolite-supported $Rh_6(CO)_{16}$ were compared with those of CO adsorbed on zeolite-supported small rhodium metal particles. The results suggest that zeolite is a suitable carrier to stabilize very small rhodium clusters.

INTRODUCTION

Within the last few years some investigations concerning the catalytic properties of metal cluster compounds have been published. It was observed that $Rh_6(CO)_{16}$ anchored to phosphinated polystyrene catalyzed the reduction of arenes (*1*). Silica-supported $Ru_3(CO)_{12}$ was found to be active in the hydrogenation and hydroisomerization of 1-butene (*2*). Homogeneous oxidation of carbon monoxide by $Rh_6(CO)_{16}$ (*3*) and hydrogenation of CO by $Ir_4(CO)_{12}$ (*4*) have been reported. These examples emphasize the potentially great value of transition metal cluster compounds in catalysis. Heterogenization of these metal clusters was expected to increase the stability of the cluster toward aggregation and also to modify its activity and selectivity. Infrared spectroscopy has been used to investigate the structure of supported metal carbonyl clusters, their interaction with the surface and the nature of the new "clusters" formed by decarbonylation. Infrared studies of alumina-supported $Rh_6(CO)_{16}$ (*5*), silica-supported $Rh_6(CO)_{16}$ (*6*), silica-supported

$Ru_3(CO)_{12}$ (*2*), silica- or alumina-supported $Ir_4(CO)_{12}$ (*7*), and zeolite-supported $Mo(CO)_6$ or $Re_2(CO)_{10}$ (*8*) have already been reported.

The present paper describes an infrared investigation of rhodium carbonyl compounds supported on zeolite. This was undertaken in order to determine the possible structure of zeolite-supported rhodium clusters formed by decarbonylation of $Rh_6(CO)_{16}$. For comparison purposes the infrared study of supported $(Rh(CO)_2Cl)_2$ and of the rhodium carbonyl species resulting from the adsorption of CO on small rhodium metal particles was carried out.

EXPERIMENTAL

Supported-rhodium carbonyl compounds were prepared by sublimation at 80°C *in vacuo* of commercial $Rh_6(CO)_{16}$ and $(Rh(CO)_2Cl)_2$ onto dehydrated carriers. The supports used were NaY, HY zeolites from Linde division and Al_2O_3 from Degussa. They were heated at 500°C *in vacuo* before use. Small rhodium metal particles (average diameter of 10 Å) sup-
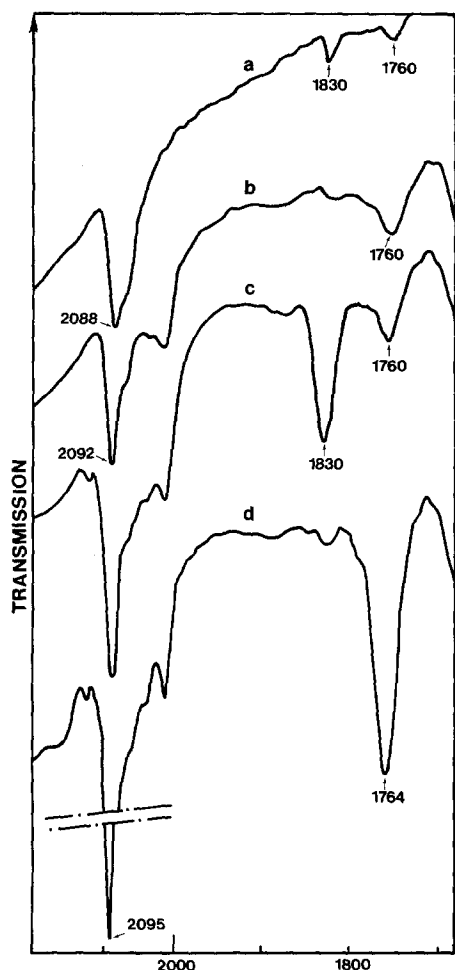
FIG. 1. IR spectra of NaY-supported $Rh_6(CO)_{16}$ sample A, 0.5% Rh): (a) pelletized in argon; (b) pelletized in air and then outgassed at 298 K; (c) after CO adsorption at 298 K; (d) after CO adsorption at 373 K.

ported on zeolite were obtained following the procedure described earlier (9).

For infrared studies the samples were pressed into thin wafers and introduced into a special infrared cell described elsewhere (10). Supported (Rh (CO)$_2$Cl)$_2$ and rhodium metal particles were prepared directly in the infrared cell while supported $Rh_6(CO)_{16}$ thin pellets were obtained by compacting the impregnated powder in argon atmosphere or in air. Electron mi-

crographs were obtained from zeolite thin cut samples.

Two NaY-supported $Rh_6(CO)_{16}$ samples with, respectively, 0.5 (A) and 1.5% (B) rhodium by weight were prepared as well as a sample Al_2O_3-supported $Rh_6(CO)_{16}$ with 1% Rh by weight.

RESULTS AND DISCUSSION

Sample A pelletized in argon exhibited an infrared spectrum showing in the carbonyl stretching region a dominant band at 2088 cm^{-1} with a shoulder at 2076 cm^{-1}, a shallow band at 2016–2020 cm^{-1}, and two weak bands at 1830 and 1760 cm^{-1} (Fig. 1a). It is known that the $Rh_6(CO)_{16}$ cluster consists of an octahedral arrangement of rhodium atoms with two terminal carbonyl groups attached to each rhodium, each of the four remaining CO being attached to three rhodium atoms (11). Its infrared spectrum in KBr presents a strong band at 2073 cm^{-1} associated with a band at 2026 cm^{-1} assigned to the terminal carbonyl groups and a sharp band at 1800 cm^{-1} due to the face-bridging carbonyls (12). The close similarity of the spectrum of Fig. 1a with that of $Rh_6(CO)_{16}$ suggests that $Rh_6(CO)_{16}$ cluster adsorbed on NaY zeolite has maintained its integrity. Our suggestion is further substantiated by the following experiments: $Rh_6(CO)_{16}$ (55 mg) was sublimed at 353 K onto a preliminarily activated NaY sample (1g). After cooling to room temperature no appreciable pressure increase could be detected. This result indicated that CO was not evolved during the adsorption of the cluster. Furthermore upon oxidation at 100°C by oxygen the amount of O$_2$ consumed and CO$_2$ formed corresponded to the stoichiometric amounts expected from the following reaction:
$Rh_6(CO)_{16} + 16 O_2 \rightarrow Rh_6(O_2)_8 + 16 CO_2$.
Dioxygen ligands were easily removed by CO with the subsequent formation of CO$_2$. The formation of rhodium–oxygen adducts during the oxidation of Al_2O_3-supported $Rh_6(CO)_{16}$ has already been suggested by

Smith et al. (5). Thus one may conclude that $Rh_6(CO)_{16}$ was relatively unaffected upon sublimation onto the zeolite in vacuo. The small ν CO shift compared with the values found for $Rh_6(CO)_{16}$ in KBr could be explained by the polarizing effects of the zeolite surface on the C–O bonds. Volumetric measurements had indicated that oxygen reacted with supported $Rh_6(CO)_{16}$ at room temperature to form CO_2 with the subsequent decarbonylation of the rhodium cluster. The decarbonylation process was further investigated by infrared spectroscopy. Sample A prepared in vacuo, was rapidly pelletized in air. The wafer was then placed in the infrared cell and outgassed at 25°C.

Figure 1b shows the resulting infrared spectrum. It is seen that this spectrum is almost identical to that of Fig. 1a except that the band at 1830 cm⁻¹ is absent. Addition of carbon monoxide to the system at room temperature increased the intensity of the bands, and simultaneously a sharp band at 1830 cm⁻¹ appeared (Fig. 1c). This latter sharp band was removed by outgassing without any further change of the infrared spectrum. The CO adsorption–desorption sequence may be repeated several times and reproducibly generated and removed the 1830-cm⁻¹ band. Since the band at 1830 cm⁻¹ disappeared rapidly when zeolite-supported $Rh_6(CO)_{16}$ was exposed to air, it was concluded that bridging carbonyls are more reactive toward oxygen than the terminal carbonyls. Furthermore the sharp band at 1830 cm⁻¹ generated by CO adsorption on the decarbonylated sample was easily removed by outgassing at 293 K which is further proof that bridging carbonyls were weakly bonded. It must also be pointed out that a partial decarbonylation of the rhodium cluster, involving all carbonyl types, had occurred during exposure to air, since in a CO atmosphere the overall spectrum intensity increased.
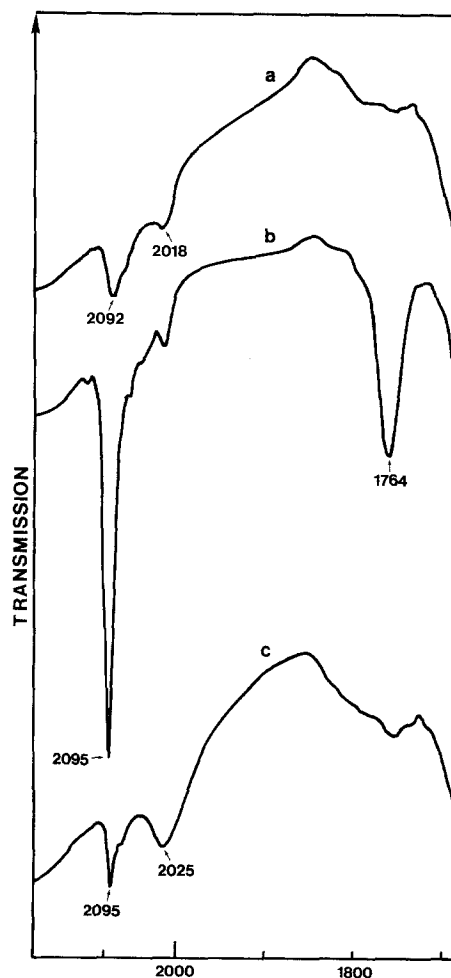
$Rh_6(CO)_{16}$ has been reported to catalyze

FIG. 2. IR spectra of NaY-supported $Rh_6(CO)_{16}$ (sample A): (a) air exposed for 24 hr and then outgassed at 298 K; (b) exposed to CO at 373 K; (c) H_2-treated at 373 K.

at 373 to 473 K the oxidation (3) or hydrogenation (4) of carbon monoxide. Thus it appeared to us important to study by infrared spectroscopy the interaction of CO with NaY-supported $Rh_6(CO)_{16}$ in the conditions of the reaction.

Sample A was pelletized in air and then treated in oxygen at 373 K to remove completely the CO ligands. The sample was then outgassed at 373 K and exposed to CO at the same temperature. The IR spectrum in the CO stretching region is shown in Fig. 1d. Two sharp and intense IR bands
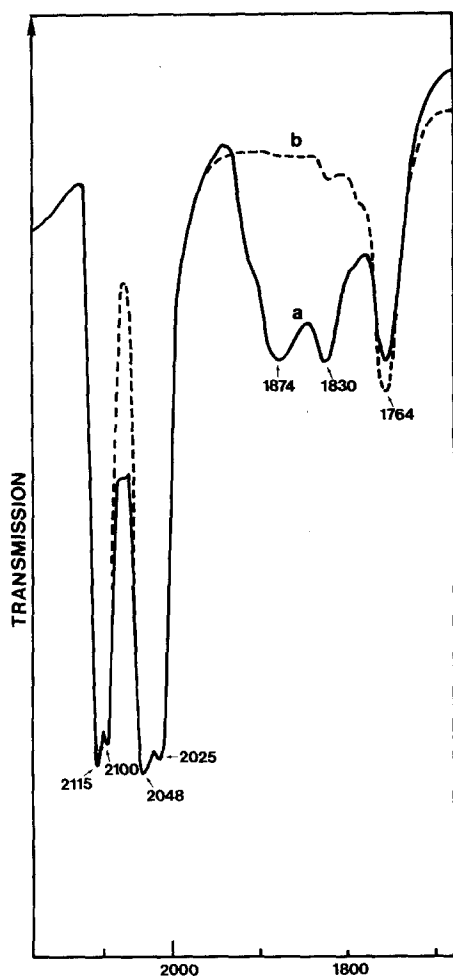
FIG. 3. IR spectra of CO adsorbed on zeolite-supported Rh metal: (a) at 298 K; (b) at 473 K.

at 2095 and 1764 cm^{-1} developed and were present along with two shallow bands at 2045 and 2018 cm^{-1}. Pumping away the excess CO at room temperature did not affect the IR spectrum. In contrast the adsorption of oxygen at 293 K progressively removed the band at 1764 cm^{-1} while the intensity of the band at 2095 cm^{-1} decreased to about two-third its initial value. The complete decarbonylation of the rhodium species was achieved by raising the temperature to 373 K as indicated by the disappearance of the 2095-cm^{-1} IR band. Again the IR spectrum of Fig. 1d was restored when the oxygen-treated sample

was reacted with carbon monoxide at 373 K. These results suggest that the rhodium carbonyl species responsible for the IR bands at 2095 and 1764 cm^{-1}, prepared by sublimation of $Rh_6(CO)_{16}$ on the zeolite surface followed by successive oxygen and carbon monoxide treatment at 373 K, may be decarbonylated and recarbonylated reversibly several times without any appreciable change in its structure and nature, as will be discussed later.

The effect of hydrogen on the rhodium carbonyl species showing the two IR bands at 2095 and 1764 cm^{-1} was also examined. Sample A pelletized in air and then outgassed (Fig. 2a) was subjected to CO adsorption at 373 K. The IR spectrum is shown in Fig. 2b. At 373 K, H_2 removed almost completely the carbonyl stretching bands (Fig. 2c). When the hydrogen-treated sample was again exposed to CO at 373 K the recorded IR spectrum was identical to that shown in Fig. 2b. These results indicated that carbonylation of the hydrogen-treated sample resulted in the formation of the same rhodium carbonyl species as that originating from the oxygen-treated sample contacted with CO at 373 K. Thus it appeared that decarbonylation of the zeolite-supported rhodium carbonyl cluster may be achieved either by oxygen or by hydrogen. The resulting rhodium carbonyl species formed by recarbonylation of the CO-stripped Rh_6 cluster was then unaffected with respect to the number and arrangement of metal atoms by successive removal and addition of CO ligands.

The infrared results shown in Fig. 1a and the volumetric data have indicated clearly that in vacuo $Rh_6(CO)_{16}$ was physically adsorbed on the zeolite without displacement of CO ligands, the structure of $Rh_6(CO)_{16}$ as a whole being relatively unaffected. That metal carbonyl clusters may be adsorbed on oxides without the liberation of CO has already been suggested by Anderson et al. (19). However, it appeared that upon decarbonylation followed by re-

carbonylation the rhodium carbonyl species showed an IR spectrum closely resembling that of solid $Rh_6(CO)_{16}$ but with CO frequencies obviously different. These results might suggest that upon the oxidative decarbonylation of $Rh_6(CO)_{16}$ supported on zeolite the rhodium cluster:

—either had maintained the octahedral arrangement of Rh_6 metal atoms, the νCO shift being interpreted by the effect of the surface crystal field on the C–O bond,

—or had been fragmented into smaller rhodium metal atom units,

—or had aggregated into metal particles,

—or had been fragmented and oxidized into Rh(I).

The two sharp bands at 2095 and 1764 cm^{-1} must obviously be attributed to terminal and bridging CO, respectively. Mononuclear $Rh(CO)_4$ shows two CO stretching modes at 2029 (m) and 2010 (s) cm^{-1} while binuclear $Rh_2(CO)_8$ gives IR bands at 2060, 2040, 1852, and 1830 cm^{-1}. Furthermore these species were relatively unstable and were transformed at room temperature into $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$(13). Consequently the species formed upon CO adsorption at 373 K on zeolite-supported Rh_6 cluster could not be attributed to mono- or dinuclear rhodium carbonyls. As stated above it may be possible that during the decarbonylation process by oxygen or hydrogen, fragmentation of the Rh_6 cluster followed by aggregation into small metal particles may have occurred. For comparison we have extended our carbonylation experiments to zeolite-supported rhodium metal and investigated high-temperature adsorption of CO.

Figure 3 shows the infrared results. At 293 K, CO adsorbed ou 5- to 10-Å-diameter rhodium particles gave two bands, each appearing as a doublet at 2115–2100 and 2048–2025 cm^{-1} of almost equal intensity, assigned to two CO groups adsorbed on a

single rhodium atom (20) along with a series of bands at 1874, 1830, and 1764 cm^{-1}, attributed to bridging CO. A weak band at 2066 cm^{-1} due to CO bonded to a single surface metal atom (9) was also present. Oxygen removed rapidly the IR bands at 2065, 1874, 1830, and 1764 cm^{-1} while the doublet at 2115–2100 and 2048–2025 cm^{-1} remained almost unchanged. The influence of the temperature at which CO was adsorbed on the infrared spectra was examined. On heating in the presence of CO, the high-frequency infrared bands remained unchanged, while there was a drastic change in the intensities of the low-frequency bands ($\nu CO < 2000$ cm^{-1}). At 473 K only the IR bands at 2115–2100, 2048–2025, and 1764 cm^{-1} remained (Fig. 3). Recent studies (9, 14) have suggested that small rhodium metal particles are partially oxidized by CO with the subsequent formation of Rh(I)(CO)$_2$ complexes responsible for the doublet at 2115–2100 and 2048–2025 cm^{-1}. The relative amounts of the linear and bridged CO adsorbed on surface metal atoms (IR bands at 2066 and less than 2000 cm^{-1}) decreased with the size of the particle and with the adsorption temperature. Therefore it is of interest to compare the results for CO adsorbed on decarbonylated zeolite-supported $Rh_6(CO)_{16}$ with those for CO adsorbed on zeolite-supported rhodium metal. With the exception of the band at 1764 cm^{-1}, it is clear that different rhodium carbonyl species were formed on the two systems. The lack of an IR doublet around 2100–2035 cm^{-1} for zeolite-supported Rh_6 cluster excludes the possible oxidation of Rh(0) during the decarbonylation process or during CO adsorption. These findings rule out the formation of small rhodium particles when $Rh_6(CO)_{16}$/NaY was decarbonylated at about 373 K by O$_2$, H$_2$, or under vacuum; such metal particles would have been oxidized by O$_2$ and CO. Moreover, it has been stated (15) that νCO is always lower for M–CO molecular species

TRANSMISSION

2020
2095
b
c   1764
2045 2020
1764
2095

2000   1800
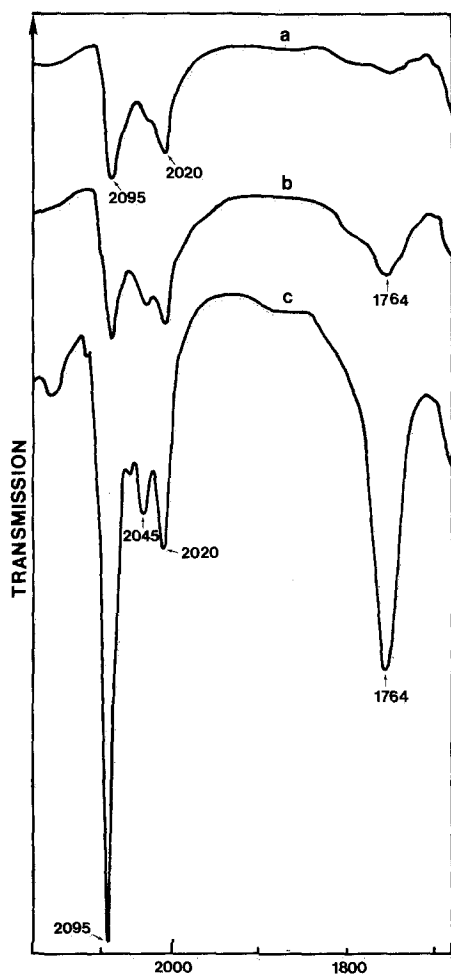
FIG. 4. IR spectra of NaY-supported $Rh_6(CO)_{16}$ (sample B, 1.5% Rh): (a) pelletized in air and then outgassed at 298 K; (b) after CO adsorption at 298 K; (c) after CO adsorption at 398 K.

precisely the structure of the rhodium carbonyl cluster entrapped within the zeolite cavities, we might suggest the formation of $(Rh)_n$ carbonyl clusters, where $n = 6$ to 13, in a hexagonal or cubic close packing arrangement of rhodium atoms. Indeed it has already been shown (13) that the stretching frequency for terminal CO increases with the number of rhodium atoms in the cluster, the reported νCO values for mono-, bi-, tetra-, and hexa-nuclear rhodium carbonyl species were 2010–2020, 2040–2060, 2035–2064, and 2040–2020 cm^{-1} (13), respectively. Thus the rhodium cluster entrapped in the zeolite should contain at least 6 rhodium atoms. The bridging νCO found for this species was lower than those reported for edge or face bridging CO (12). However, a possible interaction of the oxygen atom of bridging CO with an aluminum ion of the zeolite may account for the observed νCO shift. This type of interaction has been suggested to account for the low-frequency carbonyl stretching in iron carbonyl–Lewis acid adducts (16). While this work was in progress an analogous rhodium carbonyl cluster showing two sharp infrared bands at 2095 and 1765 cm^{-1} has been synthesized within the zeolite framework by treating $Rh^{3+}(NH_3)_6$-exchanged Y zeolite at 403 K under a pressure of 80 atm. of $CO:H_2$ mixture. The authors have suggested the possible formation of entrapped $Rh_6(CO)_{16}$ (17).

The infrared results obtained on sample B with a high rhodium loading (1.5 wt% Rh) were slightly different. Figure 4 shows the infrared spectra recorded on a sample pelletized in air and subjected to various treatments. When evacuated at room temperature the wafer showed two absorption bands each appearing as a doublet, at 2110–2095 and 2045–2020 cm^{-1}, of almost equal intensity (Fig. 4a). Contacting the sample with CO increased the intensity of these bands along with the appearance of bands at frequencies lower than 2000 cm^{-1}

than for CO linearly bonded on a single atom of a metal surface. Thus the IR band at 2095 cm^{-1} observed when CO was adsorbed at 373 K on decarbonylated $Rh_6(CO)_6/NaY$ which is at a higher frequency than that of CO adsorbed on rhodium metal (νCO = 2060 cm^{-1}) suggests the formation of polycarbonyl rhodium (0) species. Indeed it has been shown (15) that νCO increases from the monocarbonyl M–CO to the polycarbonyl $M(CO)_x$ species.

Although the infrared data presented so far are not sufficient to describe very

(Fig. 4b). If the sample was heated at 373 K in CO the two sharp bands at 2095 and 1764 cm^{-1}, previously described, developed while the twin band at 2045–2020 cm^{-1} remained almost unchanged (Fig. 4c). The absorption around 2110 cm^{-1} shown in Fig. 4b, is now probably superimposed with the sharp absorption at 2095 cm^{-1}. If the carbonylated sample was exposed to oxygen at room temperature the IR bands at 2095 and 1764 cm^{-1} were removed, leaving distinctly the doublet at 2115–2100 and 2048–25 cm^{-1}. These results reveal that at least two different rhodium carbonyl species are present on the 1.5 wt% Rh zeolite-supported rhodium cluster sample. The sharp bands at 2095 and 1764 cm^{-1} should be ascribed, as above, to the terminal and bridging CO in $Rh_n(CO)_m$ cluster entrapped within the zeolite framework. This carbonyl cluster is easily decarbonylated by oxygen. Infrared studies on rhodium (I) dicarbonyl species entrapped within the zeolite (10) and on silica-supported $(Rh(CO)_2Cl)_2$ (18) have shown two absorptions around 2100 and 2020 cm^{-1}. Furthermore our IR experiments on $(Rh(CO)_2Cl)_2$ adsorbed on NaY zeolite showed two IR bands at 2110–2095 and 2045–25 cm^{-1} attributed also to the antisymmetric and symmetric vibration modes of the terminal carbonyls. The frequencies of the two infrared absorptions recorded on 1.5 wt% Rh, $Rh_6(CO)_{16}/NaY$ sample exposed to air or oxygen appear very close to those reported above. Thus one may conclude that Rh(I) dicarbonyl species have been formed during air oxidation of the zeolite-supported rhodium cluster. Besides these $Rh(I)(CO)_2$ species, our results suggest also that decarbonylated zerovalent rhodium clusters are present which might be carbonylated at 373 K to form $Rh_n(CO)_m$-entrapped clusters.

These studies show that the retention of the cluster integrity is only possible for samples with low rhodium content. In contrast, samples loaded with a larger amount
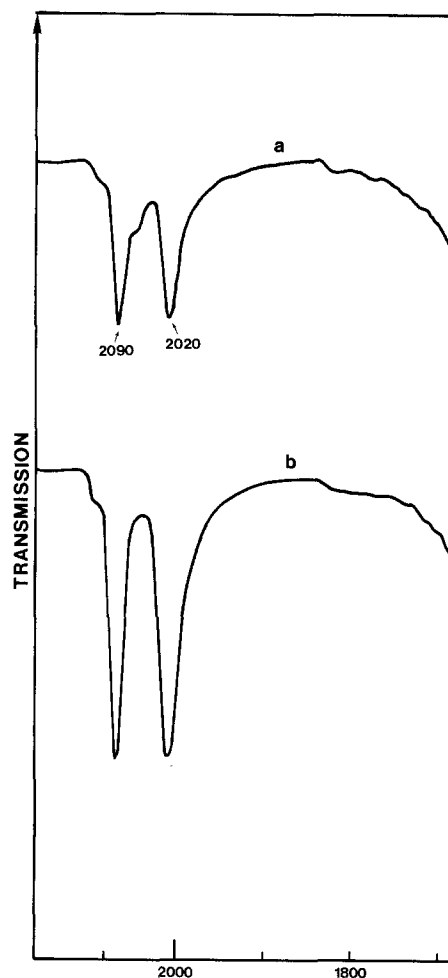

FIG. 5. IR spectra of Al_2O_3-supported $Rh_6(CO)_{16}$ (1% Rh): (a) pelletized in air and evacuated at 298 K; (b) exposed to CO at 298 K or 373 K.

of rhodium clusters form after decarbonylation and recarbonylation $Rh(I)(CO)_2$ species along with $Rh_n(CO)_m$ clusters; hence these findings imply that on the zeolite surface part of $Rh_6(CO)_{16}$ is easily fragmented and oxidized in air. The role of the zeolite in the stabilization of the rhodium cluster can be explained in the following way: $Rh_6(CO)_{16}$ has a size larger than the windows of the zeolite cavities. Thus when $Rh_6(CO)_{16}$ is sublimed on the zeolite the cluster sits on the external surface. By decarbonylation it is obvious that the size of the cluster decreases and

thus might migrate inside the zeolite cavities. This decarbonylated cluster entrapped within the zeolite cavity will be stabilized against fragmentation and oxidation. However, as the Rh cluster loading increases, part of the rhodium cluster might, upon decarbonylation, be fragmented before they migrate within the cavities. These rhodium (0) fragments are then oxidized by air to form Rh(I)OH species, which then could adsorb CO to give supported (Rh(CO)$_2$OH) complexes. The high stabilizing effect of the zeolite matrix on rhodium clusters is further shown by our results, where Al$_2$O$_3$ has been used as carrier. As for zeolite, Rh$_6$(CO)$_{16}$ was sublimed *in vacuo* on Al$_2$O$_3$ dehydrated at 773 K. The sample pelletized in argon showed sharp IR bands at 2083, 2066, 2020 cm^{-1}, and a weak band at 1830 cm^{-1}. This spectrum is very close to that previously reported by Smith *et al.* (5) and ascribed to a fully carbonylated Rh$_6$(CO)$_{16}$ supported on Al$_2$O$_3$. However, the IR spectrum of the sample pelletized in air changed drastically. Two bands of almost equal intensity at 2090 and 2020 cm^{-1} are observed with a shoulder at 2070–2060 cm^{-1}. The low-frequency band of bridging CO has completely disappeared (Fig. 5). CO adsorption at 293 K as well as at 373 K produced exclusively an increase of the band intensities. In contrast with the CO adsorption on zeolite-supported Rh$_6$(CO)$_{16}$ no sharp IR bands at 2095 and 1764 cm^{-1} appeared. The IR results indicate that on alumina Rh$_6$(CO)$_{16}$ is totally converted into Rh(I)(CO)$_2$ species upon air oxidation, Rh(I)(CO)$_2$ being responsible for the doublet at 2090 and 2020 cm^{-1}. The effectiveness of zeolite carrier for the stabilization of rhodium clusters in thus demonstrated. By far the major product formed upon recarbonylation at 373 K was Rh$_n$(CO)$_m$ cluster, the IR results

being insufficient to distinguish clearly between various possible Rh$_n$ clusters, where $n = 6$–13.

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