

An Infrared Study of Alumina- and Silica-Supported Ruthenium Cluster Carbonyls

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An investigation has been performed of the adsorption of $\text{Ru}_3(\text{CO})_{12}$, $\alpha\text{-H}_4\text{Ru}_4(\text{CO})_{12}$, and $\text{Ru}_6\text{C}(\text{CO})_{17}$ on $\gamma\text{-Al}_2\text{O}_3$ and SiO_2 , and of the structures formed upon decomposition of the initially supported clusters. The extent of $\text{Ru}_3(\text{CO})_{12}$ adsorption on $\gamma\text{-Al}_2\text{O}_3$ strongly depends on the temperature at which the support had been dehydroxylated. Infrared spectra of alumina-supported $\text{Ru}_3(\text{CO})_{12}$ suggest that the cluster is adsorbed as a result of interactions between the carbonyl ligands and hydroxyl groups and Lewis acid sites present on the support surface. Similar interactions are proposed for alumina-supported $\alpha\text{-H}_4\text{Ru}_4(\text{CO})_{12}$ and $\text{Ru}_6\text{C}(\text{CO})_{17}$. Decomposition of the supported clusters produces three surface structures, independent of the original cluster composition. The first structure is characterized by bands at 2045–2050 and 1965–1970 cm^{-1} and is represented by $[\text{Ru}(\text{CO})_2\text{X}_2]_n$. The second and third structures are characterized by bands at 2130–2140, 2060–2070, and 1990–2000 cm^{-1} and are represented by $[\text{Ru}(\text{CO})_3\text{X}_2]_n$ and $[\text{Ru}(\text{CO})_4\text{X}_2]_n$, respectively. In each of the structures X represents an oxygen atom of the alumina lattice. The nuclearity of the surface structures, n , cannot be defined from the present studies. Complete decarbonylation of the Ru surface structures induces a stronger Ru–support interaction, which may lead to the entry of Ru ions into the support lattice and the formation of surface aluminates. The aluminates are not stable, however, and the initial three structures can be regained by heating in CO. Upon reduction of the supported clusters in H_2 at temperatures above 400°C, Ru microcrystallites appear to be formed. These particles are not stable and the Ru is redispersed into smaller units if the sample is heated in CO above 200°C. By contrast with $\gamma\text{-Al}_2\text{O}_3$, the interactions of $\text{Ru}_3(\text{CO})_{12}$ with SiO_2 are very weak. As a consequence Ru microcrystallites are formed when the supported cluster is reduced in H_2 at temperatures above 400°C.

INTRODUCTION

The preparation of supported metal catalysts by the adsorption of both mono- and polynuclear (cluster) coordination complexes has been studied by a number of investigators (1–13). One of the goals of these studies has been to achieve high metal dispersion in units of defined nuclearity and composition. While the published

reports have shown that high-dispersion catalysts can be produced by the adsorption of coordination complexes, a determination of the size uniformity of the supported metal units has not yet been possible. Nevertheless, important insights have been provided regarding the interactions between the adsorbed complexes and the support surface.

In the present investigation infrared spectroscopy has been used to elucidate the interactions of $\text{Ru}_3(\text{CO})_{12}$, $\alpha\text{-H}_4\text{Ru}_4(\text{CO})_{12}$, and $\text{Ru}_6\text{C}(\text{CO})_{17}$ with the surfaces of $\gamma\text{-Al}_2\text{O}_3$ and SiO_2 .

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Al_2O_3 and SiO_2 and to identify the surface structures formed upon decomposition of the supported clusters. The results of these studies indicate that very similar structures are produced from all three complexes and that evidence exists for a strong interaction between highly dispersed Ru and $\gamma\text{-Al}_2\text{O}_3$. The interactions are found to be much weaker on SiO_2 and the formation of Ru microcrystallites is observed.

EXPERIMENTAL

Materials

Commercially available $\text{Ru}_3(\text{CO})_{12}$ (Strem Chemical Co.) was used for all of the work. The synthesis of $\alpha\text{-H}_4\text{Ru}_4(\text{CO})_{12}$ was accomplished by treating a THF solution of $\text{Ru}_3(\text{CO})_{12}$ with sodium amalgam (14). The synthesis of $\text{Ru}_6\text{C}(\text{CO})_{17}$ was carried out by thermal decomposition of $\text{Ru}_3(\text{CO})_{12}$ in dibutyl ether solution (15). Each of the clusters was purified in accordance with its method of synthesis and subsequently recrystallized. The pure clusters were identified on the basis of their infrared spectra (15, 16). Deaerated and distilled solvents were used for all of the work.

The cluster complexes were supported on either $\gamma\text{-Al}_2\text{O}_3$ (Kaiser 201) or SiO_2 (Davidson 70). Each support was first heated in vacuum at 100 to 800°C and then calcined in air at 400°C. Adsorption of the cluster was carried out by contacting the support with a saturated pentane solution of the cluster maintained under an inert atmosphere of either argon or helium. Once the support had achieved saturation adsorption, excess cluster was washed off with pentane. The quantity of supported Ru was determined by X-ray fluorescence.

To perform infrared studies a small portion of the supported cluster was pressed into a disk (6–10 mg/cm²) and suspended from a platinum wire within a glass infrared cell. The upper half of the cell contained a winch for raising and lowering the sample and was surrounded by a furnace used to heat the sample. The lower portion of the

cell was fitted with KBr windows to permit entry and exit of the infrared beam. Infrared spectra were recorded using a Fourier transform spectrometer (Digilab FTS-10M) operated with a resolution of 2 cm⁻¹.

When it was desired to avoid atmospheric contact, desorption of the clusters onto the support was carried out within the infrared cell. For this purpose, the lower half of the cell was replaced with a glass chamber into which a solution of the cluster could be transferred. Adsorption was achieved by lowering the support disk into the solution. Following this step the disk was raised into the upper half of the cell and flooded with flowing helium. The lower half of the cell was then changed back to that containing the infrared windows. At this point the cell was evacuated, and the suspended sample was freed of pentane.

RESULTS

Adsorption of $\text{Ru}_3(\text{CO})_{12}$ on $\gamma\text{-Al}_2\text{O}_3$

The interaction of $\text{Ru}_3(\text{CO})_{12}$ with $\gamma\text{-Al}_2\text{O}_3$ is strongly affected by the pretreatment of the support as shown in Fig. 1. Depending upon the temperature of dehydroxylation, the Ru loading may lie between 0.1 and 0.35 mole Ru/m² BET, which corresponds to 0.3 to 1.2 wt% Ru, and maxima in loading are observed at 150 and 600°C. Spectra of $\text{Ru}_3(\text{CO})_{12}$ adsorbed on $\gamma\text{-Al}_2\text{O}_3$ pretreated at specific temperatures are also illustrated in Fig. 1. The absorption bands associated with the cluster supported on alumina dehydroxylated at 100 to 200°C are significantly shifted downscale relative to the bands of the unsupported cluster (see Table 1). For dehydroxylation temperatures of 300°C and above, three bands are observed at 2060–2058, 2026–2023, and 2004–1998 cm⁻¹, which are in relatively good agreement with the absorption bands of the unsupported cluster. It was noted, however, that the spectra of samples prepared using Al_2O_3 dehydroxylated at temperatures below 400°C, changed considerably with time.

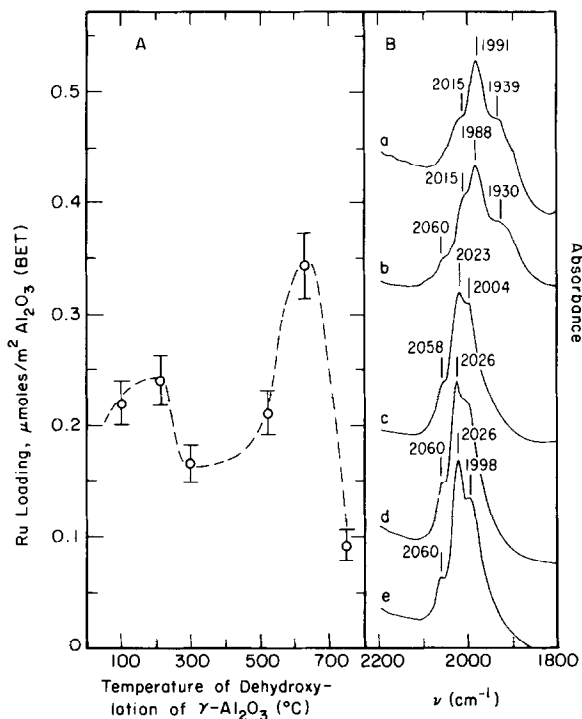


FIG. 1. (A) Dependence of $\text{Ru}_3(\text{CO})_{12}$ adsorption on $\gamma\text{-Al}_2\text{O}_3$ on the temperature of vacuum dehydroxylation. (B) Infrared spectra of $\text{Ru}_3(\text{CO})_{12}$ supported on $\gamma\text{-Al}_2\text{O}_3$ dehydroxylated at: (a) 100°C, (b) 210°C, (c) 300°C, (d) 530°C, and (e) 620°C.

The spectra in Fig. 2 show that the bands of the initially supported cluster diminish in intensity and new bands appear at 2050–2040 cm^{-1} and 1980–1970 cm^{-1} . Upon heating the sample in vacuum, two intense bands are observed at 2047 and 1967 cm^{-1} and a shoulder appears at 1990 cm^{-1} .

To eliminate the infrared bands associated with the solvent, the adsorption of $\text{Ru}_3(\text{CO})_{12}$ was also carried out by sublimation. For this purpose an alumina disk was held over a small amount of $\text{Ru}_3(\text{CO})_{12}$ heated to 50–60°C in a vacuum of 10^{-6} Torr. Figure 3 shows that the spectrum of the sample prepared by sublimation is similar to that prepared by adsorption from pentane solution with the exception that the bands are somewhat broader and occur at higher frequencies in the former case. The sample prepared by sublimation undergoes a change in structure with time, in a manner similar to that observed for samples ad-

sorbed on $\gamma\text{-Al}_2\text{O}_3$ dehydroxylated at temperatures below 400°C. A band appears at 2130 cm^{-1} , the band at 2070–2060 cm^{-1} becomes weaker, and the band at 2000–1990 cm^{-1} becomes stronger. In addition to the bands observed between 2200 and 1900 cm^{-1} weak bands were observed at 1580, 1460, and 1385 cm^{-1} , which intensifies with time.

Examination of the hydroxyl stretching region showed a slight decrease in the intensities of the hydroxyl bands following sublimation of $\text{Ru}_3(\text{CO})_{12}$ onto the support. This change suggests that a reaction may have occurred between the cluster and the hydroxyl groups.

Samples prepared by adsorption of $\text{Ru}_3(\text{CO})_{12}$ from pentane solution on $\gamma\text{-Al}_2\text{O}_3$ dehydroxylated at 600°C were very stable if held in vacuum. A spectrum of a sample taken 3 months after it had been first prepared was identical to that taken

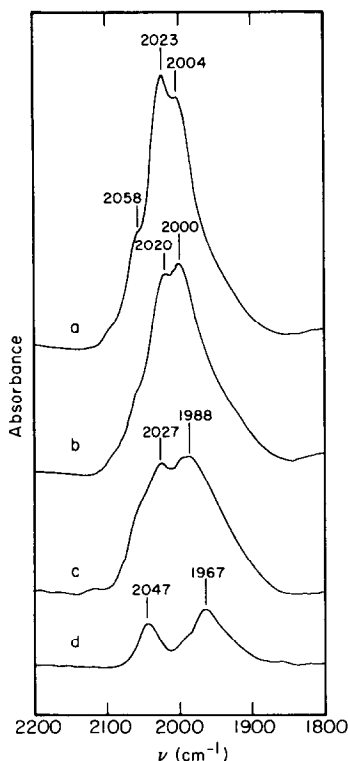


FIG. 2. Infrared spectra of $\text{Ru}_3(\text{CO})_{12}$ supported on $\gamma\text{-Al}_2\text{O}_3$ dehydroxylated at 300°C : (a) following adsorption of $\text{Ru}_3(\text{CO})_{12}$ from pentane solution; (b) after 3 hr in vacuum at 23°C ; (c) after 11 hr in vacuum at 23°C ; (d) after heating to 100°C in vacuum.

initially. The appearance of a band at 2130 cm^{-1} and changes in the bands at 2060 and 2000 cm^{-1} occurred only when the sample was heated in vacuum to $80\text{--}90^\circ\text{C}$. The high stability of $\text{Ru}_3(\text{CO})_{12}$ adsorbed from pentane is apparently due to the fact that adsorbed solvent molecules inhibit the interaction of the cluster with groups present on the support. This might be due either to blockage of sites essential for reaction or to competition with surface active groups.

Thermal Decomposition of Alumina-Supported $\text{Ru}_3(\text{CO})_{12}$

The infrared spectra of the products of thermal decomposition of $\text{Ru}_3(\text{CO})_{12}$ supported on alumina (hereafter designated $\text{Ru}_3/\text{Al}_2\text{O}_3$) are shown in Fig. 4. Heating in vacuum at $80\text{--}90^\circ\text{C}$ results in the disappear-

ance of the band at 2030 cm^{-1} and the appearance of bands at 2130 , 2050 , and 1980 cm^{-1} . Increasing the temperature to $150\text{--}170^\circ\text{C}$ leads to the disappearance of the band at 2130 cm^{-1} , and a narrowing of the band at 2050 cm^{-1} due to the elimination of the shoulder at $2070\text{--}2060\text{ cm}^{-1}$. At the same time, the band at 1980 cm^{-1} resolves into a shoulder at 1995 cm^{-1} and an intense band at 1972 cm^{-1} . Further increases in temperature result in a simultaneous decrease in the intensities of the bands appearing at 2050 , 1995 , and 1972 cm^{-1} . These bands disappear completely when the temperature is raised to $350\text{--}400^\circ\text{C}$. It should

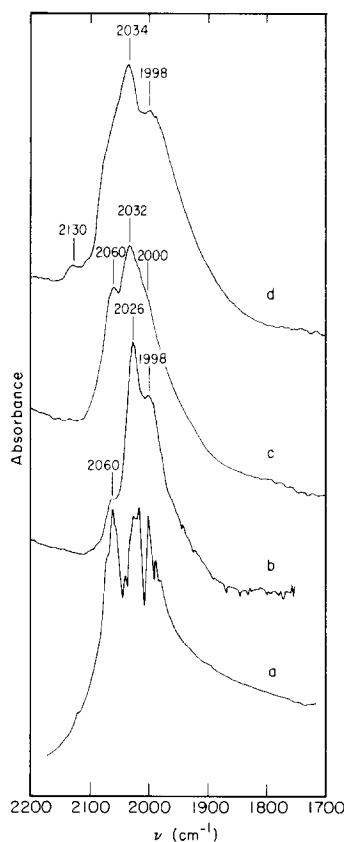


FIG. 3. Infrared spectra of unsupported $\text{Ru}_3(\text{CO})_{12}$ and $\text{Ru}_3(\text{CO})_{12}$ supported on $\gamma\text{-Al}_2\text{O}_3$ dehydroxylated at 650°C : (a) Nujol mull of $\text{Ru}_3(\text{CO})_{12}$; (b) $\text{Ru}_3(\text{CO})_{12}$ supported on $\gamma\text{-Al}_2\text{O}_3$ by adsorption from pentane solution; (c) $\text{Ru}_3(\text{CO})_{12}$ supported on Al_2O_3 by sublimation in vacuum; (d) the same as spectrum c but after 12 hr in vacuum at 23°C .

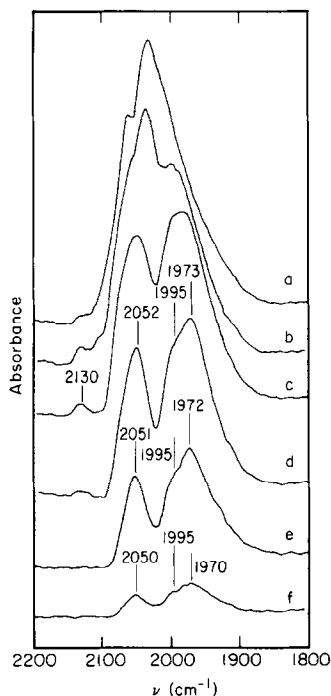


FIG. 4. Infrared spectra of products formed by thermal decomposition of $\text{Ru}_3/\text{Al}_2\text{O}_3$ in vacuum: (a) $\text{Ru}_3(\text{CO})_{12}$ supported by sublimation in vacuum; (b) 23°C for 12 hr; (c) 90°C for 1 hr; (d) 140°C for 1 hr; (e) 220°C for 1 hr; (f) 300°C for 1 hr.

be noted that samples prepared by adsorption of $\text{Ru}_3(\text{CO})_{12}$ from pentane solution and samples prepared by sublimation exhibited identical spectral changes upon heating in vacuum.

Interactions of $\text{Ru}_3/\text{Al}_2\text{O}_3$ with H_2 and CO

As shown in Fig. 5, heating $\text{Ru}_3/\text{Al}_2\text{O}_3$ in H_2 produces spectral features analogous to those observed during thermal decomposition in vacuum. However, the complete disappearance of the carbonyl bands occurs at somewhat lower temperatures, 300 – 350°C . Subsequent adsorption of CO gives rise to the appearance of five bands at 2130 , 2070 , 2053 , 2003 , and 1980 cm^{-1} .

The exposure of $\text{Ru}_3/\text{Al}_2\text{O}_3$ to CO at room temperature has a significant effect on the spectrum, as shown in Fig. 6: the relative absorbances of the bands at 2062 and 2032 cm^{-1} change; a band appears at 2130

cm^{-1} ; and a shoulder occurs at 2090 cm^{-1} , which grows with time. Concurrently, bands appear at 1780 , 1655 , 1460 , and 1233 , characteristic of CO_2 adsorbed on Al_2O_3 (17–19), and at 1600 – 1580 and 1395 – 1380 cm^{-1} , corresponding to formate groups (20). Heating in CO at 90°C leads to a broadening of the bands centered at 2135 and 2070 cm^{-1} , but when the temperature is raised to 180°C all of the bands become narrower. Further increases in the temperature, first to 240°C and then to 310°C , lead to a decrease in the intensity of the bands at 2141 , 2070 , and 2003 cm^{-1} and the appearance of shoulders at 2050 and 1973 cm^{-1} . The latter features are resolved into bands when the spectra are recorded in vacuum.

In the process of heating $\text{Ru}_3/\text{Al}_2\text{O}_3$ in CO , a considerable amount of CO_2 accumulates in the infrared cell. This component

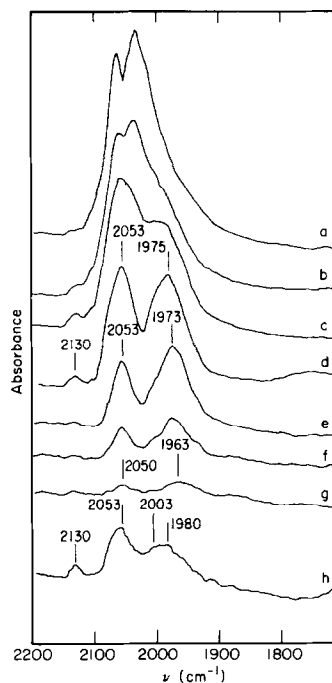


FIG. 5. Infrared spectra of products formed by reduction of $\text{Ru}_3/\text{Al}_2\text{O}_3$ in hydrogen: (a) $\text{Ru}_3(\text{CO})_{12}$ supported by sublimation in vacuum; (b) after heating in 150 Torr H_2 at 23°C for 30 min; (c) 23°C for 12 hr; (d) 90°C for 1 hr; (e) 140°C for 1 hr; (f) 220°C for 1 hr; (g) 300°C for 1 hr; (h) after exposure to 50 Torr of CO at 23°C for 24 hr.

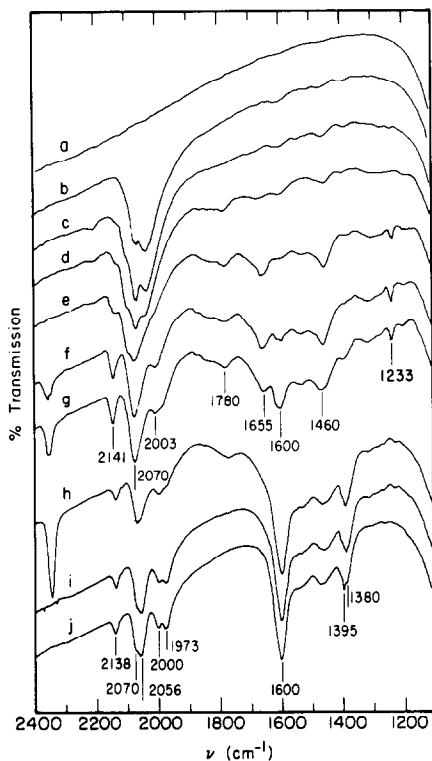


FIG. 6. Infrared spectra of products formed by heating $\text{Ru}_3/\text{Al}_2\text{O}_3$ in CO: (a) $\gamma\text{-Al}_2\text{O}_3$ dehydroxylated at 650°C ; (b) $\text{Ru}_3(\text{CO})_{12}$ supported by sublimation in vacuum; (c) after exposure to 200 Torr CO at 23°C for 30 min; (d) 23°C for 12 hr; (e) 90°C for 1 hr; (f) 180°C for 1 hr; (g) 240°C for 1 hr; (h) 310°C for 1 hr; (i) after evacuation at 70°C for 1 hr; (j) 180°C for 1 hr.

can be detected by the appearance of bands at 2346, 1780, 1655, 1460, and 1233 cm^{-1} .

Adsorption of $\alpha\text{-H}_4\text{Ru}_4(\text{CO})_{12}$ on $\gamma\text{-Al}_2\text{O}_3$

The adsorption of $\alpha\text{-H}_4\text{Ru}_4(\text{CO})_{12}$ was performed from pentane solution using $\gamma\text{-Al}_2\text{O}_3$ dehydroxylated at 650°C . Upon adsorption of the cluster the support turned orange. Analysis of the dried material indicated a Ru content of 1.1 to 1.2 wt%. The infrared spectrum of $\alpha\text{-H}_4\text{Ru}_4(\text{CO})_{12}$ supported on alumina (designated hereafter as $\text{Ru}_4/\text{Al}_2\text{O}_3$) differs significantly from the spectrum of the unsupported cluster (see Table 1). Figure 7 shows that the primary bands occur at 2037, 2018, and 2002 cm^{-1} and that two shoulders are observed at 2080 and 1978 cm^{-1} . With time, the shoulder at

2080 cm^{-1} decreases in intensity and the feature at 1978 cm^{-1} becomes more sharply resolved.

The effects of heating $\text{Ru}_4/\text{Al}_2\text{O}_3$ in vacuum and in CO are also illustrated in Fig. 7. Heating in vacuum at 80°C causes a significant rearrangement of the spectrum and a diminishment in the intensities of the high-frequency bands. A portion of the lost intensity can be regained by exposing the sample to CO, as is shown in spectra d and e. When the sample is heated in vacuum at either 180 or 230°C , two well-defined bands are observed at 2050–2048 and $1970\text{--}1968\text{ cm}^{-1}$ together with shoulders at 2075 and

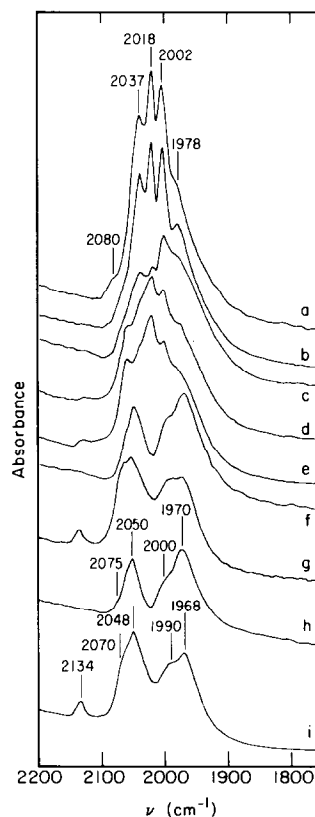


FIG. 7. Infrared spectra of $\alpha\text{-H}_4\text{Ru}_4(\text{CO})_{12}$ supported on $\gamma\text{-Al}_2\text{O}_3$ dehydroxylated at 650°C (a) $\alpha\text{-H}_4\text{Ru}_4(\text{CO})_{12}$ supported by adsorption from pentane solution; (b) after heating in vacuum at 23°C for 12 hr; (c) 80°C for 1 hr; (d) after exposure to 100 Torr of CO at 23°C for 1 hr; (e) 100°C for 1 hr; (f) after evacuation at 170°C for 1 hr; (g) after exposure to 100 Torr of CO at 180°C for 1 hr; (h) after evacuation at 230°C for 1 hr; (i) after exposure to 100 Torr of CO at 230°C for 1 hr.

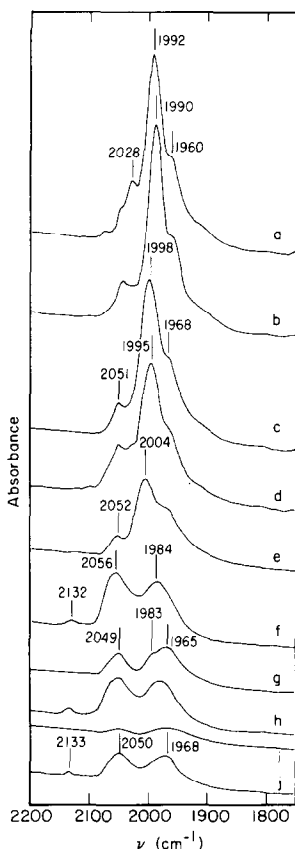


FIG. 8. Infrared spectra of $\text{Ru}_6\text{C}(\text{CO})_{17}$ supported on $\gamma\text{-Al}_2\text{O}_3$ dehydroxylated at 650°C : (a) $\text{Ru}_6\text{C}(\text{CO})_{12}$ supported by adsorption from pentane solution; (b) after heating in vacuum at 23°C for 12 hr; (c) 75°C for 1 hr; (d) after exposure to 100 Torr of CO at 85°C for 1 hr; (e) after evacuation at 165°C for 1 hr; (f) after exposure to 100 Torr of CO at 175°C ; (g) after evacuation at 230°C for 1 hr; (h) after exposure to 100 Torr of CO at 240°C for 1 hr; (i) after evacuation at 309°C ; (j) after exposure to 100 Torr of CO at 23°C for 50 hr.

2000 cm^{-1} . Exposure to CO at these temperatures produces a band at 2134 cm^{-1} and intensifies shoulders appearing at 2075 and 2000 cm^{-1} . The final spectra taken in vacuum and in the presence of CO resemble those for $\text{Ru}_3/\text{Al}_2\text{O}_3$, shown in Figs. 5 and 6.

Adsorption of $\text{Ru}_6\text{C}(\text{CO})_{17}$ on $\gamma\text{-Al}_2\text{O}_3$

The adsorption of $\text{Ru}_6\text{C}(\text{CO})_{17}$ from pentane solution was also carried out using $\gamma\text{-Al}_2\text{O}_3$ dehydroxylated at 650°C . In this instance the support turned dark red following adsorption of the cluster. The

maximum concentration of Ru in these samples was 1.2 to 1.3 wt%. The infrared spectrum of $\text{Ru}_6\text{C}(\text{CO})_{17}$ supported on $\gamma\text{-Al}_2\text{O}_3$ (designated hereafter as $\text{Ru}_6/\text{Al}_2\text{O}_3$) is shown in Fig. 8. The spectrum differs from that of the unsupported cluster (see Table 1) and is characterized by a strong band at 1992 cm^{-1} and weaker features at higher and lower frequencies. Heating the sample to 165°C causes a gradual decrease in the intensity of the carbonyl absorbances. When the sample is heated in CO at 175°C sharp changes occur in the spectrum: a weak band appears at 2132 cm^{-1} and two broad bands appear at 2056 and 1984 cm^{-1} . Upon evacuation at 230°C , the intensity of all three bands is reduced and a new band at 1965 cm^{-1} is resolved from the band at 1983 cm^{-1} . Subsequent heating in CO at 240°C reestablishes spectrum f. If the sample is then heated in vacuum at 309°C , all of the features are significantly attenuated. Finally, reexposure to CO causes a reappearance of bands at 2133 , 2050 , and 1968 cm^{-1} .

Oxidation of Supported Ru Clusters

Figure 9 illustrates the effects of oxidizing $\text{Ru}_3/\text{Al}_2\text{O}_3$ in O_2 at 23°C . Exposure of the sample to 10^{-3} Torr of O_2 results in spectrum a which exhibits a weak band at 2132 cm^{-1} and broad bands at 2050 and 1993 cm^{-1} . When the infrared cell is filled with air, the sample undergoes a progressive change until after 12 hr only two well-defined bands are observed at 2052 and 1973 cm^{-1} . A similar pattern was observed for $\text{Ru}_4/\text{Al}_2\text{O}_3$ and $\text{Ru}_6/\text{Al}_2\text{O}_3$. If oxidation was carried out at 150 to 200°C for 1 hr, the carbonyl band intensities decreased significantly and the two bands shifted to 2064 and 1992 cm^{-1} , as seen in spectrum f. More extended exposure to oxygen at 200°C led to a complete elimination of the carbonyl bands.

Surface Structures Produced by Decomposition of Alumina-Supported Ru Clusters

The results presented in the preceding

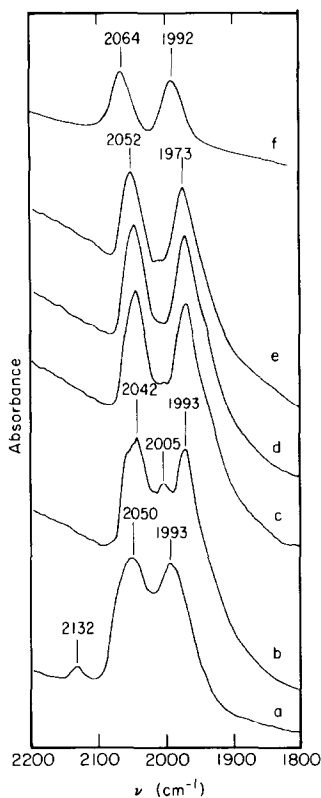


FIG. 9. Infrared spectra of the products of oxidation of $\text{Ru}_3/\text{Al}_2\text{O}_3$ and $\text{Ru}_6/\text{Al}_2\text{O}_3$: (a) $\text{Ru}_3/\text{Al}_2\text{O}_3$ after exposure to 10^{-3} Torr O_2 at 23°C for 10 hr; (b) $\text{Ru}_3/\text{Al}_2\text{O}_3$ after exposure to air at 23°C for 5 min; (c) 20 min; (d) 40 min; (e) 12 hr; (f) $\text{Ru}_6/\text{Al}_2\text{O}_3$ after exposure to a flow containing 20% O_2 in He at 200°C for 1 hr.

sections indicate that irrespective of the initial cluster composition similar structures are obtained on the alumina surface following decomposition of the cluster. These structures are characterized by two sets of bands. Heating in vacuum at 200°C , reduction in H_2 at less than 300°C , or oxidation in air at 23°C all lead to the appearance of bands at 2047 – 2052 and 1965 – 1970 cm^{-1} . These bands are designated as group I. A second group of bands, designated as group II, are observed at 2140 – 2130 , 2080 – 2070 , 2000 – 1990 cm^{-1} in addition to those of group I when the clusters are decomposed in the presence of CO at temperatures below 200°C .

The stability of the structures formed by the decomposition of Ru clusters was in-

vestigated by decarbonylation and subsequent recarbonylation of these species. Figures 10 and 11 show that the reduction of $\text{Ru}_4/\text{Al}_2\text{O}_3$ and $\text{Ru}_6/\text{Al}_2\text{O}_3$, respectively, in H_2 at 400°C leads to a complete elimination of the CO bands. Contacting of the reduced samples with CO at room temperature produces a broad band at 2050 – 2060 cm^{-1} . With time, the intensity of this band grows and broad bands become apparent in the regions of 2060 – 2070 cm^{-1} and 2000 – 1900 cm^{-1} . During this period CO_2 gradually accumulates in the cell as evidenced by the appearance of bands for adsorbed CO_2 . Heating in CO at 200°C leads to an intensification of the bands at 2047 and 1965 cm^{-1} . A comparison of spectrum i in Fig. 7 with spectra d and h in Fig. 10 and spectrum h in Fig. 8 with spectrum f in Fig. 11 shows that the structures produced by decomposition of the initial clusters in CO and

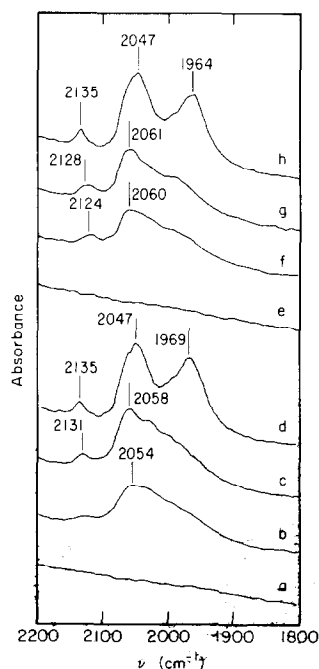


FIG. 10. Infrared spectra of CO adsorbed on $\text{Ru}_4/\text{Al}_2\text{O}_3$ reduced in H_2 : (a) $\text{Ru}_4/\text{Al}_2\text{O}_3$ reduced in H_2 at 400°C for 1 hr; (b) after exposure to 150 Torr CO at 23°C for 10 min; (c) 12 hr; (d) 200°C for 1 hr; (e) after reduction in H_2 at 490°C for 1 hr; (f) after exposure to 150 Torr CO at 23°C for 15 min; (g) 12 hr; (h) 200°C for 1 hr.

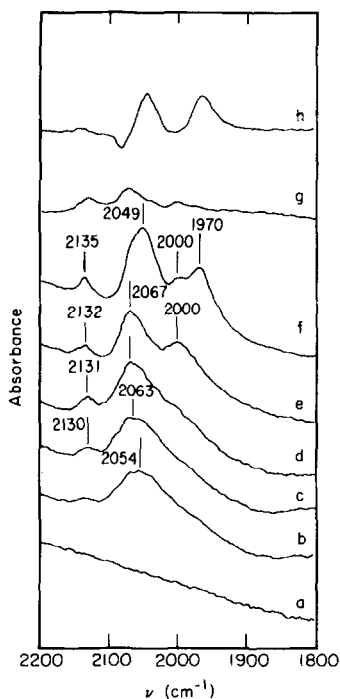


FIG. 11. Infrared spectra of CO adsorbed on $\text{Ru}_6/\text{Al}_2\text{O}_3$ reduced in H_2 : (a) $\text{Ru}_6/\text{Al}_2\text{O}_3$ reduced in H_2 at 400°C for 1 hr; (b) after exposure to 10 Torr CO at 23°C for 5 min; (c) 150 Torr CO, 23°C , 5 min; (d) 12 hr; (e) after evacuation of CO at 23°C for 2 hr; (f) after exposure to 150 Torr of CO at 200°C for 1 hr; (g) spectrum d - spectrum b; (h) spectrum f - spectrum e.

the structures obtained upon recarbonylation are virtually identical.

Spectral sequences similar to those shown in Figs. 10 and 11 were obtained if decarbonylation was achieved by either heating the sample in vacuum at above 350°C or oxidizing it at 200°C . The principal difference was that upon contacting the sample with CO at 20°C , bands characteristic of groups I and II appeared immediately rather than a single band at $2050\text{--}2060\text{ cm}^{-1}$.

Adsorption of $\text{Ru}_3(\text{CO})_{12}$ on SiO_2

In the absence of water and oxygen, $\text{Ru}_3(\text{CO})_{12}$ adsorbs very weakly on SiO_2 and can be removed by repeated washing with pentane. When $\text{Ru}_3(\text{CO})_{12}$ is supported on SiO_2 by vacuum sublimation, the spectrum of the supported cluster is identical to that

for $\text{Ru}_3(\text{CO})_{12}$ in pentane solution, as may be seen in Fig. 12. In addition, the position and intensity of the band at 3748 cm^{-1} , associated with hydroxyl groups on the silica surface, is unaffected by the presence of the cluster. These observations indicate the absence of strong interactions between the cluster and the silica surface. Nevertheless, with time there is a slight decrease observed in the intensity of the carbonyl bands associated with $\text{Ru}_3(\text{CO})_{12}$ and a simultaneous intensification of bands at 2079 , 2110 , and 2130 cm^{-1} . Heating $\text{Ru}_3(\text{CO})_{12}$ supported on SiO_2 and subsequent adsorption of CO at different temperatures lead to the appearance of a large number of bands in the region between 2150 and 1900 cm^{-1} (spectra c-i). After adsorption of CO on a sample reduced in hydrogen at 350°C , bands are observed at 2045 and 2138 cm^{-1} . Heating in CO at 200°C causes an intensification of the band at 2138 cm^{-1} and the shoulder at 2062 cm^{-1} . These bands disappear with an increase in the reduction temperature to 420°C . The final spectrum shows only a single band at 2050 cm^{-1} with a weak shoulder at 2080 cm^{-1} .

DISCUSSION

Interactions of Ru Clusters with $\gamma\text{-Al}_2\text{O}_3$ and SiO_2

The strength of adsorption of a metal carbonyl complex on an oxide support depends upon the nature of the physical and chemical interactions between the complex and the surface of the support. Several authors (1, 6, 8, 11, 12) have suggested that an important mechanism of adsorption is the reaction of the carbonyl ligands with basic hydroxyl groups present on the support surface. Anderson *et al.* (6) have proposed that the observed strong adsorption of Co, Rh, and Ir carbonyl clusters on $\gamma\text{-Al}_2\text{O}_3$ and the correspondingly weaker adsorption of these complexes on SiO_2 can be ascribed to the more nucleophilic character of hydroxyl groups on $\gamma\text{-Al}_2\text{O}_3$. The interaction of carbonyl ligands with Lewis acid sites represents a second

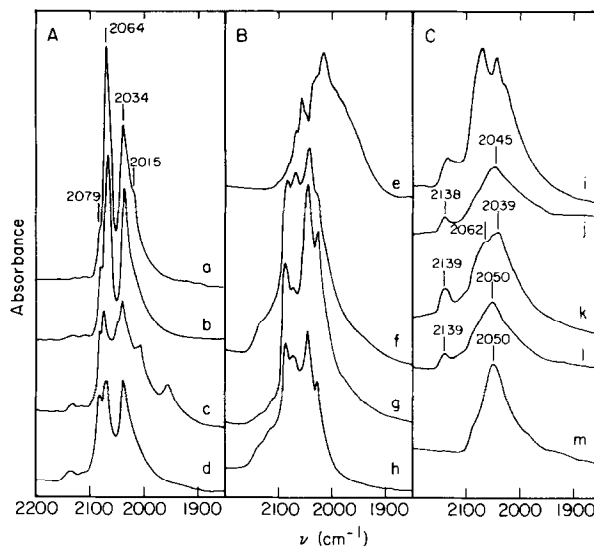
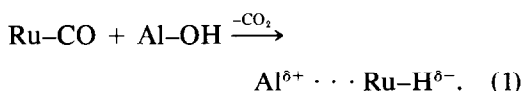


FIG. 12. Infrared spectra of $\text{Ru}_3(\text{CO})_{12}$ supported on SiO_2 : (a) $\text{Ru}_3(\text{CO})_{12}$ supported on SiO_2 by sublimation in vacuum; (b) after evacuation at 23°C for 12 hr; (c) 85°C for 1 hr; (d) after exposure to 100 Torr of CO at 95°C for 1 hr; (e) after evacuation at 200°C for 1 hr; (f) after exposure to 100 Torr of CO at 23°C for 10 min; (g) 200°C for 1 hr; (h) after evacuation at 300°C for 10 min and subsequent exposure to 100 Torr of CO at 23°C ; (i) the same as spectrum h but after 100 hr; (j) after reduction in H_2 at 350°C and subsequent exposure to 100 Torr of CO at 23°C for 1 hr; (k) after reduction in H_2 at 350°C and subsequent exposure to 100 Torr of CO at 200°C for 1 hr; (l) after reduction in H_2 at 380°C and subsequent exposure to 100 Torr of CO at 23°C for 1 hr; (m) after reduction in H_2 at 420°C and subsequent exposure to 100 Torr of CO at 23°C for 1 hr.

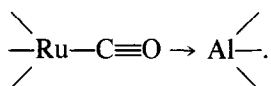
mode of binding (1, 8, 19, 21, 22). In studies of alumina-supported clusters it has been observed that clusters containing bridging carbonyls are more strongly adsorbed than clusters containing only linear carbonyls because bridging carbonyls are stronger Lewis bases (1, 6). Direct evidence for the interaction of carbonyl groups with Lewis acid sites has been observed by infrared spectroscopy for tungsten carbonyl complexes supported on $\eta\text{-Al}_2\text{O}_3$ (8). Attempts to make similar observations for complexes supported on $\gamma\text{-Al}_2\text{O}_3$ have not been successful, presumably because the Lewis acidity of $\gamma\text{-Al}_2\text{O}_3$ is less than that of $\eta\text{-Al}_2\text{O}_3$ (8).

The results presented in Fig. 1 clearly show that both the strength of adsorption of $\text{Ru}_3(\text{CO})_{12}$ and the initial spectrum of the supported cluster depend on the temperature at which the alumina has been dehydroxylated. For dehydroxylation temperatures below 250°C , the frequencies of the carbonyl bands are shifted downscale rela-

tive to those for the unsupported cluster. This is most likely due to the appearance of a negative charge on the cluster as a result of its reaction with nucleophilic hydroxyl groups present on the support surface. The formation of such anionic species is supported by the chemistry of $\text{Ru}_3(\text{CO})_{12}$ in solution. For example, it is known that upon interaction of alkali hydroxides with $\text{Ru}_3(\text{CO})_{12}$ high yields of $[\text{Ru}_4(\text{CO})_{13}]^{2-}$ and $[\text{Ru}_4(\text{CO})_{12}]^{4-}$ are obtained (14). If either $[\text{Mn}(\text{CO})_6]^-$ or $[\pi\text{-CpFe}(\text{CO})_2]^-$ is used as the nucleophile, then following acidification of the solution $\text{H}_2\text{Ru}_6(\text{CO})_{18}$ is produced (23). It is, therefore, possible that in the present instance the reduction of the cluster occurs via reaction (1), a mechanism analogous to that proposed by Basset and co-workers (11, 12) to explain the interactions of $\text{Rh}_6(\text{CO})_{16}$ with the surface of $\gamma\text{-Al}_2\text{O}_3$:



When $\text{Ru}_3(\text{CO})_{12}$ is adsorbed on $\gamma\text{-Al}_2\text{O}_3$, dehydroxylated at temperatures above 300°C , the support takes on an orange-red color, and the spectrum of the supported cluster closely resembles that of the cluster in solution. The primary difference is that the adsorption bands for the supported $\text{Ru}_3(\text{CO})_{12}$ are broader. This might be explained by the formation of surface adducts of the cluster with Lewis acid centers on the support, giving rise to bonds of the type



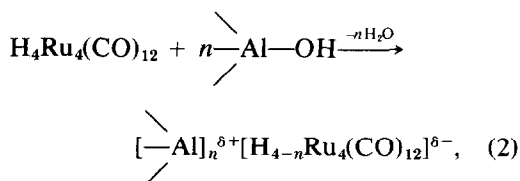
Such an adduct would be similar to that known to exist between $\text{Ru}_3(\text{CO})_{12}$ and AlBr_3 . This product is red in color and its infrared spectrum exhibits a rather strong band at 1535 cm^{-1} , characteristic of the carbonyl groups interacting with AlBr_3 (24). The strength of adducts formed between carbonyl groups and Lewis acids depends a great deal on the strength of the acid. Since the acidity of $\gamma\text{-Al}_2\text{O}_3$ is considerably lower than that of AlBr_3 , this might explain the absence of a band corresponding to the vibrations of a perturbed CO group.

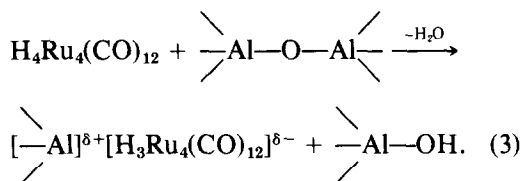
The preceding discussion indicates that the adsorption of $\text{Ru}_3(\text{CO})_{12}$ on $\gamma\text{-Al}_2\text{O}_3$ can involve both the reaction of carbonyl groups with hydroxyl groups present at the support surface and the formation of Lewis acid–Lewis base adducts. The extent to which each of these interactions contributes to the adsorption of the complex depends on the degree of dehydroxylation of the support (25–27). Parera (26) has shown that the dehydroxylation of KA-201 $\gamma\text{-Al}_2\text{O}_3$ begins at temperatures above 200°C . Initially, water is eliminated by the condensation of adjacent hydroxyl groups. This produces an O^{2-} ion in the surface and an exposed aluminum ion in a lower layer, which are Lewis basic and acid sites, respectively. These defect sites are only slightly strained and as a result the acidity or basicity associated with them is low. As the temperature increases above 300°C ,

more highly strained defects are produced because the condensing hydroxyl groups are no longer immediately adjacent. Correspondingly, the acidity of the Lewis acid sites increases. Maximum acidity for KA-201 $\gamma\text{-Al}_2\text{O}_3$ is reached at about 600°C . Above this temperature the acidity rapidly declines due migration of OH or O^{2-} groups which causes a reduction in the strain energy.

Inspection of Fig. 1 shows that the strength of $\text{Ru}_3(\text{CO})_{12}$ adsorption with increasing dehydroxylation temperature reflects the chemistry occurring at the support surface. Thus, the decline in adsorption for temperatures between 200 and 300°C can be attributed to the loss of basic hydroxyl groups, capable of reaction with the CO ligands of the complex. The trend in adsorption strength observed above 400°C directly parallels the trend in the strength of Lewis acidity reported for KA-201 alumina (26). This suggests that for dehydroxylation temperatures above 400°C , the primary mode of adsorption is the formation of acid–base adducts between the aluminum defect sites in the support and the CO ligands of the complex.

The infrared spectra of alumina-supported $\alpha\text{-H}_4\text{Ru}_4(\text{CO})_{12}$ and $\text{Ru}_6(\text{CO})_{17}$ also show a significant downscale shift of the carbonyl stretching frequencies relative to those observed for the unsupported clusters. For these complexes the shift is observed even when the alumina has been dehydroxylated at 650°C . Here again, the shift in carbonyl frequencies can be ascribed to the formation of anionic species. The charging of $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ might occur via reaction (1) or by interaction of the slightly acidic hydrogen atoms with either hydroxyl or Lewis base sites present on the alumina surface, reactions (2) and (3):





The first of these reactions has been proposed to explain the adsorption of $\text{HFeCo}_3(\text{CO})_{12}$ on γ -alumina (28). The conversion of $\text{Ru}_6\text{C}(\text{CO})_{17}$ to an anionic form might proceed through loss of a carbonyl group via reaction (1) and the subsequent reaction of the hydrido species with a hydroxyl group to produce the anion $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$. The formation of such an anion would not be surprising since its iron analog is known (29).

Table 1 lists the frequencies for carbonyl groups in various ruthenium compounds. The number and position of the bands are determined by the local symmetry and the

charge on the Ru atoms. The compounds $\text{Ru}_2(\text{CO})_6\text{X}_4$ and $\text{Ru}_3(\text{CO})_{12}\text{X}_6$ (in which X is a halogen atom) have 3 or 4 CO groups per Ru atom, respectively, and are characterized by three major absorption bands located at 2143–2133, 2075–2065, and 2015–2005 cm^{-1} . Upon lowering the electronegativity of the halogen ligands, the electron density at the Ru atoms increases. This leads to an enhancement of d_{π} -electron back-donation into the π^* orbitals of the CO groups, as a result of which the vibrational frequency of these groups shifts downscale. When the halogen groups are substituted by mercapto groups, a further downscale shift is observed. The maximum shift is observed upon introduction of nucleophilic ligands such as phosphines. Complexes containing 2 CO groups per Ru atom exhibit two major carbonyl bands, which are usually attributed to the symmet-

TABLE 1
Vibrational Frequencies for Carbonyl Ligands in Ru Complexes

Compound	ν_{CO} (cm^{-1})	References
$\text{Ru}(\text{CO})_4\text{Cl}_2$	2182 w, 2132 s, 2113 ms, 2080 s	(30)
$\text{Ru}(\text{CO})_4\text{Br}_2$	2178 w, 2124 s, 2110 m, 2078 m	(30)
$\text{Ru}(\text{CO})_4\text{I}_2$	2160 w, 2105 s, 2095 m, 2060 m	(31)
$\text{Ru}_2(\text{CO})_6\text{Cl}_4$	2143 s, 2075 s, 2015 m	(30, 32)
$\text{Ru}_2(\text{CO})_6\text{Br}_4$	2137 s, 2073 s, 2010 w	(30, 32)
$\text{Ru}_2(\text{CO})_6\text{I}_4$	2128 s, 2069 s, 2012 w	(32)
$\text{Ru}_3(\text{CO})_{12}\text{Cl}_6$	2138 m, 2068 s, 2007 m	(32)
$\text{Ru}_3(\text{CO})_{12}\text{Br}_6$	2133 m, 2065 s, b, 2009 w	(32)
$[\text{Ru}(\text{CO})_3\text{SPh}]_2$	2105 w, 2080 m, sh, 2060 s, b, 2018 m, b	(32)
$[\text{Ru}(\text{CO})_3\text{S-}i\text{-nBu}]_2$	2110 w, 2080 m, 2056 s, 2010 s, 2000 s	(32)
$[\text{Ru}(\text{CO})_3\text{PPh}_3]_3$	1982 s, 1969 s, 1935 s	(33)
$[\text{Ru}(\text{CO})_3\text{P-}i\text{-nBu}_3]_3$	2035 w, 1964 s, 1930 m	(33)
$[\text{Ru}(\text{CO})_3\text{P-(OPh)}_3]_3$	2001 s, 1985 s, 1970 m, 1945 sh	(33)
$[\text{Ru}(\text{CO})_2\text{Cl}_2]_n$	2066 m, 1988 m	(32)
$[\text{Ru}(\text{CO})_2\text{Br}_2]_n$	2059 s, 1990 m	(32)
$[\text{Ru}(\text{CO})_2\text{I}_2]_n$	2053 s, 1995 s	(32, 34)
$[\text{Ru}(\text{CO})_2(\text{SPh})_2]_n$	2105 w, 2042 s, 1985 s, 1945 sh	(32)
$[\text{Ru}(\text{CO})_2(\text{S-}i\text{-nBu})_2]_n$	2100 w, 2022 s, 1962 s, 1930 w	(32)
$[\text{Ru}(\text{CO})_2(\text{S-Et})_2]_n$	2096 w, 2023 s, 1963 s, 1932 w	(32)
$[\text{Ru}(\text{CO})_2(\text{SMe})_2]_n$	2102 w, 2022 s, 1962 s, 1930 sh	(32)
$\text{Ru}_5(\text{CO})_{12}$	2062 s, b, 2055 s, 2017 s, b, 1998 vs, 1987 vs, 1982 s, 1978 s	(35)
$\text{H}_2\text{Ru}_4(\text{CO})_{13}$	2083 s, 2068 s, 2056 s, 2033 m, 2026 s, 2008 w, 1880 w	(14)
$\alpha\text{-H}_4\text{Ru}_4(\text{CO})_{12}$	2084 m, 2067 s, 2063 s, 2033 s, 2026 s, 2013 m	(14)
$\text{Ru}_5\text{C}(\text{CO})_{15}$	2066 vs, 2034 s, 2016 m	(24)
$\text{Ru}_6\text{C}(\text{CO})_{17}$	2064 s, 2049 s, 2007 w, 1993 w, 1958 w, 1845 w	(15)
$\text{H}_2\text{Ru}_6(\text{CO})_{18}$	2060 s, 2054 s, 2008 m	(29)

ric and antisymmetric vibrations of the $\text{Ru}(\text{CO})_2$ fragment with *cis* orientation of the CO groups. The positions of these bands are also determined by the nature of the ligands binding the Ru atoms together.

In the present studies of alumina-supported clusters five principal bands were identified which could be divided into two groups, designated I and II. The bands associated with group I appeared at 2045–2050 and 1965–1970 cm^{-1} . Comparison with Table 1 suggests that these bands can be assigned to a surface structure of the type $[\text{Ru}(\text{CO})_2\text{X}_2]_n$, identified as structure 1, in which the electrophilic ligands are likely to be the oxygen atoms of the support. By similar reasoning, the bands at 2130–2140, 2060–2070, and 1990–2000 cm^{-1} , associated with group II, can be assigned to surface structures of the form $[\text{Ru}(\text{CO})_3\text{X}_2]_n$ and $[\text{Ru}(\text{CO})_4\text{X}_2]_n$, identified as structures 2 and 3, respectively. The proposed assignments suggest that the Ru atoms present in the structures stabilized on the alumina surface interact closely with oxygen atoms in the support lattice, and

that each Ru atom is capable of adsorbing 2 or more molecules of CO. The value of n in the proposed structures cannot be specified. If the clusters are molecularly dispersed, then n might be expected to lie between 1 and the number of Ru atoms present in the original cluster (i.e., 3, 4, or 6). On the other hand, if cluster aggregates are formed, then the value of n could become much higher. Unfortunately, it is not possible on the basis of the present data to establish the extent to which cluster aggregation occurs.

The interrelationships between the proposed surface structures are summarized in Fig. 13. Structure 1, $[\text{Ru}(\text{CO})_2\text{X}_2]_n$, can be obtained from the initially supported clusters by oxidation in air, thermal decomposition in vacuum, or reduction in H_2 at temperatures below 300°C. The stability of the initial cluster to thermal decomposition appears to increase with increasing number of Ru atoms present in the cluster, as evidenced by the increase in the temperature at which decomposition begins. The carbon atom present in the center of $\text{Ru}_6\text{C}(\text{CO})_{17}$

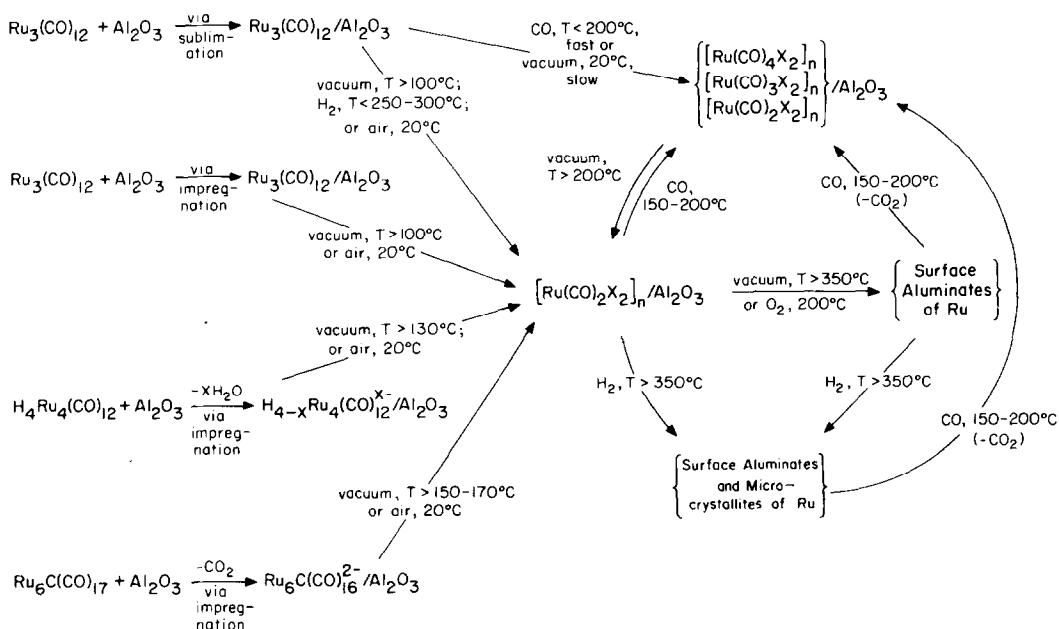


FIG. 13. Interrelationships between structures formed by decomposition of alumina-supported Ru clusters.

may further aid in stabilizing this particular complex. Structures 2 and 3, $[\text{Ru}(\text{CO})_3\text{X}_2]_n$ and $[\text{Ru}(\text{CO})_4\text{X}_2]_n$, are formed when structure 1 is heated in the presence of CO. This transformation is reversible and structure 1 can be regenerated by heating the more fully carbonylated structures in vacuum above 200°C.

Upon complete removal of the CO ligands by either thermolysis or oxidation, the Ru atoms in the surface structure become coordinatively unsaturated and very likely interact more strongly with the oxygen present in the alumina lattice. It is anticipated that when this occurs Ru–Ru bonds are broken and individual Ru atoms or ions may penetrate into the lattice to form surface aluminates. Evidence for such interactions has been observed with other transition metals supported on alumina (37–39). The CO_2 observed when CO is contacted with the fully decarbonylated material may arise from a partial removal of lattice oxygen atoms which strongly interact with the Ru atoms. Alternatively, CO_2 might be formed via reaction of CO with surface hydroxyl groups.

The pattern of $\text{Ru}_3(\text{CO})_{12}$ decarbonylation observed here is consistent with that noted by Courdurier *et al.* (5). In that study $\text{Ru}_3(\text{CO})_{12}$ was introduced into the cages of HY zeolites (Linde SK 40) by means of vapor transport. The supported cluster was then heated in a closed vessel and the amount of CO liberated was determined volumetrically. Heating to 200°C released 3 CO molecules per original molecule of the complex, producing a residual structure with the stoichiometry of $\text{Ru}_3(\text{CO})_9$. Since the evolved CO was not evacuated, comparison with the present work is best made by examining the results obtained when alumina-supported $\text{Ru}_3(\text{CO})_{12}$ is heated in the presence of CO. As seen in Fig. 13, heating at temperatures of 150 to 200°C leads to structures containing on the average 3 CO ligands per Ru atom. Courdurier *et al.* (5) found further that the initially produced residue was stable up to 300°C.

At higher temperatures further decarbonylation occurred and complete decarbonylation was achieved at 450°C. In the present work complete decarbonylation was achieved at temperatures above 350°C. The lower value may be due to the fact that the evolved CO was continually removed by evacuation.

Evidence for the formation of Ru crystallites comes from an examination of CO adsorption following the reduction of either structure 1 or the surface aluminate formed by decarbonylation of structure 1. The spectra presented in Figs. 10 and 11 indicate that upon initial contact of the reduced material with CO, a band is observed at 2050–2060 cm^{-1} . Both the position and the shape of this band are identical to that reported by Dalla Betta (40) for CO adsorption on alumina-supported Ru crystallites prepared by reduction of RuCl_3 . The stability of the crystallites obtained from the Ru clusters does not appear to be very high since heating in CO results in the reappearance of bands characteristic of structures 1, 2, and 3. The formation of CO_2 during recarbonylation again suggests either the removal of oxygen from the alumina lattice or the reaction with surface hydroxyl groups.

Assignment of CO Bands for Silica-Supported $\text{Ru}_3(\text{CO})_{12}$

The studies of $\text{Ru}_3(\text{CO})_{12}$ supported on SiO_2 show that the adsorption of CO following H_2 reduction at 350°C results in the appearance of bands at 2139, 2063, and 2039 cm^{-1} . When the reduction temperature is increased to 420°C, the two high-frequency bands become practically undetectable. These observations are in good agreement with those obtained in previous investigations of CO adsorption on silica-supported Ru (41–45). Table 2 summarizes the assignments proposed for CO vibrations reported in those studies, and provides a basis for interpreting the bands observed in Fig. 12. Accordingly, the band observed at 2039–2050 cm^{-1} can be as-

TABLE 2

Assignment of Infrared Bands for CO Adsorbed on Silica-Supported Ru

Catalyst	ν_{CO} (cm^{-1})	Assignment	Reference
0.8% Ru/SiO ₂	2151, 2083	Not given	(41)
1.5% Ru/SiO ₂	2143, 2083	Not given	(41)
13% Ru/SiO ₂	2010–1990, 1970–1870	Ru–CO, Ru ₂ –CO	(42)
0.1% Ru/SiO ₂	Two bands between 2010 and 1900	Ru–(CO) ₂ , Ru–(CO) ₃	(43)
6.0% Ru/SiO ₂	2030 2080	Ru–CO Ru–CO perturbed by a nearby O atom	(44)
	2135	CO adsorbed on a RuO surface site	
4.0% Ru/SiO ₂	2140 2130, 2070	Ru–CO Ru ^{δ+} –(CO) ₂	(45)

signed to CO adsorbed on reduced Ru particles, while the bands at 2139 and 2062 cm^{-1} can be assigned to CO adsorbed on partially oxidized Ru particles. The strong similarity between the present results and those reported for low-dispersion silica-supported Ru suggests that Ru₃(CO)₁₂ forms microcrystallites of Ru during reduction at high temperature. Such a process would not be unexpected since the interactions between SiO₂ and Ru₃(CO)₁₂ are very weak. It should be noted that the band attributed to CO adsorbed on reduced Ru occurs at a somewhat higher frequency (2039–2050 cm^{-1}) than that reported in previous studies (2030–2040 cm^{-1}). This might be explained by a partial transfer of charge from the Ru atoms to the support, a process which would be more likely to occur in the present work because of the low metal loadings used ($\leq 1\%$). This interpretation is further supported by the TEM observations of Prestridge *et al.* (46) which show that Ru microcrystallites smaller than 40 Å form two-dimensional rafts on the surface of SiO₂, and the EXAFS studies of Lytle *et al.* (47) which show evidence for Ru–O bonds formed between Ru and oxygen atoms present at the silica surface.

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