Surface Characterization of the Ru$_3$(CO)$_{12}$/Al$_2$O$_3$ System

I. Interaction with the Hydroxylated Surface

A. ZECCHINA AND E. GUGLIELMINOTTI

Istituto di Chimica Fisica, Università di Torino, Corso M. d'Azeglio 48, 10125 Torino, Italy

AND

A. BOSSI AND M. CAMIA

Istituto "G. Donegani" S.p.A., Via G. Fauser 4, 28100 Novara, Italy

Ru$_3$(CO)$_{12}$ adsorbed on hydrated Al$_2$O$_3$ is transformed under the action of atomspheric oxygen into an anchored mononuclear dicarbonylic species (Ru$_B$). In the absence of O$_2$, OH groups of the surface act as oxidizing agents at $T > 373$ K leading to a variety of oxidized species, whose structure and relative concentration depend upon the treatment conditions. *In vacuo* and in the temperature range 673–423 K, dicarbonylic Ru$_A$, Ru$_B$, and Ru$_C$ anchored species characterized by well-defined ir bands at 2138–2075, 2072–2005, 2054–1977 cm^{-1}, respectively, are prevalently formed. At higher temperature the decarbonylation is complete but the ruthenium is prevalently in an oxidized form. Decarbonylation in a flow of hydrogen favours the formation of Ru$_C$ species at intermediate temperatures and of metallic ruthenium at the highest temperatures.

INTRODUCTION

The interaction of carbonylic complexes with oxidic surfaces is a topic of growing interest (*1–14*). The studies have revealed that complex reactions take place over hydroxyl-covered surfaces leading to new surface carbonylic complexes and to oxidized low-valency ions. Due to the extensive interaction with the surface ligands, the integrity of the carbonylic compounds is often lost with formation of a variety of interaction products. If metal-cluster carbonyls are used, the important question arises as to whether the metallic skeleton resists the surface attack or whether fragmentation occurs leading to products of different nuclearity. In order to investigate this point the trimetallic Ru$_3$(CO)$_{12}$ cluster has been chosen because of its simple structure and well-known chemical behaviour. Moreover the interaction of Ru$_3$(CO)$_{12}$ with Al$_2$O$_3$ has been already studied by Kuznetsov *et al.* (*14*), so providing a good starting point for a further and more detailed investigation.

Following the previous considerations, a full spectroscopic investigation has been carried out on the Ru$_3$(CO)$_{12}$/Al$_2$O$_3$ system in order to define the following matters:

(i) the nature of the interaction with the surface OH groups, with particular attention to the rupture or the preservation of the metallic skeleton;

(ii) the effect of the progressive vacuum removal of the CO ligands on the dispersion and valence state of the decarbonylated ruthenium;

(iii) the effect of the initial carbonyl concentration on the aggregation state of the partly or totally decarbonylated ruthenium. The results are reported and discussed in this paper.

EXPERIMENTAL

Sample preparation. The support was Degussa P110 (Alon C), a nonporous alumina (SA 100 m^2/g), and was usually

225

used without any pretreatment. $Ru_3(CO)_{12}$ was dissolved in chloroform or n-heptane and then mixed with the appropriate amount of alumina to form a slurry. The slurry was freed from the solvent by room-temperature (RT) outgassing. As an ageing process takes place, three different samples were studied, namely, P—used immediately after the solvent evaporation; Q—after 2 hr standing in air; R—after 1-month storage in air. In one case samples were prepared by impregnating RT and 423 K outgassed Alon C with $Ru_3(CO)_{12}$ in an argon stream in order to avoid contact with the oxygen of the atmosphere (sample E). Two Ru concentrations have been used (0.33 and 1.57 wt%).

Infrared spectra. Disks for ir spectra were obtained by pressing 20 mg/cm^2 powder under 100 kg/cm^2 pressure. The disks were then inserted in a silica cell equipped with NaCl windows connected to a vacuum manifold where decarbonylation *in vacuo* $(10^{-4}-10^{-5}$ Torr) at any given temperature was carried out. A double-beam Beckman IR 12 spectrometer and a Perkin–Elmer 180 spectrometer have been used.

Reflectance spectra. For reflectance spectra the powder was inserted into a silica cell equipped with a Suprasil window where the thermal treatments *in vacuo* were carried out. The spectrometer was a Beckman DK2 equipped with the reflectance accessory.

Mass spectra. Mass spectra have been obtained with a Quadrupole Residual Gas Analyzer Centronic model Q 806 permanently connected to the vacuum manifold where the decarbonylations were carried out.

Volumetric measurements. The volumetric measurements have been carried out in a conventional apparatus equipped with capacitive manometers (MKS Baratron with 310 BHS head gauge and digital readout Unit 170 M-27B).

RESULTS

Figure 1a shows the effect on the ir spec-

tra of a 0.33% sample of ageing the powder under normal atmosphere. With respect to the $Ru_3(CO)_{12}$ spectrum in heptane solution (spectrum S) it can be noted that:

(i) the spectrum of sample P shows the characteristic peaks of the unreacted complex (*15*) only slightly broadened by the interaction with the surface;

(ii) the spectrum of sample R shows only a pair of bands (hereafter denoted the B pair) at 2072 and 2005 cm^{-1}, with an intensity ratio ~1, due to new surface species;

(iii) the spectrum of sample Q shows an intermediate situation which can be interpreted as the superposition of bands of the unreacted $Ru_3(CO)_{12}$ and of the new species.

Exposure to air for several months leads to the total disappearance of the B pair, leaving a very weak component at 1890 cm^{-1}. A schematic description of the behaviour of the bands is shown in the inset to Fig. 1a. On R samples strong bands at 1570 and 1465 cm^{-1} are detected (the spectra are not reported for the sake of brevity) which on the contrary are very weak on freshly prepared P samples and are absent on pure Al_2O_3.

Figure 1b shows the ageing effect on the reflectance spectra in the visible and near infrared. With respect to the $Ru_3(CO)_{12}$ spectrum in n-heptane solution (spectrum S) the relevant features are:

(i) spectrum P (freshly prepared sample) shows a band at 25,000 cm^{-1} which is characteristic of the unreacted $Ru_3(CO)_{12}$ (*15*) physically adsorbed on the surface;

(ii) in spectra Q and R, the band of the unreacted complex decreases in intensity while a new, very broad, band of lower intensity centered at 20,000 cm^{-1} becomes clearly visible (for a schematic description see inset).

This band at 20,000 cm^{-1} is probably due to transformation products of the original carbonylic complex. These products are not necessarily the same as those responsible for the bands of the B pair (Fig. 1a) as ir-inactive, completely decarbonylated, spe-
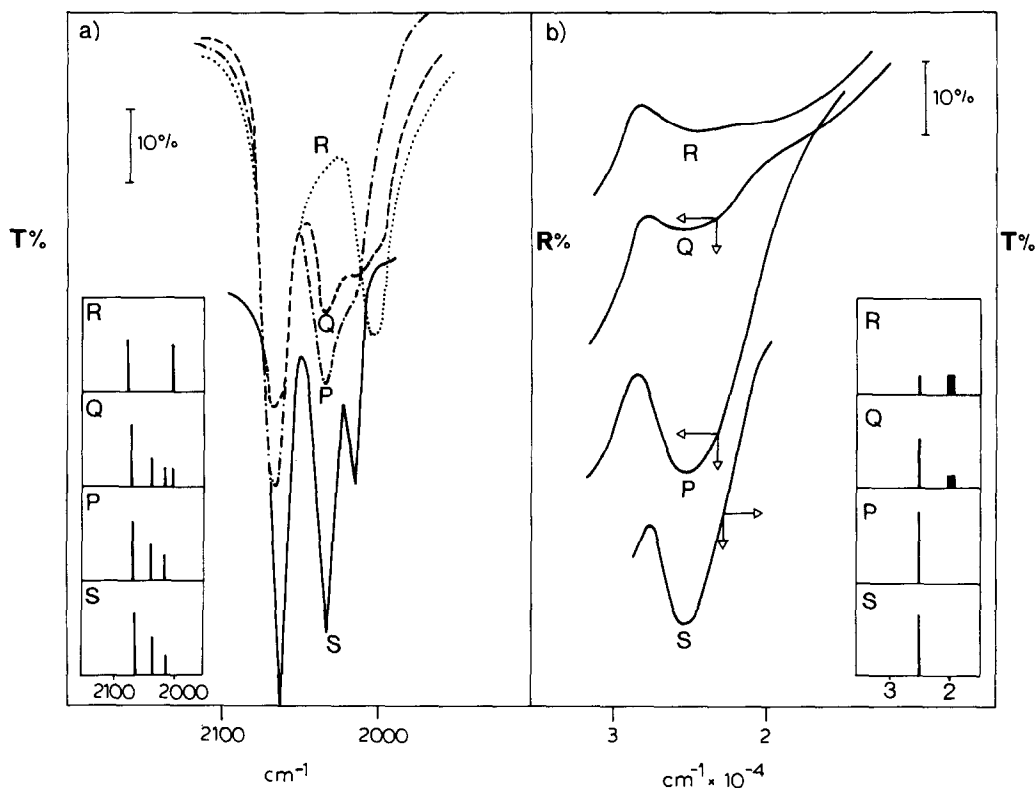
FIG. 1. (a) Infrared spectra of $Ru_3(CO)_{12}$ (0.33%) on Al_2O_3. Spectrum S: $Ru_3(CO)_{12}$ in heptane; spectrum P: $Ru_3(CO)_{12}$ on Al_2O_3 immediately after impregnation; spectrum Q: $Ru_3(CO)_{12}$ on Al_2O_3 after 2 hr; spectrum R: after 1 month. (b) Reflectance spectra of $Ru_3(CO)_{12}$ (0.33%) on Al_2O_3. Spectrum S: $Ru_3(CO)_{12}$ in heptane; spectrum P: $Ru_3(CO)_{12}$ on Al_2O_3 immediately after impregnation; spectrum Q: after 2 hr; spectrum R: after 1 month.

cies can contribute. In all spectra a sharp edge is observed at ~30,000–32,000 cm^{-1} which is apparently unaffected by the chemical transformations occurring on the sample. It must be mentioned at this point that if the impregnation is carried out in total absence of oxygen (sample E) the typical spectrum of the $Ru_3(CO)_{12}$ complex (both in the ir and in the visible) is maintained much longer so showing that, once deposited on the hydroxylated Al_2O_3 surface, the carbonyl becomes oxygen sensitive.

In Fig. 2a is illustrated the effect on the ir spectrum of a P (0.33%) sample of decarbonylation *in vacuo* at increasing temperatures, while Fig. 2b shows the effect of subsequent exposure to CO at the beam temperature (~323 K). It can be seen that by decarbonylation at the beam temperature (side a: dashed curve) the overall intensity of the bands decreases and a new spectrum arises, characterized by bands at 2100 (very weak), 2065 (medium), and 2030 cm^{-1} (medium) and shoulders at 2090, 2005, and 2000 cm^{-1}. Moreover, the relative intensity of the 2065- and 2030-cm^{-1} bands is influenced by the evacuation time. By subsequent exposure to CO at the same temperature (side b: dashed curve) a spectrum similar in shape (but with lower intensity) to that of the $Ru_3(CO)_{12}$ is restored. This shows that by degassing at the beam temperature the adsorbed carbonyl loses CO ligands; however, the metallic skeleton of a large fraction of the original clusters is
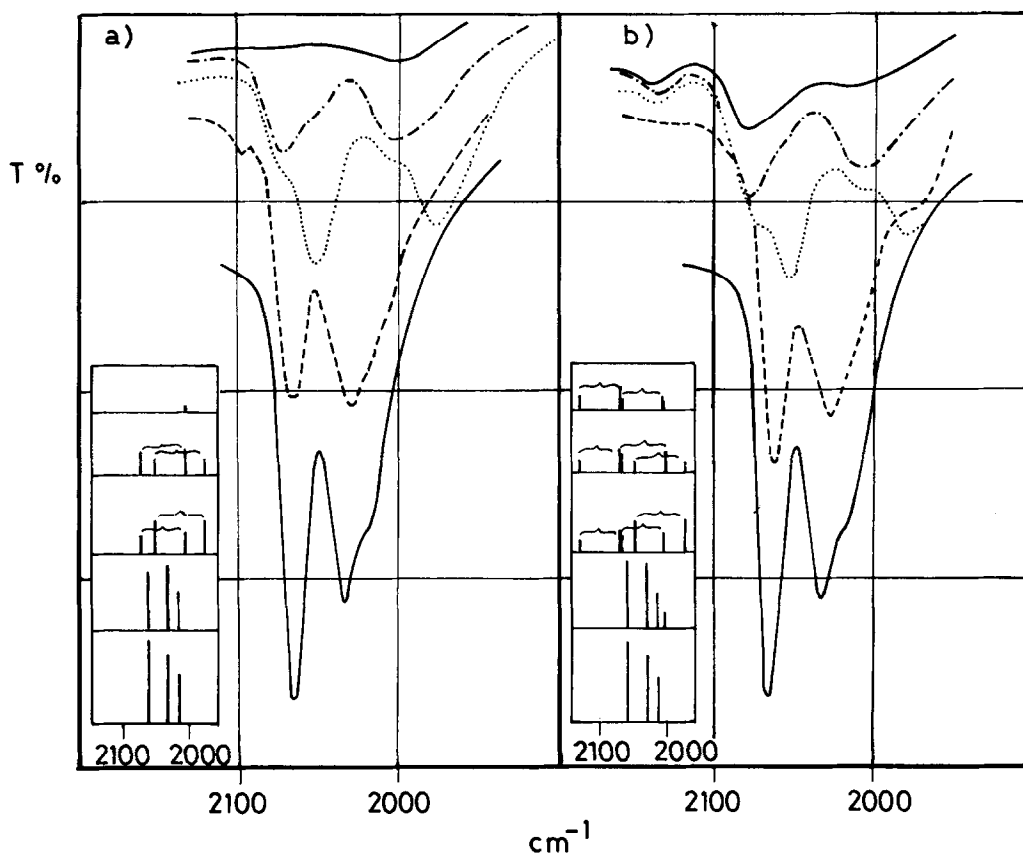
FIG. 2. (a) —— (lower): $Ru_3(CO)_{12}$ (0.33%) on Al_2O_3 immediately after impregnation; ———: after decarbonylation *in vacuo* at 323 K; · · ·: at 423 K; —·—: at 523 K; —— (upper): at 623 K. (b) —— (lower): $Ru_3(CO)_{12}$ (0.33%) on Al_2O_3 immediately after impregnation; all other spectra obtained after exposure to CO (P = 5.3 kPa) of the samples outgassed as illustrated in side a.

probably preserved, as is suggested by the immediate formation of the $Ru_3(CO)_{12}$ bands upon subsequent CO contact. Decarbonylation at 423 K *in vacuo* is described by the dotted curve of Fig. 2a. A new pair of bands at 2054 and 1977 cm^{-1} (hereafter denoted the C pair) with intensity ratio ~1 is now observed, together with two shoulders at ~2072 and ~2005 cm^{-1}. The overall intensity, however, is largely decreased so suggesting that further loss of CO ligands has occurred. Subsequent exposure to CO at the beam temperature (~323 K) leads to the dotted curve of side b. The band pair at 2054 and 1977 cm^{-1} is apparently unchanged, while a new weak band is formed at 2138 cm^{-1} together with an intensity en-

hancement at ~2075 cm^{-1} and in the range 2040–2000 cm^{-1}. The absence, after CO adsorption, of the characteristic bands of the $Ru_3(CO)_{12}$ cluster, shows that, after decarbonylation at 423 K, the original cluster is not appreciably restored. The spectrum after CO adsorption is much weaker than that of the freshly impregnated sample: this fact suggests that even on the CO-covered sample, the CO/Ru ratio is far from 4. Decarbonylation at 523 K is illustrated by the dot-dashed curve (side a). The band pair C has disappeared (only two weak shoulders are now visible in the same position) while a weak band pair at 2072 and 2005 cm^{-1} (B pair: intensity ratio ~1) represents the only clearly detectable feature of the spectrum.

In contrast with the lower decarbonylation temperatures (where evolution of CO was mainly observed) a mass spectrometric analysis of the evolved gases showed that H_2, CO_2, and H_2O are the main products. Exposure to CO at this stage (side b) (5.3 kPa) generates a band at 2138 cm^{-1}; an intensity enhancement at 2075 cm^{-1} is also observed. Also in this case the $Ru_3(CO)_{12}$ bands are not appreciably reformed. Finally, heating *in vacuo* at 623 K (side a: bold solid curve) causes the disappearance of all bands (with the exception of a very weak residual component at 2000 cm^{-1}, i.e., full decarbonylation). As in the previous stage, H_2, H_2O, and CO_2 are evolved from the surface. Exposure to CO after this stage gives rise to a pair of bands (A pair: intensity ratio ~2.5) at 2138 and 2075 cm^{-1} and a very weak and complex absorption at lower frequencies with shoulders at ~2054 and ~1977 cm^{-1}. No band due to $Ru_3(CO)_{12}$ is detected.

Volumetric measurements of the CO adsorbed after this decarbonylation stage showed that only ~0.9 CO molecule per Ru atom is present at the surface, in agreement with the low intensity of the spectrum. The A pair is mainly observed in the presence of a CO pressure: this is due to its weak resistance to outgassing at 323 K (the experiments are not described for the sake of brevity). We anticipate that A, B, and C band pairs are associated with three well-defined surface carbonylic species: evidence for this will be found in the following paragraphs and in the succeeding papers (Parts II and III). On this basis the spectra observed before and after exposure to CO on P (0.33%) samples decarbonylated at T > 423 K can be interpreted as mainly due to the contemporary presence of the three complexes in variable proportions (see insets). A-type complexes are the predominant species on CO-covered samples activated at 623 K; B complexes are abundant on samples treated at 523 K, while C complexes are found only on samples outgassed at 423 K. A, B, and C species show no

appreciable tendency to add CO at RT to form the original cluster. As to the samples outgassed at the beam temperature, more than one surface species is likely to be present because the spectrum is very complex and the relative intensity of some of the components changes with the outgassing time. However, these species add CO to form the original cluster. Finally, the very weak component at ~2000 cm^{-1} observed on samples outgassed at 623 K is due to very resistant CO ligands.

In Fig. 3a the effect of the decarbonylation procedure on the reflectance spectra of a P (0.33%) sample is illustrated, while in Fig. 3b the spectra obtained after subsequent exposure to CO are reported. With respect to the freshly impregnated sample (side a: upper solid curve) the sample outgassed at 323 K (side a: dashed curve) (which is the temperature of the sample under the ir beam) shows a strong decrement of the unreacted $Ru_3(CO)_{12}$ bands at 25,000 cm^{-1} and the presence of two new absorptions at 31,000 and 20,000 cm^{-1}, together with a shoulder at 16,000 cm^{-1}. Exposure to CO (side b: dashed curve) causes a strong increase of the 25,000-cm^{-1} band
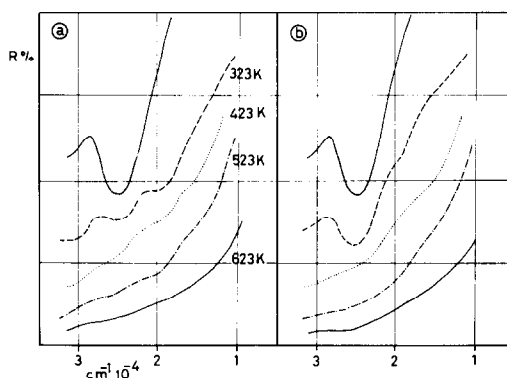

FIG. 3. (a) ——— (upper): Reflectance spectra of $Ru_3(CO)_{12}$ (0.33%) on Al_2O_3 immediately after impregnation; ———: after decarbonylation *in vacuo* at 323 K; ···: at 423 K; – · –: at 523 K; ——— (lower): 623 K. (b) ——— (upper): Reflectance spectrum of $Ru_3(CO)_{12}$ (0.33%) on Al_2O_3 immediately after impregnation; all other spectra obtained after successive exposure to CO (P = 5.3 kPa) of the samples outgassed as in side a.

and a contemporary decrement of the 20,000- and 31,000-cm⁻¹ bands, while the shoulder at 16,000 cm⁻¹ is unaffected. The 31,000- and 20,000-cm⁻¹ bands are thus associated with those species which can add CO to regenerate the original cluster, already observed in ir measurements. Decarbonylation at 423 K causes the nearly complete disappearance of the 25,000-cm⁻¹ band (side a: dotted curve) so showing that a very small amount of unreacted $Ru_3(CO)_{12}$ is left on the surface. Also the bands at 31,000 and 20,000 cm⁻¹ are less prominent, i.e., the species formed in the initial decarbonylation step at 323 K tend to disappear under more severe conditions. The products of this further decarbonylation probably absorb in the whole range

16,000–31,000 cm⁻¹. Exposure to CO (side b: dotted curve) causes a small increment of the 25,000-cm⁻¹ absorption and the disappearance of the residual 20,000-cm⁻¹ band, while the other parts of the spectrum are practically unaffected. These facts indicate that if a very moderate carbonylation still occurs leading to small amounts of the original cluster, the broad absorption extending from 33,000 to 16,000 cm⁻¹ is largely unaffected, so showing that it is associated with irreversibly decarbonylated species. The effects of the decarbonylation at 523 and 623 K and of the subsequent exposure to CO are illustrated in Fig. 3 by the dot-dashed and lower solid curves, respectively. It can be seen that upon decarbonylation at 523–623 K, the spectrum be-
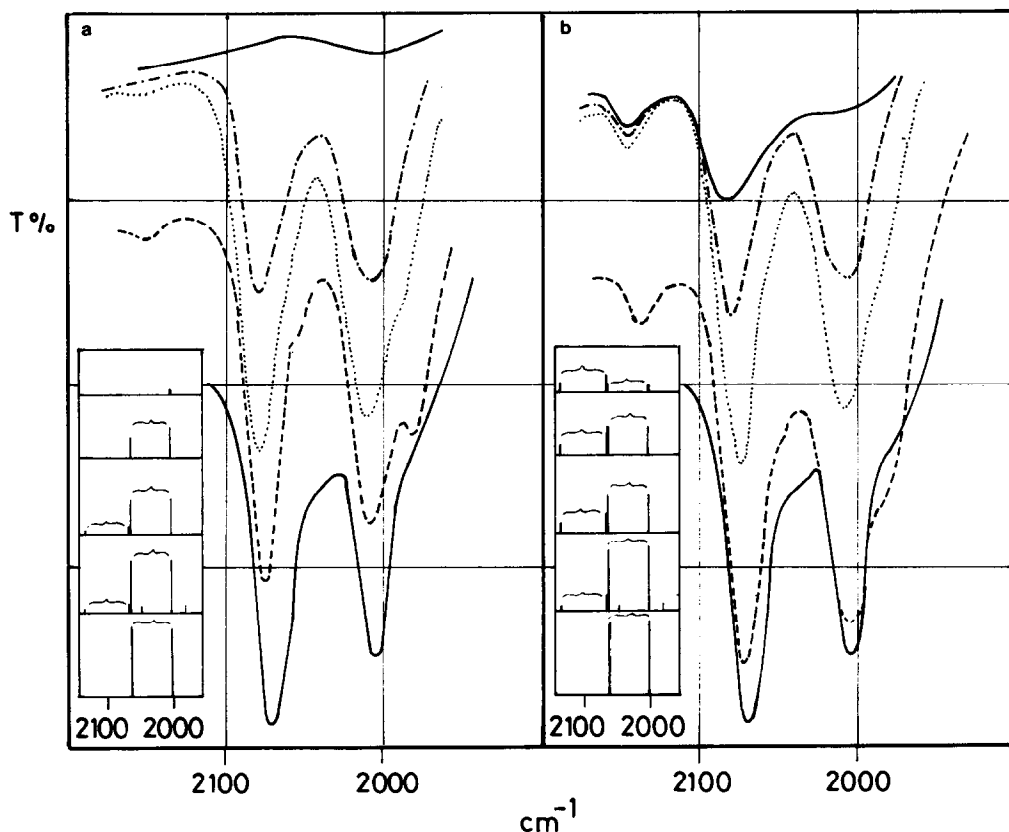

FIG. 4. (a) —— (lower): $Ru_3(CO)_{12}$ (0.33%) on Al_2O_3 after 1 month; ———: after decarbonylation *in vacuo* at 323 K: ····: at 423 K: –·–: at 523 K: —— (upper): at 623 K. (b) —— (lower): $Ru_3(CO)_{12}$ (0.33%) on Al_2O_3 after 1 month; all other spectra taken after exposure to CO ($P = 5.3$ kPa) of the samples decarbonylated as in side a.

comes broader and extends to even lower frequencies. Broad features at ~31,000, 27,000, 20,000, 19,000, and 16,000 cm^{-1} are probably still present on the 523 K outgassed sample: however, because they are not destroyed by exposure to CO, they are also due to irreversibly decarbonylated species. Exposure to CO causes an increment of the optical density in the whole range 33,000–16,000 cm^{-1} with a maximum increase at ~25,000 cm^{-1}.

In Fig. 4 are reported the ir spectra concerning the decarbonylation–carbonylation sequence for an R sample, i.e., a sample which contains mainly B species. The effect of outgassing at the beam temperature is shown by the dashed curve (side a): no significant change of the B pair intensity is observed; however, the weak bands at 2138, 2054, and 1977 cm^{-1} indicate the presence of A species and small amounts of C species. Exposure to CO (side b) only causes an intensity enhancement of the A pair. By outgassing at 423 K the A and C pairs disappear (side a: dotted curve) while by subsequent CO adsorption only A pairs are formed with greater intensity. Decarbonylation at 523 K is described by the dot-dashed curve (side a) where only B species are observed, although with lower intensity. After subsequent CO adsorption (side b) only A species are formed, while B species are left practically unaltered. Finally the effect of the nearly total decarbonylation at 623 K is illustrated by the upper solid curve (side a): as in the previous case (P samples) only a weak residue at 2000 cm^{-1} is observed. CO adsorption (side b) causes the usual formation of the A species as a major product; however, due to the presence of a weak and broad adsorption at lower frequencies the presence of small amounts of the others is not excluded. Also in this case independent volumetric measurements showed that the amount of CO adsorbed per Ru atom was ~0.8–1. The constant value of the adsorptive capacity towards CO of P, Q, and R samples (0.8–1.0) apparently suggests that the final state

of the active Ru after total decarbonylation is fairly independent of the preparation conditions. This observation agrees with the ir evidence that, on totally decarbonylated samples, CO adsorption mainly gives rise to the same bands (A pair) with comparable intensity.

In Figs. 5a and b a parallel desorption–adsorption experiment carried out in a reflectance cell is described. It can be noted that the weak band at 25,000 cm^{-1} associated with residual unreacted Ru$_3$(CO)$_{12}$ gradually disappears upon decarbonylation in the temperature interval 323–623 K (side a) leaving a broad maximum centered at ~20,000 cm^{-1} and an absorption edge at ~31,000 cm^{-1}. A shoulder at ~16,000 cm^{-1} is also observed. Both these features were found also on freshly prepared P samples (Fig. 3a); however, a comparison between the two series of spectra reveals that an apparent reflectance maximum at 27,000 cm^{-1} is present on R samples. An intermediate situation was observed on Q samples. Exposure to CO after each outgassing stage (side b) induces an absorption increase in the range 30,000–10,000 cm^{-1}, the maximum change being observed in all cases at ~25,000 cm^{-1}. The shapes of the spectra,
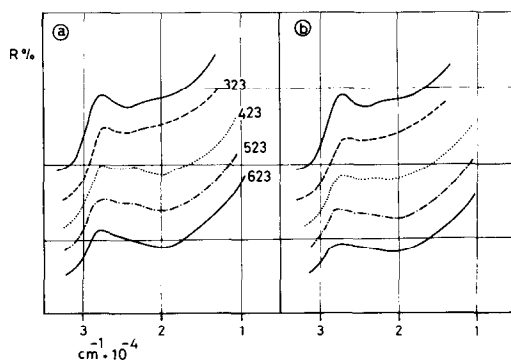

FIG. 5. (a) —— (upper): Reflectance spectrum of Ru$_3$(CO)$_{12}$ (0.33%) on Al$_2$O$_3$ after 1 month; ——: after decarbonylation *in vacuo* at 323 K; ···: at 423 K; —·—: at 523 K; —— (lower): at 623 K. (b) —— (upper): Reflectance spectrum of Ru$_3$(CO)$_{12}$ (0.33%) on Al$_2$O$_3$ after 1 month; all other spectra taken after exposure to CO (P = 5.3 kPa) of the samples decarbonylated as in side a.

however, are not greatly altered and so they remain different with respect to the analogous ones observed on P samples. This observation implies that totally decarbonylated P and R samples, although very similar from the adsorptive point of view (similar CO coverages and identical CO adsorbed species), contain a different distribution of Ru species. In particular, unknown Ru species absorbing at ~27,000 cm^{-1} are definitely more abundant on P samples.

In Fig. 6 the decarbonylation of an R (0.33%) sample in H_2 flow is illustrated. At the beam temperature no difference exists between this experiment and the analogous one carried out *in vacuo* (Fig. 5a). At higher temperatures, however, dramatic differences are observed. In fact in the presence of H_2, C species (practically absent on R samples *in vacuo*) become predominant on the 523 K-treated samples and disappear only at higher temperatures. This suggests that C species can be formed from the B species by the effect of H_2 reduction at $T \geq$ 423 K.

In another series of experiments, more concentrated (1.57%) samples have been investigated. For the sake of brevity, we shall report only the main results. In particular:

(i) as to the ageing effect in air, the behaviour of 1.57% samples is essentially identical to that illustrated in Fig. 1;

(ii) the decarbonylation patterns are also similar and identical species (A,B,C) can be identified;

(iii) CO adsorption on partially or totally decarbonylated samples reveals different features.

In order to illustrate this point, the decarbonylation–carbonylation sequence of an R (1.57%) sample is described in Figs. 7a and b. The original sample shows two extremely strong peaks at 2075 and 2005 cm^{-1} (side a: lower solid curve) due to B species formed from $Ru_3(CO)_{12}$ under the action of the oxygen of the atmosphere. Moreover, an evident shoulder at 1990–1980 cm^{-1} is

present which was not so pronounced on more diluted samples. As this additional feature is present only on aged samples, it is probably due to a transformation product of the original cluster. Outgassing at the beam temperature (side a: dashed curve) causes the appearance of an absorption at 2132 cm^{-1} which can be considered as the highest mode of A-type species. The intensity of this absorption slightly increases upon CO exposure (side b) while its maximum moves to 2135 cm^{-1}.

By 423 K decarbonylation the B peaks and the shoulder at 1990–1980 cm^{-1} (side a: dotted curve) are definitely weakened; moreover, also the 2135-cm^{-1} band is eliminated. Subsequent exposure to CO (side b) not only restores the 2135-cm^{-1} band (with enhanced intensity) but also causes an ab-
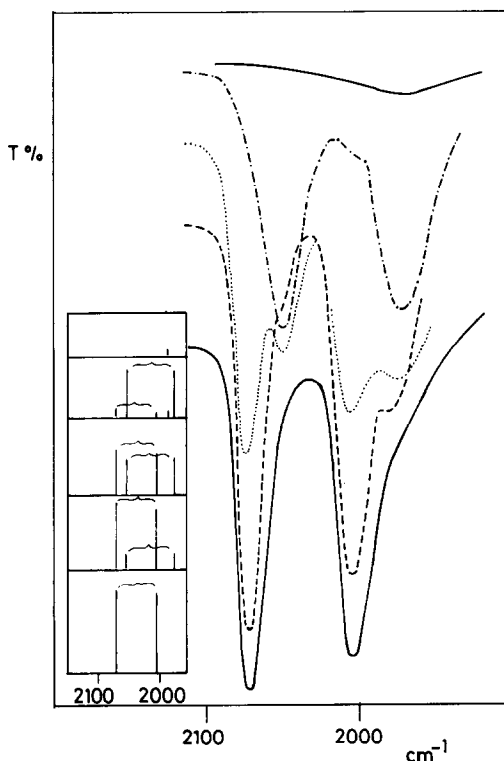

FIG. 6. Decarbonylation in flowing H_2 of an aged $Ru_3(CO)_{12}/Al_2O_3$ sample. —— (lower): $Ru_3(CO)_{12}$ (0.33%) on Al_2O_3 after 1 month; ———: decarbonylated at 323 K; ····: at 423 K; – · –: at 523 K; —— (upper): at 623 K.
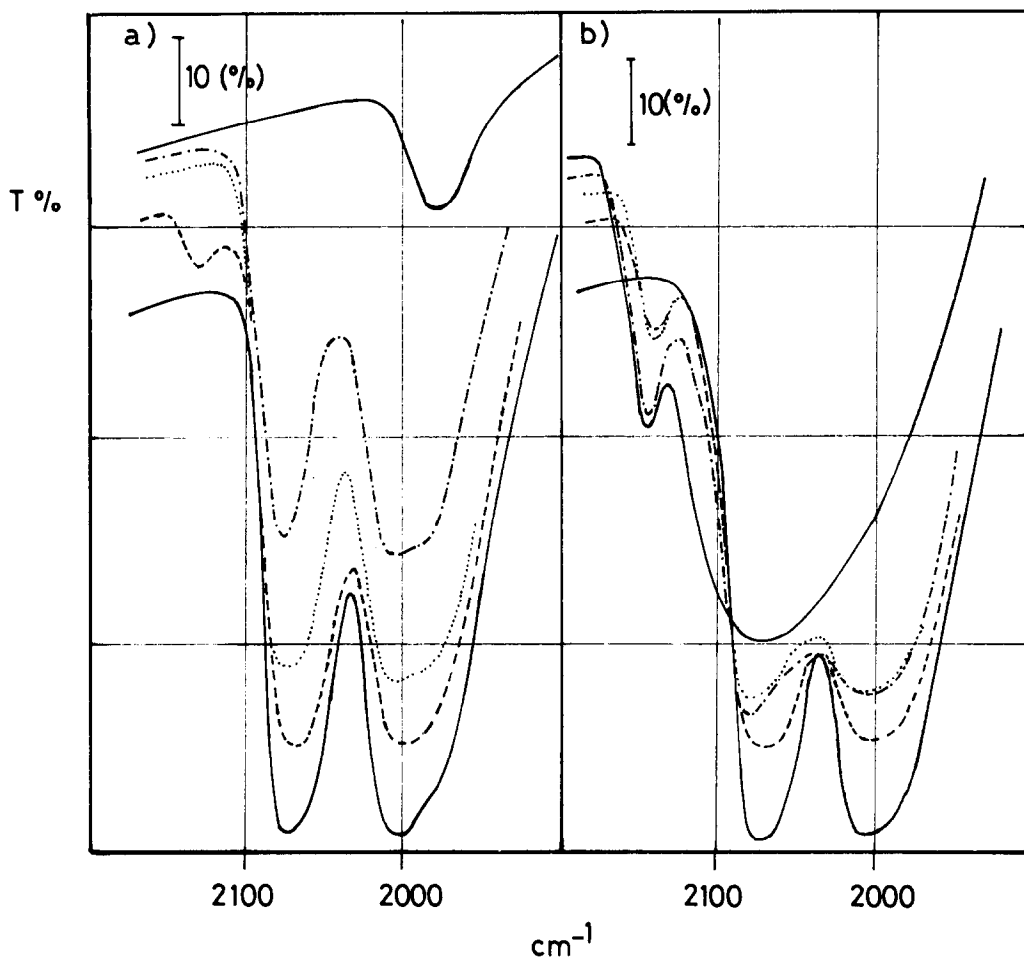
FIG. 7. (a) ——— (lower): $Ru_3(CO)_{12}$ (1.57%) on Al_2O_3 after 1 month; ———: after decarbonylation *in vacuo* at 323 K; ···: at 423 K; – · –: at 523 K; ——— (upper): at 623 K. (b) ——— (lower): $Ru_3(CO)_{12}$ (1.57%) on Al_2O_3 after 1 month; all other spectra taken after exposure to CO ($P = 5.3$ kPa) of the samples decarbonylated as in side a.

sorption increment at 2075 cm⁻¹ (where the low-frequency component of the A pair is expected) and at 2070–2000 cm⁻¹. In particular it can be observed that the absorption minimum at 2040 cm⁻¹ (side a: dotted curve) is strongly attenuated due to the formation of species absorbing in this region. Decarbonylation at 523 K is illustrated by the dot-dashed curve (side a): the B bands at 2075 and 2005 cm⁻¹ together with the shoulder at 1990–1980 cm⁻¹ are severely weakened. Subsequent CO adsorption (side b) causes the formation of a peak at 2140 cm⁻¹ (highest component of an A-type

pair), and a parallel optical density increase at 2075 cm⁻¹ (where the second component of the A pair is expected) and in the range 2070–2000 cm⁻¹ (as in the previous case). Finally the effect of the decarbonylation at 623 K is illustrated by the last curve (upper solid curve). All bands are completely eliminated and only a weak residue is observed at ~1980 cm⁻¹ which is particularly strong on this sample because of the high Ru concentration. This isolated band is due to residual monocarbonylic species which are very resistant to outgassing. Comparison with the initial intensity of the $Ru_3(CO)_{12}$

carbonylic bands and with the intensity of the bands due to CO adsorbed on decarbonylated samples (see below) indicated that this species involves a very small fraction of sites. For this reason no attempts of detailed assignment will be made in the following. CO adsorption on this decarbonylated sample gives rise to the corresponding spectrum of side b which is characterized by a peak at 2140 cm^{-1} (highest mode of an A-type pair) and by a broad absorption ($\Delta \bar{\nu}_{1/2} = 150$ cm^{-1}) with an apparent maximum at ~2070 cm^{-1} and a shoulder at ~1990 cm^{-1}. In conclusion, the comparison between the spectra of CO adsorbed on 0.33 and 1.5% fully decarbonylated R samples demonstrates that Ru concentration is an important factor which strongly influences the properties of dispersed ruthenium.

DISCUSSION

The Ageing Effect

As shown in Fig. 1a, $Ru_3(CO)_{12}$ on Al_2O_3 under the influence of atmospheric oxygen undergoes an "oxidative" transformation leading to the total disappearance of the bands characteristic of the original cluster and to the formation of the characteristic B pair. Parallel uv–visible reflectance experiments show the simultaneous disappearance of the 25,000-cm^{-1} band of the starting carbonyl. As this transition is due to a $\sigma \rightarrow \sigma^*$ transition in the trimetallic skeleton (16) it is inferred that the Me–Me bands are broken. The resulting product, however, is still carbonylated and must have a well-defined structure because of the constancy of the frequencies and intensity ratio of the carbonylic bands. By anticipating a conclusion which will be fully demonstrated in Part II, we will hereafter assume that the new carbonylic species (Ru_B complexes) contain a pair of coupled linear CO oscillators bonded to an oxidized ruthenium atom. Due to the mild oxidizing conditions, it can be inferred that the Ru ions derived from oxidative rupture of the original trimetallic

skeleton will not be so very distant from the starting complex; for instance, they may be disposed in a chain where the ruthenium ions are bonded via oxygen or hydroxyl bridges. The presence of strong bands at 1570 and 1465 cm^{-1} on aged samples (which are due to carbonate or carboxylate species) suggests the following reaction scheme:

$$(1)$$
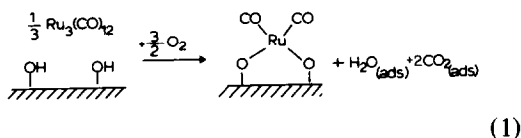
where the adsorbed CO_2 is in carbonate or carboxylate form on Ru-free portions of the Al_2O_3 surface and the Ru is in the divalent state. The problem of the structure of such species will be discussed in more detail in Part II.

Decarbonylation in Vacuo

(1) P (freshly prepared) samples. It has been shown that adsorbed $Ru_3(CO)_{12}$ loses CO ligands by simple outgassing at RT. As the complex is very stable at RT, both in a crystalline form or in solution, it is inferred that this process is not a simple decomposition. The surface of virgin alumina is very rich in OH groups which represent potential ligands; as a consequence the most likely reaction is a ligand displacement as in scheme (2):

$$Ru_3(CO)_{12} + x(OH) \rightleftharpoons$$
$$Ru_3(CO)_{12-x}(OH)_x + xCO, \quad (2)$$
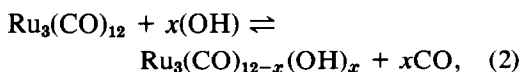
where the skeleton is preserved and the number of OH surface ligands can vary depending upon the residual CO pressure. In favour of this hypothesis the following arguments can be mentioned:

(i) Similar ligand displacement reactions between CO and nucleophilic ligands are known to occur for $Ru_3(CO)_{12}$ in homogeneous solution (17).

(ii) The reflectance data obtained after RT desorption (new bands at 30,000 and 20,000 cm^{-1} in Fig. 3), are also in favour of

this because $Ru_3(CO)_9L_3$ (L = $PEtPh_2$, PPh_3) complexes show a pair of transitions in a very similar position.

(iii) A simple decarbonylation with formation of unsaturated subcarbonylic species is absolutely unlikely on hydrated alumina where a monolayer of OH ligands is present. Moreover, it has been shown (*18*) that in CO-deficient subcarbonylic clusters adsorbed on surfaces, edge or face bridged CO groups (ir bands at $\bar{\nu} \leq 1900$ cm^{-1}) should be present after partial decarbonylation, in contrast with the experimental data.

(iv) The hypothesized scheme easily explains the infrared data characterized by band intensity strongly influenced by the outgassing time.

(v) Reaction (1) can be reversed by increasing the CO pressure, in agreement with the above results.

The presence of the weak band at 2100 cm^{-1} also suggests the formation of other surface compounds. On the basis of the similarity of the ir spectra they could be similar to those found for $Os_3(CO)_{12}$ adsorbed on η-Al_2O_3 and which are formed upon oxidative addition of surface OH groups to the trimetallic skeleton with release of two CO per each added OH group (*19, 20*) following the scheme:


$$(3)$$
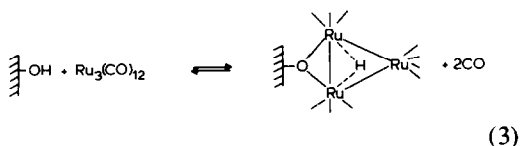
The previous considerations are valid only for extremely dilute samples (0.33%). On the more concentrated ones agglomeration must also be taken into account as a possible effect of the removal of CO ligands.

Further loss of CO (achieved by increasing the temperature *in vacuo*) leads to the formation of two new band pairs (B and C). The weak B pair which is the same prevalently found on an aged sample, reveals that during this decarbonylation stage some oxidation has occurred. Also the completely

new C pair belongs to surface carbonylic complexes formed during the thermal treatment *in vacuo*. By anticipating information contained in Parts II and III, we will hereafter assume that the C pair belongs to a new Ru_C complex containing two coupled linear CO oscillators. The frequency of the bands (lowered with respect to those of the Ru_B complexes) suggests that the ruthenium centre is in a more reduced form. As $Ru_3(CO)_{12}$ not only undergoes ligand displacement reactions with preservation of the metallic skeleton, but also, under more severe conditions, with skeleton fragmentation (*17*), we hypothesize that Ru_C complexes (formed at 423 K *in vacuo*) do not contain the original triangular skeleton.

After decarbonylation at 423 K also CO-free unsaturated Ru species are formed which are revealed by successive exposure to CO. In fact under these conditions another pair of absorption bands is quickly formed (A pair) at higher frequencies (2138 and 2075 cm^{-1}). These or very similar bands have already been reported on Ru/Al_2O_3 (*21*) and Ru/SiO_2 (*22*) and ascribed by Davydov and Bell (*22*) to complexes containing two coupled linear CO groups and the ruthenium atom in an oxidized state. This tentative assignment has been confirmed in Part II by means of ^{13}CO isotopic substitution, so the A pair will hereafter be ascribed to a Ru_A complex. In conclusion, the structure of the complexes Ru_A, Ru_B, and Ru_C is very similar and can be schematically represented by the formula

$$(L)_yRu(CO)_2,$$
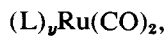
where L is a surface ligand and ruthenium is in different oxidation states. Due to this structural similarity (which implies a similar molecular orbital picture) the frequency of the ir bands can be considered as a qualitative measure of the extent of electronic back-donation from the metal to the antibonding π^* orbital of the CO molecule. The following back-donation sequence can thus be established:

$$Ru_C > Ru_B > Ru_A$$

which implies an identical sequence as far as the electron density on the central atom is concerned. The oxidation state of ruthenium is then in the sequence

$$Ru_A > Ru_B > Ru_C.$$

In conclusion, by decarbonylation at 423 K of $Ru_3(CO)_{12}$ a distribution of dicarbonylic complexes of ruthenium in different oxidation states is formed. Due to the absence of O_2, the oxidation agents are undoubtedly the OH groups of the surface as documented by the evolution of hydrogen and carbon dioxide. A similar reaction has been observed also in similar systems $[Mo(CO)_6-Al_2O_3]$ (23).

By further decarbonylation at 523 K the C pair disappears. As in the previous case the reaction is not a simple decarbonylation leading to unsaturated intermediates. In fact reexposure to CO does not restore the original bands and, as before, hydrogen, CO_2, and small amounts of CH_4 are evolved from the surface. Finally outgassing at 623 K eliminates also the residual B pair. In both cases oxidized ruthenium is formed as proved by the successive exposure to CO where mainly Ru_A complexes are formed. It must be noted that after total decarbonylation some ruthenium must be present also in an even higher oxidation state (probably in tetravalent form). This is supported by the observation that, after an initially rapid growth, the bands of the A pair continue to increase with the contemporary formation of surface carbonates (bands at 1600–1300 cm^{-1}) which undoubtedly monitor the reduction of ruthenium to an oxidation state characteristic of Ru_A complexes. Temperature-programmed reduction (TPR) experiments confirm this observation (Part III). The presence of small amounts of metallic aggregates formed upon destruction of Ru_C complexes is not excluded. In fact the ir spectra of CO adsorbed on fully decarbonylated P samples show, together with the bands of the Ru_A species, a weaker and broad absorption at lower frequencies probably associated with CO adsorbed on metallic ruthenium (21, 22).

The reflectance spectrum of fully decarbonylated samples (P and R) is very similar to the spectra of complexes of Ru^{III} (24, 25). In particular all spectra, often characterized by the lack of well-resolved bands in the whole range 35,000–10,000 cm^{-1}, show transitions at 15,000–16,000, 20,000–24,000, and 33,000 cm^{-1}. This result strongly suggests the oxidation state III for Ru_A species. All the conclusions previously described are summarized in Table 1.

(2) Q and R (aged) samples. On the basis of the previous discussion, the results obtained for Q and R samples can be interpreted as follows:

(i) On both samples a decarbonylation occurs accompanied by oxidation, as documented by the appearance, after CO adsorption, of the Ru_A bands at all decarbonylation stages.

(ii) Ru_C complexes are absent on R oxidized samples, in agreement with the low Ru oxidation number (as shown in the previous paragraph).

(iii) By comparison of the spectra in Figs. 6 and 3, it can be seen that the most important difference is represented by the presence of a relative reflectance maximum at ~27,000 cm^{-1} on aged samples. From the previous discussion we have seen that P, Q, and R samples differ in the relative proportion of ruthenium in different states; the amount of ruthenium in low or zero oxidation number is in the order:

$$P > Q > R.$$

Thus it can be hypothesized that the absorption at ~27,000 cm^{-1} is associated with zero oxidation states of Ru in Ru_C complexes and/or very small aggregates. Clusters of small dimensions can show $\sigma \rightarrow \sigma^*$ transitions localized in Me–Me bonds at such low frequency (16, 25). This consideration suggests that in Ru_C complexes Me–Me bonds are still present. Examination of Fig. 4 also shows that Ru_A species are al-

TABLE 1

Ru Species Formed during the Decarbonylation Process

Outgassing	P samples	R samples
323 K	Ligand displacement and insertion reactions; skeleton totally or partially preserved	Oxidized Ru_B species only; skeleton not preserved
423 K	Intermediate oxidized (Ru_A, Ru_B) and reduced (Ru_C) dicarbonylic species formed; skeleton not preserved	Evidence of further oxidation by OH groups (Ru_A and Ru_B)
523 K⎤ 623 K⎦	Extensive oxidation of the intermediate dicarbonylic species; H_2 and CO_2 evolved; metallic particles not excluded on the most concentrated samples	Extensive oxidation leading mainly to Ru_A species and to Ru^{IV}

Note. In hydrogen flow, reduced dicarbonylic Ru_C species are predominant at intermediate temperatures. From their decarbonylation at higher T, metallic ruthenium mainly is formed.

ready present on the initial sample outgassed at RT (both *in vacuo* or in CO), so suggesting that both Ru_A and Ru_B complexes are simultaneously formed upon oxidation of $Ru_3(CO)_{12}$ deposited on the surface. All these considerations are summarized in Table 1.

Decarbonylation in Hydrogen

As shown in Fig. 6 the decarbonylation in hydrogen of an R sample follows a different path. In fact, unlike the vacuum case (Fig. 4) the predominant species at intermediate decarbonylation stages are the Ru_C dicarbonylic entities. This result definitely confirms that ruthenium in the Ru_C species is in a low oxidation state. Moreover, the total absence of Ru_B complexes at the highest decarbonylation temperatures strongly suggests that the samples fully decarbonylated in hydrogen are in the lowest valency state. This fact implies that in the presence of hydrogen the oxidation products of the reaction with the surface OH groups are immediately reduced or the reaction itself is strongly inhibited. At this stage of the discussion it is not possible to state the value of the oxidation state of all dicarbonylic complexes.

The Behaviour of the More Concentrated Samples

As shown in Fig. 7a there is no basic difference between the decarbonylation patterns of 0.33 and 1.57% R samples. Similarly equivalent patterns where obtained on the P and Q samples. Important differences on the other hand are observed in the ir spectra of CO adsorbed after partial or total decarbonylation. For the sake of brevity in the following we shall discuss the spectra of CO adsorbed only on fully decarbonylated R 1.57% samples. The essential difference between this spectrum and the equivalent one obtained on a 0.33% R sample is represented by the extremely large width ($\Delta\bar{\nu}_{1/2} = 150$ cm^{-1}) and intensity of the component at $\sim$2070 cm^{-1}. As the peak at 2140 cm^{-1} (highest mode of the Ru_A complexes) has the usual width, this implies that, besides the second component of the Ru_A doublet, in the range 2100–2000 cm^{-1} there is a broad absorption which is much less visible in more dilute samples and whose presence is favoured by the high loadings. This observation is of great help for a plausible assignment. In fact when $Ru_3(CO)_{12}$ is decarbonylated *in vacuo* the following phenomena can in principle occur:

(i) CO is lost and the so-formed unsaturated entities saturate their ligand vacancies by inserting surface ligands (OH) or by forming new metal–metal bonds in a clustering process;

(ii) CO is lost because of an oxidation reaction favoured by the temperature increase with suitable surface OH and subsequent formation of surface compounds of oxidized ruthenium.

The experimental data obtained on 0.33% samples suggest that both reactions occur in proportions which are strongly influenced by the initial state of the ruthenium catalyst. The extent of the oxidative decarbonylation is limited by the concentration of active OH groups (which is probably a limited fraction of the total) present on the surface. Once this fraction has been consumed, the decarbonylation will follow preferentially path (i), which is consequently the favoured one at the highest loadings. Hence the higher the Ru concentration the easier the clustering between unsaturated entities: as a consequence on concentrated samples metallic agglomerates will become definitely favoured. On this basis the broad adsorption in the range 2100–2000 cm^{-1} can be assigned to linear CO species adsorbed on metallic particles. This assignment entirely agrees with the data reported in the literature (21, 22).

CONCLUSIONS

$Ru_3(CO)_{12}$, which is a stable compound, becomes oxygen sensitive once deposited on the Al_2O_3 hydrated surface. The new dicarbonylic surface species so formed (Ru_B) probably contain ruthenium atoms in oxidation state II. Freshly prepared samples decarbonylated *in vacuo* at 323–423 K lose CO following two different paths which lead to both oxidized (Ru_A and Ru_B) and zero-valent (Ru_C) dicarbonylic compounds. The formation of oxidized compounds is due to a chemical reaction with active OH groups of the surface. Me–Me bonds are likely to be present in Ru_C and absent in

Ru_A and Ru_B complexes. By further decarbonylation of dilute samples at higher temperature, an oxidized surface phase is mainly formed together with minor amounts of metallic aggregates. On more concentrated samples the fraction of ruthenium in the metallic state becomes predominant. Decarbonylation in flowing hydrogen mainly gives rise to dicarbonylic Ru_C complexes at intermediate temperatures and metallic ruthenium at the highest temperatures.

REFERENCES

1. Smith, G. C., Chojnack, T. D., Dasputa, S. R., Iwatabe, K., and Watters, K. L., *Inorg. Chem.* **14**, 1479 (1975).
2. Basset, J. M., and Ugo, R., *in* "Aspects of Homogeneous Catalysis" (R. Ugo, Ed.), Vol. III. Reidel, Dordrecht, 1976.
3. Ichikawa, M., *J. Chem. Soc. D* **11**, 26 (1976).
4. Burwell, R. L., and Brenner, A., *J. Mol. Catal.* **1**, 77 (1976).
5. Coudurier, G., Gallezot, P., Praliaud, H., Primet, M., and Imelik, B., *C.R. Acad. Sci. Ser. C* **282**, 311 (1976).
6. Anderson, J. R., Elmes, P. S., Howe, R. F., and Mainwaring, D. E., *J. Catal.* **50**, 508 (1977).
7. Smith, A. K., and Basset, J. M., *J. Mol. Catal.* **2**, 229 (1977).
8. Bilhou, J. L., Theolier, A., Smith, A. K., and Basset, J. M., *J. Mol. Catal.* **3**, 245 (1977).
9. Brenner, A., and Burwell, R. L., *J. Catal.* **52**, 353 (1978).
10. Bilhou, J. L., Bilou-Bougnol, V., Graydow, W. F., Basset, J. M., Smith, A. K., Zanderighi, G. M., and Ugo, R., *J. Organomet. Chem.* **153**, 73 (1978).
11. Smith, A. K., Theolier, A., and Basset, J. M., *in* "Proceedings, 4th Soviet-French Sem. on Catal., Metsniereba, Tiblisi, 1978."
12. Smith, A. K., Theolier, A., Basset, J. M., Ugo, R., Commerenc, D., and Chauvin, Y., *J. Amer. Chem. Soc.* **100**, 2590 (1978).
13. Ichikawa, M., *J. Catal.* **56**, 127 (1979).
14. Kuznetsov, V. L., Bell, A. T., and Yermakov, Y. I., *J. Catal.* **65**, 374 (1980).
15. Yawney, D. B., and Stone, F. G. A., *J. Chem. Soc. A*, 502 (1969).
16. Tyler, R., Levenson, R. A., and Gray, H. B., *J. Amer. Chem. Soc.* **100**, 7888 (1978).
17. Chini, P., *Inorg. Chim. Acta Rev.*, 31 (1968).
18. Guglielminotti, E., Zecchina, A., Boccuzzi, F., and Borello, E., *in* "Proceedings, 32nd Interna-

tional Meeting on Growth and Properties of Metal Clusters, Lyon, 1979," p. 165. Elsevier, Amsterdam, 1980.

19. Smith, A. K., Besson, B., Basset, J. M., Psaro, R., Fusi, A., and Ugo, R., *J. Organomet. Chem.* **192,** C31 (1980).

20. (*a*) Watson, P. L., and Schrader, G. L., *J. Mol. Catal.* **9,** 129 (1980). (*b*) Deeba, M., and Gates B. C., *J. Catal.* **67,** 303 (1981).

21. Della Betta, R. A., *J. Phys. Chem.* **79,** 2519 (1975).

22. Davydov, A. A., and Bell, A. T., *J. Catal.* **49,** 332 (1977).

23. Bowman, R. G., and Burwell, R. L., Jr., *J. Catal.* **63,** 463 (1980).

24. Hazzion, Z., and Navon, G., *Inorg. Chem.* **19,** 2236 (1980).

25. Clark, R. J., and Franks, M. L., *J. Chem. Soc. Dalton Trans.* 1825 (1976).