Silica and Lanthanum Oxide Supported Ruthenium Species Derived from $Ru_3(CO)_{12}$ and $RuCl_3$; a FT-IR Study

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Abstract

$Ru_3(CO)_{12}$ adsorbs physically on silica to give μ-$HRu_3(CO)_{10}(OSi\leqslant)$ at 100 °C and decarbonylates completely at 200 °C. Readsorption of CO at 150 °C gives di- and tricarbonyl species of which the dicarbonyl is very stable. By comparing with the spectra of adsorbed CO on Ru/SiO_2, it is concluded that treatment with CO at 150 °C reduces ruthenium to the zerovalent state that stabilizes the dicarbonyl species. Carbon monoxide adsorbed on oxidized ruthenium is far less stable. On lanthanum oxide, the cluster breaks up at room temperature giving the dicarbonyl surface species. Although the tricarbonyl spectrum is not shown, the completely decarbonylated species after reduction with hydrogen followed by CO adsorption at 100 °C shows a mixture of di- and tricarbonyl ruthenium on the surface. As compared to adsorbed CO on Ru/SiO_2, adsorbed CO on lanthanum oxide supported ruthenium is less reactive towards hydrogen.

Introduction

Interaction of metal cluster carbonyls with oxide supports has a two-fold interest in catalysis. Firstly, it may produce surface-anchored metal carbonyl species (with or without the cluster being retained) that may be catalytically active. Secondly, their complete decarbonylation on mild heating under vacuum may lead to the formation of highly dispersed supported metals.

Interaction of $Ru_3(CO)_{12}$ with silica has been investigated by several authors [1–3]. Most of the workers reported that the initially physisorbed $Ru_3(CO)_{12}$ on thermoevacuation gives mononuclear carbonyl species. Only recently, Theolier *et al.* [4] reported the formation of μ-$HRu_3(CO)_{10}(OSi\leqslant)$ analogous to the corresponding osmium species by carrying out the preparation in the total absence of moisture and oxygen.

Interaction of $Ru_3(CO)_{12}$ with an alumina surface has been studied by several authors [1, 5–8]. It is generally concluded that the interaction leads to the breaking of the cluster forming several monoruthenium carbonyl species bound to the surface.

Interaction of a carbonyl cluster is often dependent on the basicity of the support. A recent study by Chakrabarty and Desai has shown that although $Os_3(CO)_{12}$ reacts with silica forming μ-$HOs_3(CO)_{10}(OSi\leqslant)$, on dehydrated lanthanum oxide the cluster breaks down to form monoosmium carbonyls [9]. Use of hydrated lanthanum oxide, on the other hand, allowed the hydritotriosmium species to be formed [10]. Similar results were obtained for the interaction of $Os_3(CO)_{12}$ with hydrated and dehydroxylated magnesium oxide [11]. This work has been undertaken with the aim of examining the effect of the basicity of the support on its interaction with $Ru_3(CO)_{12}$ by selecting silica and lanthanum oxide as supports. One drawback of studying such an interaction by infrared spectroscopy is the low transmittance resulting in a poor quality spectrum. This problem has been overcome by using FT-IR spectroscopy. The spectra of adsorbed CO on the completely decarbonylated samples and also on supported ruthenium obtained from $RuCl_3$ are reported with the intention of studying the reactivity of the various adsorbed CO species and partly to confirm (or otherwise) the earlier reports.

Experimental

$Ru_3(CO)_{12}$ was obtained from Strem Chemicals. The supports (silica – Davison 979, specific surface 280 m^2 g^{-1} and La_2O_3 – Indian Rare Earths, 99.9% purity, specific surface 12 m^2 g^{-1}) were treated in a furnace at 450 °C and stored in a desiccator. The support was treated at 450 °C in the reaction tube in a stream of helium for 2 h, cooled to 25 °C and then a solution of $Ru_3(CO)_{12}$ in dry hexane was added. After keeping the mixture in flowing helium for an hour, the solvent was removed by vacuum evaporation. Loading was one weight per cent of ruthenium. $Ru_3(CO)_{12}/La_2O_3$ was also prepared in the open by using lanthanum oxide that had been exposed to 15 torr of water vapour for several hours.

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A thin wafer of the sample (5 mg cm^{-2}) was pressed and loaded in a high vacuum infrared cell that could be evacuated to 10^{-4} torr and could be heated upto 400 °C. Spectra were recorded on a Fourier transform infrared spectrometer Nicolet-170SX at a resolution of 2 cm^{-1}. All spectra were recorded at the beam temperature under vacuum. Spectra were also recorded as Nujol mulls after heating the supported $Ru_3(CO)_{12}$ to various temperatures under vacuum.

Results and Discussion

Silica Support

Figure 1 shows the spectra of $Ru_3(CO)_{12}/SiO_2$ after various treatments. Fresh $Ru_3(CO)_{12}/SiO_2$ (Fig. 1a) shows three bands (2065s, 2028m and 2016sh) due to physically adsorbed $Ru_3(CO)_{12}$. (All band positions are in wave numbers.) On heating under vacuum at 100 °C it shows bands at 2080, 2060, 2016 and 1978 and a very weak band at 2150. This is quite similar to the spectrum of $HOs_3(CO)_{10}(OSi\lessgtr)$ [4, 9, 12] that showed infrared bands at 2114vw, 2078s, 2064s, 2010sh and 1984m [4]. The weak band at 2114 might have been masked by the strong 2080 band. This is also not much different from the spectrum of molecular $HRu_3(CO)_{10}(SC_2H_5)$ reported by Crooks *et al.* [13]. This can be assigned to μ-$HRu_3(CO)_{10}(OSi\lessgtr)$. The very weak band at 2150 may be due to partial breaking of the cluster.

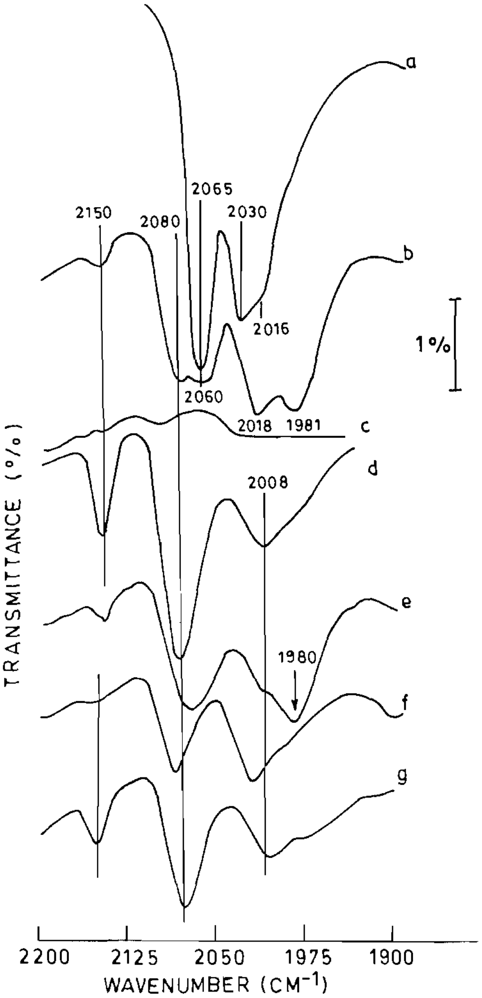

Fig. 1. Infrared spectra of a self-supported disc of $Ru_3(CO)_{12}/SiO_2$: (a) fresh sample; (b) evacuated at 150 °C; (c) at 200 °C; (d) treated with 100 torr CO at 150 °C; (e) 100 torr H_2 at 200 °C; (f) evacuated at 200 °C; (g) reduced in 100 torr H_2 at 350 °C, evacuated and treated with 100 torr CO at 150 °C.

Decarbonylation is complete at 200 °C before which the three-band spectrum attributed to surface bound $Ru(II)(CO)_3$ and $Ru(II)(CO)_2$ was observed. When the completely decarbonylated species is treated with CO (100 torr) at 150 °C, the three-band spectrum (2150s, 2080vs and 2008m, br) appears (Fig. 1d). On treatment with H_2 (100 torr) at 200 °C, the band at 2150 nearly disappears and that at 2080 loses intensity drastically. A new band also appears at 1980. Prolonged evacuation at 200 °C leaves a two-band spectrum (2085m, 2020m) of equal intensity (Fig. 1f). Treatment of this with 100 torr CO at 150 °C regenerates the three-band spectrum.

For comparison, we recorded the spectrum of adsorbed CO on the Ru/SiO_2 sample prepared from $RuCl_3$ by impregnation followed by reduction in hydrogen at 400 °C. The wafer after loading in the cell was again reduced in H_2 (100 torr) at 350 °C, evacuated and cooled to room temperature. CO was then adsorbed at 150 °C and 100 torr. The spectra presented in Fig. 2 is after subtracting the Ru/SiO_2 background. It can be seen that on treatment with CO at 150 °C, a two-band spectrum (2075s, 2005m) appears initially. On further treatment it changes to three bands with the new band at 2140. On treatment with H_2 at 100 °C, the band at 2140 disappears and that at 2075 is drastically reduced in intensity. Oxidation of this by oxygen at 100 °C followed by readsorption of CO at 150 °C restores the original three bands (Fig. 2d).

The spectra of adsorbed CO on Ru/SiO_2 derived from $Ru_3(CO)_{12}$ will be discussed first. After complete decarbonylation, adsorption of CO at 150 °C gives a three-band spectrum. By comparing with those of $[Ru(CO)_3Cl_2]_2$ (2143s, 2082s) [14], we conclude that this spectrum is due to a mixture of di- and tricarbonyl ruthenium. The dicarbonyl $[Ru(CO)_2(OSiPh_3)_1]_n$ is known to give two bands at 2062s and 1995s [4]. The tricarbonyl reacts with hydrogen as indicated by the disappearance of the 2150 and weakening of the 2080 bands. The dicarbonyl species, however, is very stable and does not react completely with hydrogen even at 200 °C. Treatment with hydrogen generates a new band at 1980 that we assign to linearly adsorbed CO on the ruthenium metal [4].

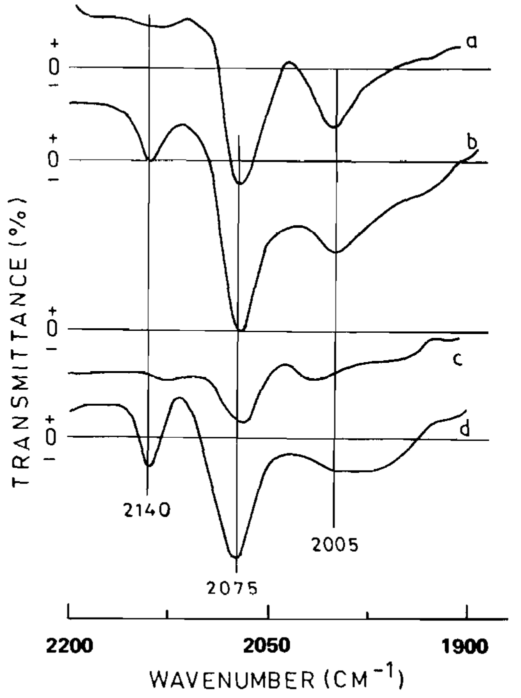

Fig. 2. Infrared spectra of Ru/SiO$_2$ prepared from RuCl$_3$ after the following treatments (background subtracted): (a) 100 torr CO at 150 °C for 1 h; (b) same as (a) for 2 h; (c) 100 torr H$_2$ at 100 °C; (d) oxidized with 100 torr of oxygen at 100 °C followed by 100 torr CO at 150 °C.

While the di- and tricarbonyl ruthenium formed by thermal degradation of ruthenium carbonyl Ru$_3$(CO)$_{12}$/SiO$_2$ decompose completely at 200 °C, the dicarbonyl formed on readsorption of CO is stable. Davydov and Bell [15] while studying CO adsorption on Ru/SiO$_2$ prepared by reduction of RuCl$_3$/SiO$_2$ observed that CO adsorbed on oxidized ruthenium can be easily removed but not CO adsorbed on reduced ruthenium. As suggested earlier, thermal decomposition of supported Ru$_3$(CO)$_{12}$ gives Ru(II)(CO)$_2$. We conclude that readsorption of CO at 150 °C leads to the formation of reduced ruthenium carbonyl species. This will be further supported by the results of CO adsorption on hydrogen reduced Ru/SiO$_2$.

Adsorption of CO on RuCl$_3$/SiO$_2$ reduced by hydrogen at 350 °C gives the same three-band spectrum (Fig. 2a). After oxidation of the surface and readsorption of CO, an identical spectrum results without any change in the band positions. This proves that carbon monoxide treatment at 150 °C reduces back the ruthenium, possibly to the zero oxidation state.

Lanthanum Oxide Support

Ru$_3$(CO)$_{12}$ supported on dehydroxylated lanthanum oxide shows only two bands at 2062 and 1980 with equal intensity. On heating under vacuum, the intensity gradually decreases but the intensity ratio is maintained at one. The carbonyl bands disappear above 250 °C (Fig. 3). The features of the two-band spectrum are the same irrespective of whether the spectrum is recorded inside the cell or in the open as Nujol mull. Readsorption of CO at 200 °C regenerates the spectrum with a marginal frequency shift to the higher side (2066s, 1986s). Treatment with hydrogen at 100 °C reduces the intensity of the peaks. Treatment with oxygen followed by CO adsorption shifts the bands to a lower frequency (2048s and 1962s) (Fig. 4e). Subsequent reduction with hydrogen at 350 °C followed by CO adsorption at 150 °C shifts back the peaks to 2070 and 1990 and a new peak appears at 2130.

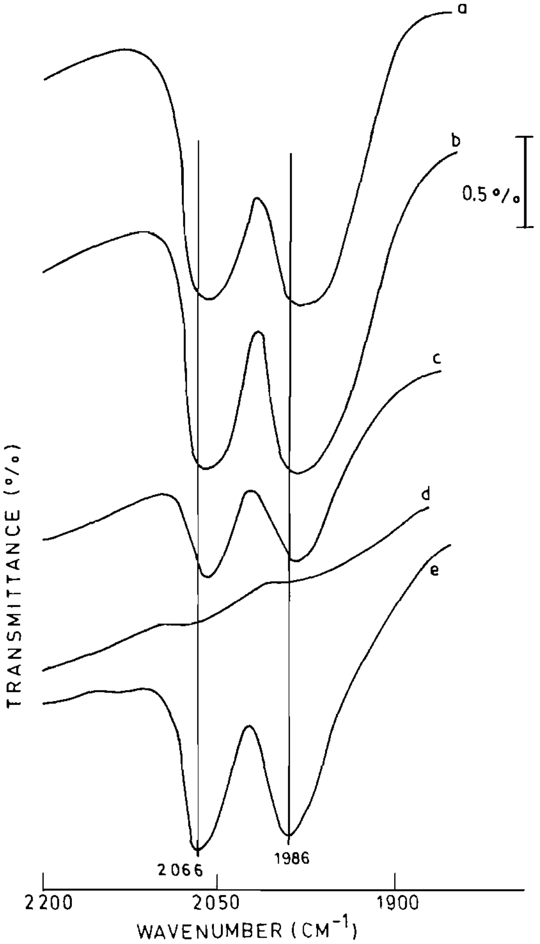

Fig. 3. Infrared spectra of Ru$_3$(CO)$_{12}$/La$_2$O$_3$: (a) fresh sample; (b) heated under vacuum at 150 °C; (c) at 200 °C; (d) 250 °C; (e) 100 torr CO at 200 °C.

The two-band spectrum can be assigned to the mononuclear dicarbonyl ruthenium on the surface showing that the cluster breaks up immediately on contact with the lanthanum oxide support. The result is similar to that observed for Os$_3$(CO)$_{12}$ on dehydroxylated lanthanum oxide [9]. After mild

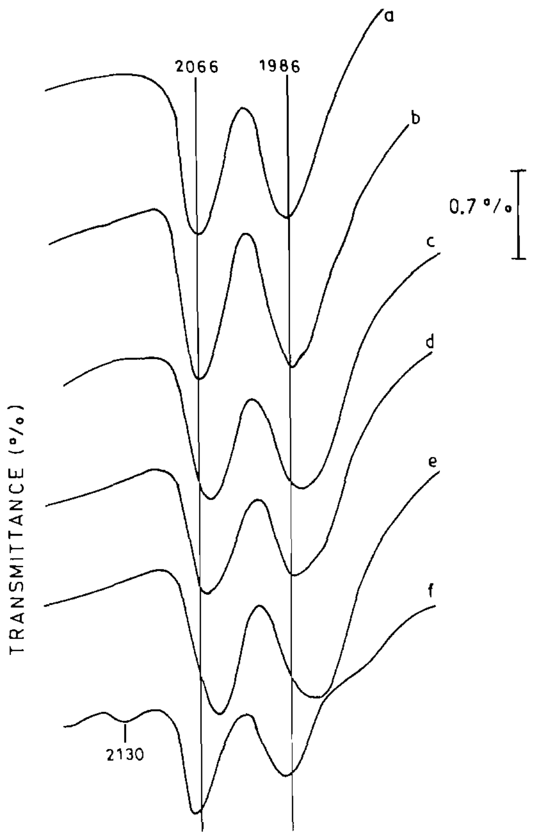

Fig. 4. Infrared spectra of Ru/La_2O_3 obtained from $Ru_3(CO)_{12}$/La_2O_3 by thermoevacuation inside the cell: (a) 100 torr CO at 200 °C; (b) 100 torr H_2 at room temperature; (c) 50 torr H_2 at 100 °C; (d) air at room temperature; (e) 100 torr CO at 200 °C; (f) reduced in 100 torr H_2 at 350 °C, evacuated and treated with 100 torr CO at 150 °C.

oxidation, readsorption of CO shifts the bands to a lower wave number that most likely is due to the change in the oxidation state of ruthenium to a more positive value thus reducing back donation of electrons from the metal to carbon monoxide. Treatment with hydrogen at a high temperature followed by CO adsorption gives the three-band spectrum as we have seen in the case of reduced ruthenium on silica support. This suggests the formation of di- and tricarbonyl species on low-valent (possibly zero-valent) ruthenium.

The use of hydrated lanthanum oxide support does not make any difference in the nature of the species formed and hence the results are not reported separately. It is to be recalled that $Os_3(CO)_{12}$ on hydrated lanthanum oxide forms μ-$HOs_3(CO)_{10}$-$OSi\leqslant$) on mild heating. The lower bond energy of the Ru–Ru bond does not allow the corresponding ruthenium species to be formed except on a highly acidic support like silica.

Conclusions

Interaction of triruthenium dodecacarbonyl with silica at about 100 °C converts the physisorbed starting compound to a surface bound species μ-$HRu_3(CO)_{10}(OSi\leqslant)$. Further heating leads to the break up of the cluster and readsorption of CO at 150 °C to form di- and tricarbonyl ruthenium in which ruthenium is possibly in the zero oxidation state. With hydrogen, the tricarbonyl is far more reactive than the dicarbonyl ruthenium. On lanthanum oxide, both dehydrated and hydroxylated, the cluster breaks up immediately giving the dicarbonyl ruthenium. The dicarbonyl can be regenerated on adsorption of CO on the completely decarbonylated species. The tricarbonyl can be formed only under more drastic reducing condition. The dicarbonyl shows much greater stability to heat and hydrogen.

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