

The chemical and photochemical reactions of metal carbonyl cluster compounds on solid surfaces

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Abstract - EXAFS spectroscopy by use of synchrotron radiation provides information about the local structure surrounding metal atoms in metal carbonyl cluster compounds adsorbed on the surface of a support and those in the chemical species derived from them. The structural changes caused by thermal treatments were systematically investigated by employing EXAFS and other spectroscopic techniques on the chemical species formed by the adsorption of $\text{Ru}(\text{CO})_{12}$, $\text{Os}(\text{CO})_{12}$, $\text{Fe}(\text{CO})_{12}$, $\text{Rh}_x\text{Co}_y(\text{CO})_{12}$ and other metal carbonyl cluster compounds on silica, alumina and a variety of metal oxide supports.

Discussion will be given also on the photochemical changes induced by the UV or visible irradiation of $\text{Fe}(\text{CO})_5$, $\text{Fe}_2(\text{CO})_9$, $\text{Fe}_3(\text{CO})_{12}$, $\text{Os}_3(\text{CO})_{12}$ and other metal carbonyl cluster compounds adsorbed on silica.

1. INTRODUCTION

There is an increasing interest in the application of metal carbonyl cluster compounds in heterogeneous catalysis. Many metal carbonyl cluster compounds are known to be active in a variety of homogeneous catalyses¹). By use of the reaction of a metal carbonyl cluster compound with support surface, one may attach a catalytic active metal carbonyl species onto the support surface. Another important application is to use metal carbonyl cluster compounds as a precursor to prepare a highly- and uniformly-dispersed supported metal catalyst.

From these interests, extensive investigations have been made on a variety of the catalysts prepared by use of metal carbonyl cluster compounds. While thermal treatment is usually used to take off the CO ligands from a metal carbonyl cluster, decarbonylation can be also performed by means of photochemical process. The latter may have several advantages over the thermal process, because extremely small metal clusters could be produced at low temperature without any sintering effect, and furthermore an unstable metal carbonyl species could be grafted onto the support by utilizing a photochemical reaction.

In order to understand the chemical and photochemical behaviors of metal carbonyl cluster compounds on solid surfaces, it is of vital importance to characterize the chemical species formed in each treatment. Spectroscopic methods such as UV-visible diffuse reflectance spectroscopy and FT-IR spectroscopy, have been mostly used for this purpose²). But it is often hard to obtain a definite structural model only by these methods. The analysis of extended X-ray absorption fine

structure (EXAFS) has been proved to be a powerful tool for the structural study of supported metal catalysts. In particular, by use of synchrotron radiation, one can obtain high-quality EXAFS data on a supported metal catalyst system even in the case of low metal loading. When the data by other spectroscopic methods are combined with the structural information obtainable from EXAFS, one can get a fairly clear structural model for the chemical species formed on a support surface. Using such approach, we have carried out a systematic study on the chemistry and photochemistry on a series of metal carbonyl cluster compounds supported on the surfaces of silica, alumina and so on. This article provides a review of those investigations. First we will take up $\text{Ru}_3(\text{CO})_{12}$ supported on the surfaces of various different oxides to demonstrate the effect of the metal-support interaction. Then we will discuss the thermal and photochemical processes of $\text{Fe}_3(\text{CO})_{12}$, $\text{Fe}_2(\text{CO})_9$, and $\text{Os}_3(\text{CO})_{12}$ on silica and alumina. Finally, we will discuss the photochemical behaviour of $\text{H}_2\text{FeOs}_3(\text{CO})_{13}$ supported on silica.

2. $\text{Ru}_3(\text{CO})_{12}$

The catalytic activities and selectivities of the supported Ru catalysts prepared from $\text{Ru}_3(\text{CO})_{12}$ are known to vary markedly depending on the nature of the support³⁻⁹. By use of EXAFS spectroscopy, we studied the structures of the Ru species which are formed from $\text{Ru}_3(\text{CO})_{12}$ on a series of supports such as SiO_2 , Al_2O_3 , TiO_2 , V_2O_5 , MgO and MnO_2 ^{10,11}.

$\text{Ru}_3(\text{CO})_{12}$ was put onto the support surface by immersing the support in a *n*-pentane solution of $\text{Ru}_3(\text{CO})_{12}$ under Ar atmosphere. Decarbonylation was done by heating the sample to 473 K except for the case of SiO_2 where it was done at 398 K. In each case, the reduction was performed by heating the sample to 723 K in H_2 . EXAFS data were obtained by use of the EXAFS spectrometer¹² at BL 10-B of Photon Factory in National Laboratory for High-Energy Physics (PF-KEK).

Figure 1 shows the Fourier transform of Ru K-edge EXAFS oscillation of $\text{Ru}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3$. In the as-supported state, Fourier transform shows three main peaks due to Ru-C, Ru-Ru and Ru-(C)-O. The Ru-Ru peak disappears after the pyrolysis indicating the formation of a mono-nuclear Ru species. The Fourier transform shows two prominent peaks, the one due to Ru-C(-O) and Ru-O(support) and the other due to Ru-(C)-O. Finally, the Fourier transform of the sample after the H_2 reduction shows peaks attributable to Ru-Ru and Ru-O(support). We carried out the curve-fitting analysis on each peaks of those Fourier transforms. The coordination number (*N*) and bond distance (*R*) obtained by the curve-fitting analysis are listed in Table 1 for $\text{Ru}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3$ and $\text{Ru}_3(\text{CO})_{12}/\text{SiO}_2$ systems. Both in $\text{Ru}_3(\text{CO})_{12}/\text{SiO}_2$ and in $\text{Ru}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3$, Ru-C and Ru-(C)-O coordination numbers decreased to 2 after the pyrolysis while they were 4 in the as-supported state, indicating a partial decarbonylation had taken place during the pyrolysis. Note that, in the case of $\text{Ru}_3(\text{CO})_{12}/\text{SiO}_2$, Ru-Ru bond remains unbroken after the pyrolysis, but no Ru-O(support) bond is formed.

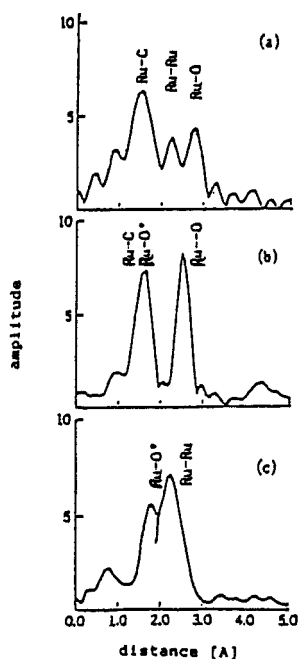


Fig.1
Fourier transform of Ru K-edge EXAFS
of $\text{Ru}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3$
(a) as supported,
(b) after pyrolysis at 573 K,
(c) H_2 reduced

Table 1 Curve-fitting analysis of Ru K-edge EXAFS

| | Ru-C | | Ru-(C)-O | | Ru-Ru | | Ru-O(*) | |
|---|------|--------|----------|------|-------|--------|---------|------|
| | N | R[Å] | N | R[Å] | N | R[Å] | N | R[Å] |
| <u>$\text{Ru}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3$</u> | | | | | | | | |
| pyrolysis | ~2 | 1.90 | ~2 | 2.97 | --- | --- | ~2 | 2.17 |
| H_2 reduction | --- | --- | --- | --- | 2.5 | 2.62 | ~2 | 2.15 |
| <u>$\text{Ru}_3(\text{CO})_{12}/\text{SiO}_2$</u> | | | | | | | | |
| pyrolysis | ~2 | 1.84 | ~2 | 2.99 | 1.2 | 2.76 | --- | --- |
| H_2 reduction | --- | --- | --- | --- | ~4.4 | 2.68 | --- | --- |
| [references] | | | | | | | | |
| Ru metal | | | | | (12) | (2.68) | | |
| $\text{Ru}_3(\text{CO})_{12}$ powder | (4) | (1.93) | (4) | 3.06 | (2) | 2.85 | | |

Ru-O(*): bonding between Ru and O(support)

These facts show that a partially decarbonylated Ru carbonyl species, such as $\text{Ru}_3(\text{CO})_9$, is kept on SiO_2 surface without forming Ru-O(support) bonding. This is markedly different from the $\text{Ru}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3$ system. Both in $\text{Ru}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3$ and $\text{Ru}_3(\text{CO})_{12}/\text{SiO}_2$, Ru-Ru bond appears after the H_2 reduction. In the case of the H_2 reduced state of $\text{Ru}_3(\text{CO})_{12}/\text{SiO}_2$, the Ru-Ru coordination number was found to be six, indicating the formation of small Ru metal particles, no indication being found for the formation of Ru-O(support) bonding. The situation is very different in $\text{Ru}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3$, where Ru-Ru coordination number is only about 2.5 and each Ru atom has about two Ru-O(support) bondings.

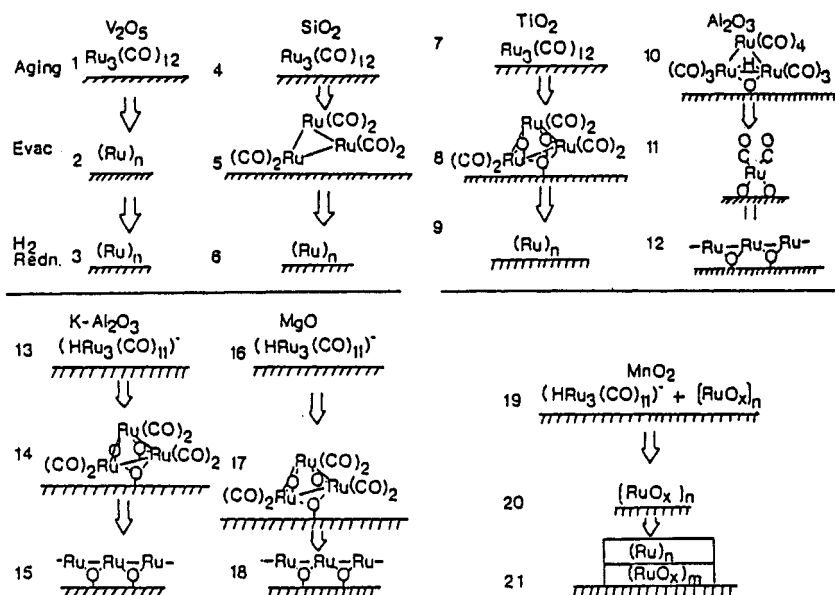


Fig.2 Structure models for the supported Ru species derived from $\text{Ru}_3(\text{CO})_{12}$

By combining the structural informations derived from EXAFS with those obtainable from other spectroscopic methods, we concluded that the structural change of Ru species taken place on oxide surfaces can be described as those illustrated in Fig.2¹¹⁾.

After the aging at 313 K, $\text{Ru}_3(\text{CO})_{12}$ is supported without any significant change in its molecular structure on V_2O_5 , SiO_2 and TiO_2 , but it is in the state of a surface complex $\text{Ru}_3(\text{CO})_{10}(\text{H})(-\text{O}-\text{Al} \leq)$ on Al_2O_3 and in the state of $[\text{HRu}_3(\text{CO})_{11}]^-$ ion on MgO as well as on K-added Al_2O_3 . This difference seems to be primarily determined by the basicity of the support surface. In the H_2 reduced state, flat Ru clusters with Ru-O(support) bondings are formed on Al_2O_3 , K-added Al_2O_3 and MgO , while a little larger Ru metal particles without Ru-O(support) bonding are formed on V_2O_5 , SiO_2 , TiO_2 .

3. $\text{Fe}(\text{CO})_5$, $\text{Fe}_2(\text{CO})_9$ AND $\text{Fe}_3(\text{CO})_{12}$

First we will take up $\text{Fe}_3(\text{CO})_{12}/\text{SiO}_2$ and $\text{Fe}_3(\text{CO})_{12}/\gamma\text{-Al}_2\text{O}_3$ systems. $\text{Fe}_3(\text{CO})_{12}$ was put on the support surface by the dry process. Namely, its powder was well mixed with the support and the mixture was aged by heating to 313 K for 2 hours¹³⁾. In the case of $\text{Fe}_3(\text{CO})_{12}/\text{SiO}_2$ thus prepared, both FT-IR and uv-visible diffuse reflectance spectrum are almost the same as $\text{Fe}_3(\text{CO})_{12}$, indicating that the carbonyl molecules are in the molecularly dispersed state without a significant change of the molecular structure. The results of the analysis of Fe K-edge EXAFS also support the above conclusion. In the case of $\text{Fe}_3(\text{CO})_{12}/\gamma\text{-Al}_2\text{O}_3$, there was CO evolution in the aging process, the amount of the evolved gas being 1 mole CO per one mole of $\text{Fe}_3(\text{CO})_{12}$. The analysis of Fe K-edge EXAFS showed the presence of tri-nuclear Fe skeleton with Fe-Fe distance of 2.47 Å, which is significantly smaller than the corresponding distance in the original metal carbonyl cluster molecule (2.61 Å). It was reported by Hugues et al that $[\text{HFe}_3(\text{CO})_{11}]^-$ attached to the support is formed on the surface of $\eta\text{-Al}_2\text{O}_3$ ¹⁴⁾. The FT-IR as well as UV-visible diffuse

reflectance spectra are quite different from those of $[\text{HFe}_3(\text{CO})_{11}]^-$. By combining these observations, we concluded that $\text{Fe}_3(\text{CO})_{12}$ forms a surface complex of the structure illustrated in Fig.3 on Al_2O_3 when aged at 313 K, while it is just physically adsorbed on SiO_2^{13} .

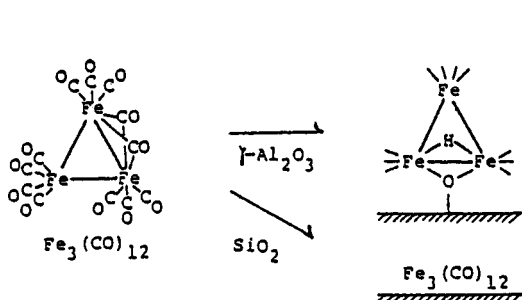


Fig.3

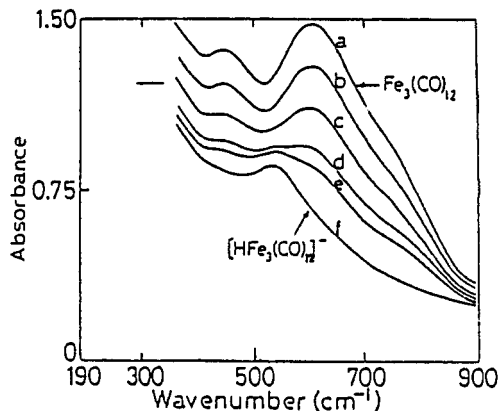


Fig.4 Change of UV-visible diffuse reflectance spectrum of $\text{Fe}_3(\text{CO})_{12}/\text{SiO}_2$
Irradiation time:(a) 0 h,(b)4 h,(c) 20 h,
(d)55 h,(e) 88 h,(f) 160 h

A complete decarbonylation occurs as $\text{Fe}_3(\text{CO})_{12}/\text{SiO}_2$ is heated to 473 K. The Fourier transform of the Fe K-edge EXAFS of the sample after the above treatment, showed only the peaks due to Fe-Fe and Fe-O(support). Fe-Fe and Fe-O(support) distances were found to be 2.46 and 1.83 Å, respectively. The Fe-Fe coordination number was about 2 in this state. These results derived from EXAFS show that trinuclear Fe cluster are fixed on silica surface forming Fe-O(support) bondings¹⁵.

When $\text{Fe}_3(\text{CO})_{12}/\text{SiO}_2$ is irradiated with visible light in the wavelength region of 400-500 nm, the color of the sample changes from dark green to rose color. The change of the UV-visible diffuse reflectance spectrum is shown in Fig.4¹⁶. By the light irradiation, the 450 nm band ($\sigma \rightarrow \sigma^*$ transition) and the 610 nm band ($\sigma^* \rightarrow \sigma^*$ transition) decrease their intensities and a new band grows up at 540 nm. The FT-IR spectrum of the final product of the light irradiation has peaks at 2050 and 2002 cm^{-1} . The photoproduct thus formed cannot be extracted by pure dichloromethane, but can be extracted when tetramethyl-ammonium chloride is added to the solvent. The IR spectrum of the photo-irradiated sample as well as that of the extracted species agrees well with the spectrum of the solution of $[\text{Et}_4\text{N}]^+[\text{HFe}_3(\text{CO})_{11}]^-$ ¹⁷. Thus the photoproduct is concluded to be $[\text{HFe}_3(\text{CO})_{11}]^-$ with an ionic bond to silica surface.

$\text{Fe}(\text{CO})_5$ molecules can be put onto SiO_2 surface by exposing the support to $\text{Fe}(\text{CO})_5$ vapor. It was reported by Jackson and Trusheim^{18,19} that $\text{Fe}(\text{CO})_5$ physically adsorbed on silica is selectively converted to $\text{Fe}_3(\text{CO})_{12}$ when $\text{Fe}(\text{CO})_5/\text{SiO}_2$ is irradiated with the 337 nm light from N_2 gas laser. We confirmed also that $\text{Fe}(\text{CO})_5/\text{SiO}_2$ can be efficiently converted to $\text{Fe}_3(\text{CO})_{12}/\text{SiO}_2$ as the former is irradiated with the light from KrF excimer laser (246 nm). When irradiated with visible light, the $\text{Fe}_3(\text{CO})_{12}/\text{SiO}_2$ system thus produced by the photochemical

process undergoes the same photochemical change to yield $[\text{HFe}_3(\text{CO})_{11}]^-$ ionically attached to SiO_2 surface as in the case of the $\text{Fe}_3(\text{CO})_{12}/\text{SiO}_2$ sample prepared directly by putting $\text{Fe}_3(\text{CO})_{12}$ onto silica surface by means of the dry process, .

Naturally, the products produced by thermal treatment as well as those formed by the photochemical process are dependent of the nature of the support surface. We can prepare the silica whose surface is covered with $\text{HSi}\equiv$ by treating it at the room temperature with a pentane solution of $\text{HSi}(\text{OC}_2\text{H}_5)_3$. In the same way, the silica whose surface is covered with $\text{H}_2\text{Si}<$ can be prepared by the treatment with the solution of $\text{H}_2\text{Si}(\text{OC}_2\text{H}_5)_2$. Hereafter, we will denote the former surface-modified silica as " $\text{HSi}-[\text{SiO}_2]$ " and the latter as " $\text{H}_2\text{Si}-[\text{SiO}_2]$ ". We put iron carbonyl cluster compounds onto these surface-modified silica by means of the dry process with an thermal aging at 318 K for several hours. In the cases of $\text{Fe}(\text{CO})_5$ and $\text{Fe}_3(\text{CO})_{12}$, the iron carbonyl molecules are confirmed to be just physically adsorbed on the support surface. The situation was different in the case of $\text{Fe}_2(\text{CO})_9$. The FT-IR spectrum of $\text{Fe}_2(\text{CO})_9/\text{HSi}-[\text{SiO}_2]$ exhibits broad strong bands at 2025 and 2000 cm^{-1} and a weak band at 2110 cm^{-1} . A similar FT-IR spectrum was observed also for $\text{Fe}_2(\text{CO})_9/\text{H}_2\text{Si}-[\text{SiO}_2]$. The evidence for the formation of Fe-Si bond in these samples could be obtained by ^{29}Si NMR, Mossbauer spectroscopy and EXAFS²⁰).

The Fourier transform of Fe K-edge EXAFS of $\text{Fe}_2(\text{CO})_9/\text{HSi}-[\text{SiO}_2]$ is shown in Fig.5(a). The first peak at the distance below 2 Å can be attributed to Fe-C (and partly to Fe-Si) and the second peak at above 2 Å to Fe-Fe. A complete decarbonylation occurs as the sample is heated to 573 K in He atmosphere. The Fourier transform of this state shows only one prominent peak attributable to Fe-Si. In contrast

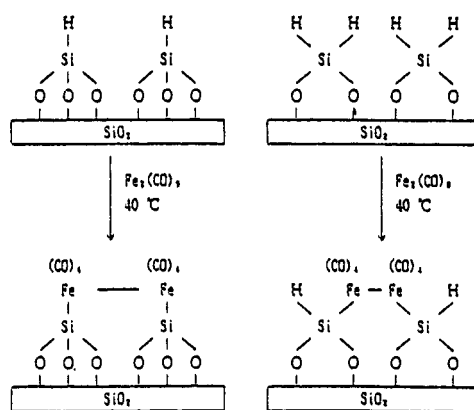
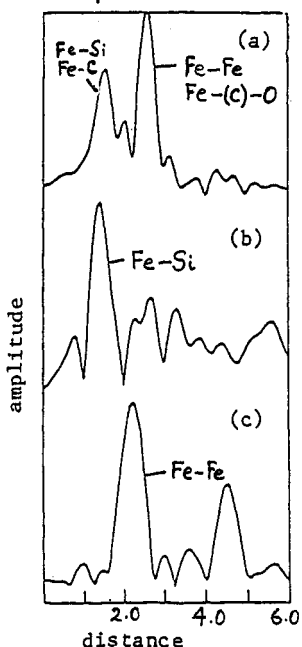


Fig.6

Fig.5
Fourier transform of Fe K-edge EXAFS of
 $\text{Fe}_2(\text{CO})_9/\text{HSi}-[\text{SiO}_2]$
(a) as supported, (b) H_2 reduced, (c) Fe_2^- -
 H_2 reduced state of $\text{Fe}_2(\text{CO})_9/\text{SiO}_2$ (normal)

to this, the sample where $\text{Fe}_2(\text{CO})_9$ is put on the ordinary silica whose surface is covered with OH groups, gives the Fourier transform shown in Fig.5(c) after the same heat-treatment. Only Fe-Fe peak appears in this case showing the formation of Fe metal particles.

It was also confirmed by the observation with electron microscope that Fe metal particles have been formed in the latter sample while no indication was found for the formation of Fe metal particles in the former sample.

Summarizing all the results mentioned above, we concluded that $\text{Fe}_2(\text{CO})_9$ which is known to be reactive toward H-Si bond^{21,22}), reacts with H-Si \leq or H₂Si \leq groups of the surface modified silica to form binuclear carbonyl complex having Fe-Si bonding as illustrated in Fig.6.

As mentioned already, both $\text{Fe}(\text{CO})_5$ and $\text{Fe}_3(\text{CO})_{12}$ are physically adsorbed on HSi-[SiO₂]. Photochemical change takes place when $\text{Fe}(\text{CO})_5/\text{HSi}-[\text{SiO}_2]$ is irradiated with the light in the wavelength region of 300-400 nm and the final photoproduct in this photo-irradiation gives the UV-visible reflectance spectrum almost the same as $\text{Fe}_2(\text{CO})_9/\text{HSi}-[\text{SiO}_2]$. Similarly, as $\text{Fe}_3(\text{CO})_{12}/\text{HSi}-[\text{SiO}_2]$ is irradiated with the light above 600 nm, the diffuse reflectance spectrum changes with irradiation time to give again the spectrum almost the same as $\text{Fe}_2(\text{CO})_9/\text{HSi}-[\text{SiO}_2]$. Although the photoproduct in the $\text{Fe}(\text{CO})_5/\text{SiO}_2$ system is $\text{Fe}_3(\text{CO})_{12}$, as we have already mentioned, the primary product in the photochemical process of $\text{Fe}(\text{CO})_5$ in solution is known to be $\text{Fe}_2(\text{CO})_9$ ²³). Thus it is most likely that, by some reason, $\text{Fe}(\text{CO})_5$ is first converted photochemically to $\text{Fe}_2(\text{CO})_9$ on the surface of HSi-[SiO₂] like in the photochemical process in solution, which then react with the H-Si groups on the support surface to form the binuclear complex. In the case of $\text{Fe}_3(\text{CO})_{12}/\text{HSi}-[\text{SiO}_2]$, we should also consider that $\text{Fe}_2(\text{CO})_9$ is photochemically formed from $\text{Fe}_3(\text{CO})_{12}$ and then react with H-Si groups on the modified silica surface, but at this moment we are not sure if $\text{Fe}_2(\text{CO})_9$ is directly produced by a single photochemical process from $\text{Fe}_3(\text{CO})_{12}$, or by two photochemical steps involving the formation of $\text{Fe}(\text{CO})_5$ as the first step.

4. $\text{Os}_3(\text{CO})_{12}$

When the system where $\text{Os}_3(\text{CO})_{12}$ is supported on silica or alumina is heat-treated to above 473 K, it becomes to be the state which is stable up to 673 K. Several different structural models have been proposed for this state^{4,24-26}). In order to clarify their structures, we studied the Os K-edge EXAFS on $\text{Os}_3(\text{CO})_{12}/\text{SiO}_2$ and $\text{Os}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3$ systems.

We prepared the samples by immersing the support in a dichloromethane solution of $\text{Os}_3(\text{CO})_{12}$. Each sample was heat-treated at 523 K in the nitrogen atmosphere, and the reduction was performed by heating the sample to 625 K in H₂.

The Fourier transform of Os K-edge EXAFS oscillation observed for the heat-treated sample of $\text{Os}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3$ is shown in Fig.7²⁷), which is markedly different from that of $\text{Os}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3$ before the pyrolysis. The most prominent peak in the Fourier transform is the

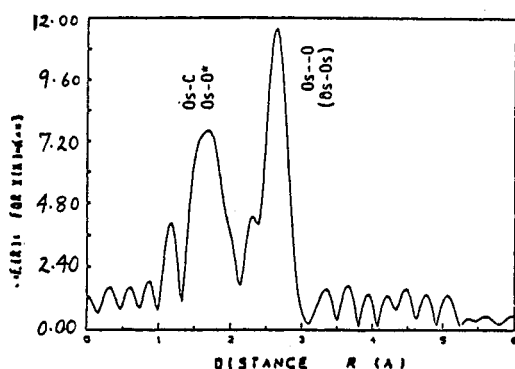


Fig.7 Fourier transform Os K-edge EXAFS of $\text{Os}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3$ of $\text{Os}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3$ after pyrolysis

one due to Os-(C)-O and the peaks in the region of 1.5-20 Å are due to Os-C and Os-O(support). There is no peak attributable to Os-Os. This result clearly shows that Os₃ skeleton has been broken to give a mono-nuclear carbonyl species by the heat-treatment. The results of the curve-fitting analysis are given in Table 2, which show that, after the pyrolysis at 523 K, a mono-nuclear carbonyl species, such as Os(CO)₂ or Os(CO)₃ are attaching onto Al₂O₃ surface by forming Os-O(support) bondings with the bond distance of 2.10 Å. Os-Os bond reappears after the H₂ reduction with the coordination number of about 3. There exist Os-O(support) bondings in this state.

In the case of Os₃(CO)₁₂/SiO₂, Os-Os bond is not completely broken by the 523 K treatment, the Os-Os coordination number being about one as shown in Table 2. In this case also, Os-O(support) bondings are formed after the pyrolysis, but they are broken and Os atoms aggregate to form small Os metal particles after the H₂ reduction.

Table 2 Curve-fitting analysis of Os K-edge EXAFS

| | Os-C | | Os-(C)-O | | Os-Os | | Os-O(*) | |
|--|------|---------|----------|------|-------|---------|---------|------|
| | N | R[Å] | N | R[Å] | N | R[Å] | N | R[Å] |
| <u>Os₃(CO)₁₂/Al₂O₃</u> | | | | | | | | |
| pyrolysis | 2~3 | 1.83 | 2~3 | 3.00 | --- | --- | ~2 | 2.10 |
| H ₂ reduction | --- | --- | --- | --- | ~3 | 2.63 | ~1 | 2.10 |
| <u>Os₃(CO)₁₂/SiO₂</u> | | | | | | | | |
| pyrolysis | 2~3 | 1.90 | 2~3 | 3.00 | ~1 | 2.87 | ~2 | 2.08 |
| H ₂ reduction | --- | --- | --- | --- | ~6 | 2.64 | --- | --- |
| [reference] | | | | | | | | |
| Os metal | | | | | (12) | (2.705) | | |
| Os ₃ (CO) ₁₂ powder | (4) | (1.929) | (4) | 3.09 | (2) | 2.89 | | |
| KOsO ₂ (OH) ₂ powder | | | | | | | (4) | 2.00 |

Os-O(*); bonding between Os and O(support)

When the sample of the as-supported Os₃(CO)₁₂/SiO₂ is irradiated with the 351 nm line of XeF excimer laser, which is in the region of the $\sigma \rightarrow \sigma^*$ band of Os₃(CO)₁₂, UV-visible diffuse reflectance spectrum changes with the irradiation time as shown in Fig.8^{16,28}. There are clear isosbestic points in this spectral change, indicating that only one kind of photoproduct is formed by this light irradiation. After a long light irradiation, FT-IR spectrum changes to the spectrum (b) in Fig.9, which is quite different from the spectrum of the non-irradiated sample (the spectrum (a) in Fig.9).

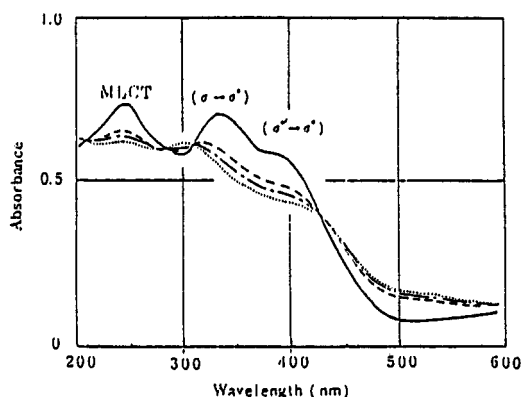


Fig.8 Change of UV-visible diffuse reflectance spectrum of $\text{Os}_3(\text{CO})_{12}/\text{SiO}_2$ caused by light irradiation.

Irradiation time (min.):
 (—) 0, (---) 10, (-·-·) 20, (····) 30.

The spectrum shows peaks at 2030(s), 2065(s), 2081(s) and 2115(w) cm^{-1} . These peaks agree well with those reported for the hydrido triosmium dodecacarbonyl complex attached to silica^{24,25,29}, of which structure is illustrated in Fig.9. On the other hand, when irradiated with the 246 nm light of KrF excimer laser, which is in the region of the MLCT band, the final photoproduct gives the spectrum (c) in Fig.9, having peaks at 2125(w), 2040(s, broad) cm^{-1} and a shoulder at 1975 cm^{-1} . This spectrum correspond to the mono-nuclear Os carbonyl species attached to silica³⁰.

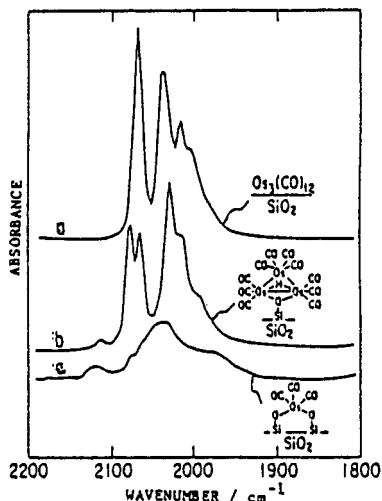


Fig.9 FT-IR spectra of the photoproducts of $\text{Os}_3(\text{CO})_{12}/\text{SiO}_2$: (a) as supported, (b) after the irradiation with 351 nm light. (c) after the irradiation with 246 nm light.

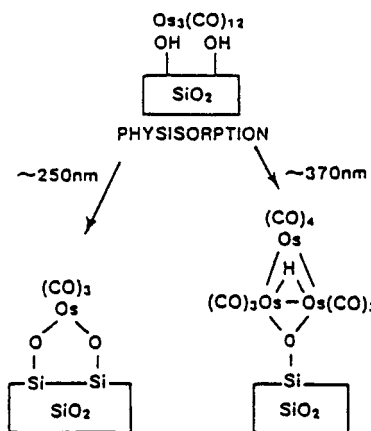


Fig.10

No further change occurs when the sample where all $\text{Os}_3(\text{CO})_{12}$ is converted to the hydrido triosmium dodecacarbonyl complex, is irradiated further with the 351 nm light, but mono-nuclear Os carbonyl species are formed when irradiated with the 248 nm light. Thus different Os carbonyl species attached to silica surface can be produced by selecting the wavelength of the irradiating light as illustrated in Fig.10. The photochemical change was found to be quite different in the case of $\text{Os}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3$ system from those described above. In this case, the irradiation with the 351 nm light resulted in the formation of mono-nuclear Os carbonyl species.

5. $\text{H}_2\text{FeOs}_3(\text{CO})_{13}$

It is known for $\text{H}_2\text{FeOs}_3(\text{CO})_{13}/\text{SiO}_2$ that, when heated to 403 K, Fe-Os bond is broken to give a tri-nuclear carbonyl complex attached to silica, $\text{Os}_3(\text{CO})_{10}(\text{H})(-\text{O}-\text{Si})$ and Fe metal particle, and the former is further decomposed to the mono-nuclear Os carbonyl species when heated to 573 K³⁰).

Figure 11 shows the change of FT-IR spectrum of $\text{H}_2\text{FeOs}_3(\text{CO})_{13}/\text{SiO}_2$ during the irradiation with visible light above 400 nm. The spectral change shows clear isosbestic point suggesting the formation of one kind of photoproduct. The gas evolved during the photo-irradiation entirely composed of CO, and its amount is one mole CO per one mole of the supported $\text{H}_2\text{FeOs}_3(\text{CO})_{13}$. No indication was found for the evolution of H_2 .

The Fourier transforms of the Fe K-edge EXAFS of $\text{H}_2\text{FeOs}_3(\text{CO})_{13}$ before and after the light irradiation are shown in Fig.12 together with that of $\text{H}_2\text{FeOs}_3(\text{CO})_{13}$ powder. The Fourier transform of the non-irradiated sample resembles that of the original carbonyl cluster compound, indicating that $\text{H}_2\text{FeOs}_3(\text{CO})_{13}$ molecules are supported on silica surface without significant change in its molecular structure. Fourier transform changes a little after the light irradiation, but the main feature of Fourier transform remain unchanged.

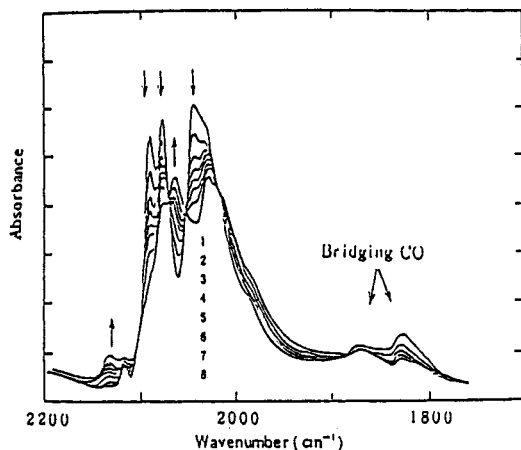


Fig.11 Change of FT-IR spectrum of $\text{H}_2\text{FeOs}_3(\text{CO})_{13}/\text{SiO}_2$ under the light irradiation.

Irradiation time (min.): (1) 0, (2) 2, (3) 4, (4) 6, (5) 8, (6) 10, (7) 15, (8) 60.

From the curve-fitting analysis, Fe-Os_p distance and its coordination number were concluded to be 2.66 Å and 2 ± 1 , respectively, which are 2.68 Å and 2 ± 1 in the case of the non-irradiated sample. This means that FeOs₃ skeleton of $\text{H}_2\text{FeOs}_3(\text{CO})_{13}$ molecule remains unbroken in the photoproduct. The appearance of the Raman bands characteristic of the metal-metal stretching vibrations in the resonance Raman spectrum of the photo-irradiated sample of $\text{H}_2\text{FeOs}_3(\text{CO})_{13}/\text{SiO}_2$ shown in Fig.13, also provides the evidence for the presence of FeOs₃ skeleton in the photoproduct.

When the photo-irradiated sample was put into dry and deaerated *n*-hexane, it is decolorized and *n*-hexane got yellow color. The IR spectrum of the extracted species agrees well with the spectrum of the photoproduct formed in $\text{H}_2\text{FeOs}_3(\text{CO})_{13}/\text{SiO}_2$. Seemingly, the photoproduct formed on silica surface can be easily extracted into *n*-hexane. This fact shows that the photoproduct is only loosely bound onto silica surface without forming chemical bond with the support.

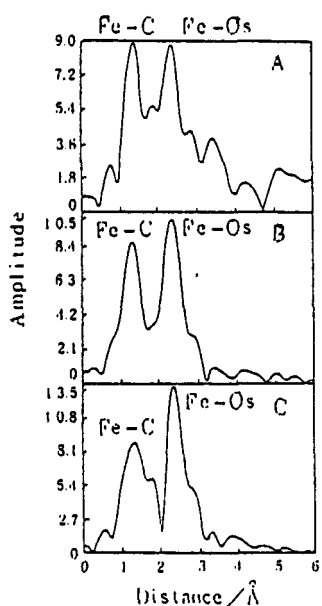


Fig.12 Fourier transform of Fe K-edge EXAFS of $\text{H}_2\text{FeOs}_3(\text{CO})_{13}/\text{SiO}_2$: (A) light irradiated, (B) non-irradiated, (C) $\text{H}_2\text{FeOs}_3(\text{CO})_{13}$

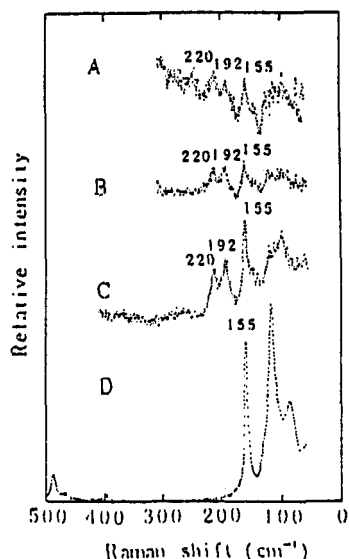


Fig.13 Raman spectra of $\text{H}_2\text{FeOs}_3(\text{CO})_{13}/\text{SiO}_2$, observed with 514.5 nm line of argon ion laser: (A) irradiated, (B) non-irradiated, (C) $\text{H}_2\text{FeOs}_3(\text{CO})_{13}$, (D) $\text{Os}_3(\text{CO})_{12}$

According to the photochemical study of $\text{H}_2\text{FeOs}_3(\text{CO})_{13}$ in solution, one CO ligand is lost from $\text{H}_2\text{FeOs}_3(\text{CO})_{13}$ in the primary photochemical process³¹. The photoproduct thus formed is very reactive, and forms $\text{H}_4\text{FeOs}_3(\text{CO})_{12}$ in the presence of H_2 in the solution. It was also reported that the break-down of the metal skeleton takes place in the presence of CO. Recently we found that the coordinatively unsaturated carbonyl species, $\text{H}_2\text{FeOs}_3(\text{CO})_{12}$ was formed as the 3-methylpentane frozen glass containing $\text{H}_2\text{FeOs}_3(\text{CO})_{13}$ was irradiated with visible light at 77 K. On warming up the frozen glass, this photoproduct goes back to $\text{H}_2\text{FeOs}_3(\text{CO})_{13}$ by the recombination with CO having been trapped at a near-by site. The IR spectrum of this coordinatively unsaturated carbonyl species produced in the frozen glass agrees well with the spectrum of the photoproduct formed in $\text{H}_2\text{FeOs}_3(\text{CO})_{13}/\text{SiO}_2$. Thus it is most likely that the same coordinatively unsaturated carbonyl species is formed in $\text{H}_2\text{FeOs}_3(\text{CO})_{13}/\text{SiO}_2$ by the irradiation with visible light. Probably, this unsaturated carbonyl species is more or less stabilized by the interaction with OH groups on silica surface, which prevent the progress of secondary reactions. This might be the reason why the coordinatively unsaturated $\text{H}_2\text{FeOs}_3(\text{CO})_{12}$ which is unstable, can be efficiently formed in $\text{H}_2\text{FeOs}_3(\text{CO})_{13}/\text{SiO}_2$ by the light irradiation even at the room temperature.

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