JOURNAL OF CATALYSIS 71, 337–347 (1981)

Infrared Characterization of Mononuclear Osmium Carbonyl Species on Alumina

HELMUT KNÖZINGER[1] AND YAPING ZHAO[2]

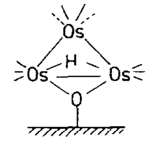
Institut für Physikalische Chemie, Universität München, Sophienstrasse 11, 8000 Munich 2, West Germany

Received October 24, 1980; revised May 22, 1981

$Os_3(CO)_{12}$ was attached to Al_2O_3 surfaces by different reaction routes. An initially formed triosmium cluster undergoes thermal degradation at temperatures below 470 K. Degradation products are mononuclear tri- and dicarbonyl osmium complexes which can be reversibly interconverted. Metal aggregation does not occur below 770 K. A detailed analysis of the infrared carbonyl spectra permits the estimation of geometric parameters of the osmium complexes. A tentative model of the catalyst structure is presented and the stabilization of a monoatomic dispersion is interpreted as being due to an extremely strong osmium–oxygen interaction and the steric repulsion between carbonyl ligands of neighboring surface complexes.

I. INTRODUCTION

The relations between molecular clusters and small metallic particles have attracted increasing interest during the last few years (*1*). Moreover, it has been demonstrated that supported metal catalysts derived from carbonyl cluster compounds may develop unique catalytic properties which are not achieved by conventionally prepared metal catalysts (*2–5*). The reason for this is suggested to be due to the very high dispersion and small particle size of catalysts derived from zero-valent metal cluster compounds (*5*). Supported osmium catalysts have found little attention in the past. Carbonyl infrared spectra of CO adsorbed on supported osmium metal have been published (*6, 7*) and Sinfelt and co-workers (*8, 9*) reported on a very elegant electron microscopic study of supported osmium particles. These catalysts were prepared conventionally by impregnation with H_2OsCl_6 and subsequent high-temperature reduction. The successful attachment of molecular triosmium carbonyl clusters onto ligand-modified silica supports was described recently by Brown and Evans (*10*) and by Pierantozzi *et al.* (*11*). Basset and Ugo and their co-workers (*12–14*) were the first to report on the reaction from solution of $Os_3(CO)_{12}$ with unmodified hydroxylated SiO_2 and Al_2O_3 surfaces. Deeba and Gates (*15*) reported ir spectra of the same cluster adsorbed on the surfaces of SiO_2, Al_2O_3, TiO_2, and ZnO and Watson and Schrader (*16*) demonstrated that the Al_2O_3-supported catalysts developed alkene hydrogenation activity under mild conditions. A molecular trinuclear cluster compound attached to the oxide surfaces was detected as the initial reaction product by infrared spectroscopy (*12–16*), quantitative gas analysis (*13, 14*), and EXAFS (*14*). The structure of this compound can be described as follows (A):



and has well-defined molecular analogues (*17*). This surface cluster was decomposed on heating and the resulting surface complex gave three infrared carbonyl bands at 2118–2135, 2034–2052, and 1955–1970 cm^{-1}

---

[1] To whom correspondence should be addressed.

[2] Permanent address: Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, Peoples Republic of China.

0021-9517/81/100337-11$02.00/0

(*13*, *15*). The corresponding carbonyl spectrum was compared with the authentic spectrum of $[Os(CO)_3X_2]_2$ species (X = halogen) and the formation of a mononuclear carbonyl osmium surface species was postulated on that basis. However, it was not checked in all cases whether the three observed bands did indeed belong to a single species (*15*), although the possible existence of interconvertible mononuclear di- and tricarbonyl species was mentioned by Smith *et al.* (*13*).

The two very recent communications by Basset and Ugo and their co-workers (*13*, *14*) were not known to us when this work was first submitted for publication. Therefore, some of our experimental data parallel their results, and others are complementary. The main emphasis of the present contribution is a careful ir study of the osmium carbonyl surface complexes on Al_2O_3 during their decarbonylation and recarbonylation. The vibrational analysis in the carbonyl stretching region permitted estimation of some structural parameters from which a tentative model of the surface complexes is deduced. The present paper goes beyond the conclusions drawn by Smith *et al.* (*13*) at least with respect to the ir analysis and the description of a model structure of the catalysts.

II. EXPERIMENTAL

$Os_3(CO)_{12}$ was received from Strem Chemicals and used without further purification. $H_2Os_3(CO)_{10}$ was prepared according to the procedure described by Knox *et al.* (*18*). The Al_2O_3 used as support was Al_2O_3 P 110C1 from Degussa, West Germany. This material is prepared by flame hydrolysis of $AlCl_3$ and consists of small nonporous spherical particles (5–30 nm diameter). Its BET surface area was 100 m^2/g.

The support was first heated in O_2 at 670 K to remove contaminated hydrocarbons and then heated *in vacuo* (<10 N m^{-2}) at a predetermined temperature (usually 670 K) for 10 h. After cooling the support to room temperature, it was contacted with the cluster solution under dry N_2. The reaction of the cluster compounds with the support surface was carried out in two ways, either by simply stirring the suspension at room temperature for 15 h (the solvents were either hexane or octane) or by refluxing it in dry octane (bp 398 K) under dry N_2 for 3 h. The materials obtained were thoroughly washed with the solvents to remove unreacted, weakly adsorbed clusters, and dried *in vacuo*. Table 1 summarizes the samples which were prepared and gives the preparation conditions and support pretreatment temperatures. Thin self-supporting wafers were pressed in air and placed into a previously described (*19*) transmission infrared cell, which permits *in situ* heat treatments and chemisorption experiments to be carried out.

The infrared spectra were recorded on a

TABLE 1

Characterization of Supported Osmium Catalysts

Sample	Original cluster	Support and pretreatment temp. (K)	Attachment procedure
Ia	$Os_3(CO)_{12}$	Al_2O_3 (370)	Reflux in octane at 398 K
Ib	$Os_3(CO)_{12}$	Al_2O_3 (670)	Reflux in octane at 398 K
Ic	$Os_3(CO)_{12}$	Al_2O_3 (870)	Reflux in octane at 398 K
IIa	$Os_3(CO)_{12}$	Al_2O_3 (670)	Room-temperature adsorption from octane solution
IIb	$Os_3(CO)_{12}$	Al_2O_3 (870)	Room-temperature adsorption from octane solution
III	$H_2Os_3(CO)_{10}$	Al_2O_3 (670)	Room-temperature adsorption from octane solution
IV	$Os_3(CO)_{12}$	SiO_2 (670)	Reflux in octane at 398 K

Perkin–Elmer spectrophotometer type 225. Before exposing the sample to the infrared beam the system was pumped at room temperature to avoid any interference of oxygen. Moreover, to reduce possible heat effects induced by the infrared beam the light source was usually run at only about 20% of its maximum power. The spectral slitwidth in the carbonyl stretching region was typically 3 cm^{-1}.

III. RESULTS AND DISCUSSION

1. Infrared Characterization

Sample IV, which was prepared by refluxing SiO_2 with an octane solution of $Os_3(CO)_{12}$, showed ir carbonyl bands at 2117, 2078, 2068, 2030, 2015, and 1998 cm^{-1}. This set of bands was obtained after pressing the self-supporting wafer in air. The bands compare well with the set of bands reported by Basset and Ugo and their co-workers (*12–14*), by Deeba and Gates (*15*), and by Watson and Schrader (*16*). They also correlate with ir carbonyl spectra of the authentic reference compounds $[HOs_3(CO)_{10}(OCH(CH_3)_2)]$ (*21*), $[HOs_3(CO)_{10}OH]$ (*22*), $[HOs_3(CO)_{10}SR]$ (*23*), $[HOs_3(CO)_{10}(HN\text{-}n\text{-}Bu)]$ (*17*), and $[HOs_3(CO)_{10}\text{–}O\text{–}Si(Ph)_3]$ (*13, 14*). It can therefore be consistently assumed that structure **A** as suggested first by Basset and Ugo and co-workers (*12–14*) is being formed in agreement with the conclusions of Deeba and Gates (*15*) and of Watson and Schrader (*16*).

The Al_2O_3-supported clusters developed the same set of carbonyl bands irrespective of the synthesis route when the samples were not contacted with the ambient atmosphere. If the samples were exposed to air during the preparation of the self-supporting wafers, additional bands near 2130, 2030–2050, and 1940–1970 cm^{-1} were observed in addition to the characteristic carbonyl bands of structure **A**. This behavior had been reported previously and the additional bands can be interpreted as being indicative for a cluster degradation to mononuclear carbonyl surface species (*13, 15*). The relative degree of cluster degradation clearly depended on the pretreatment temperature (i.e., the surface hydroxyl content) of the Al_2O_3 support prior to the cluster adsorption. Sample IIb was prepared after dehydroxylation at 870 K which results in a residual hydroxyl density of only about 2.5×10^{14} OH/cm^2 corresponding to approximately 17% of a theoretical monolayer (*20*). This sample showed much less cluster degradation than sample IIa (dehydroxylation at 670 K) which contained initially 5.5×10^{14} OH/cm^2 corresponding to 38% of the theoretical monolayer capacity (*20*).

It is interesting to note that these trends can be observed although the samples had been exposed to the atmosphere during the preparation of the ir wafers. Atmospheric water and/or oxygen may thus influence the stability of structure **A**; the oxidative degradation of the cluster structure by surface hydroxyl groups, however, must also be an important process for the cluster degradation. This was further supported by independent experiments using a fluorinated Al_2O_3 surface from which the most basic hydroxyl groups were eliminated. Structure **A** was strongly stabilized on this support, probably due to the fact that the remaining hydroxyl groups had properties comparable to those of SiO_2 surfaces which obviously favor the formation of structure **A** even after exposure to air for short periods of time. However, it cannot be excluded that adsorbed water may be involved in the cluster degradation when heating the samples.

The ir carbonyl spectra obtained for the degradation products were practically identical to those reported by Smith *et al.* (*13*) who have handled their samples without exposure to air before thermal decomposition. Since this work aimed at a more detailed structural analysis of the final degradation products rather than an understanding of the mechanism of this process, severe precautions against exposure to the atmosphere were not considered necessary. Nevertheless the samples were stored under dry N_2 and only exposed during the short time period needed to prepare the self-supporting wafers.

2. *Thermal Decomposition*

Ugo *et al.* (*12*) and Smith *et al.* (*13*), reported on the thermal decomposition of $Os_3(CO)_{12}$ attached to SiO_2 surfaces. They observed the evolution of CH_4, CO, CO_2, and C_2 and higher hydrocarbons on heating $Os_3(CO)_{12}$ on SiO_2 at 443 K under argon. The yield of C_2 and higher hydrocarbons decreased in favor of CH_4 on increasing the decomposition temperature; even under these conditions the osmium species were not transformed into metallic Os particles.

Figure 1 shows the result of a temperature-programmed decomposition experiment of sample Ib, in which the parent peaks of CH_4, CO, CO_2, and H_2O were recorded continuously on a quadrupole mass spectrometer while the sample was heated in a helium stream at a heating rate of 15 K min^{-1}. Full mass spectra were recorded occasionally for the detection of further components in the evolved gas. The signals for the various components in Fig. 1 cannot be compared quantitatively, since the mass spectrometer was coupled to the helium stream via a jet separator which works mass specifically and therefore leads to a perturbation of the real composition. Hydrogen which was probably also evolved (*12, 13*), could not be detected in the presently used system. Figure 1 shows the evolution of CH_4, CO, and CO_2 in various stages. Carbon monoxide shows a very pronounced evolution peak at 445 K with a shoulder at about 370 K and is then evolved continuously as the temperature is increased with a shoulder at 715 K followed by a steep rise up to 770 K. The CO_2 evolution curve shows maxima at 370 and 700 K before it rises steeply above 730 K. Methane is continuously produced above 340 K and also shows a steep increase at

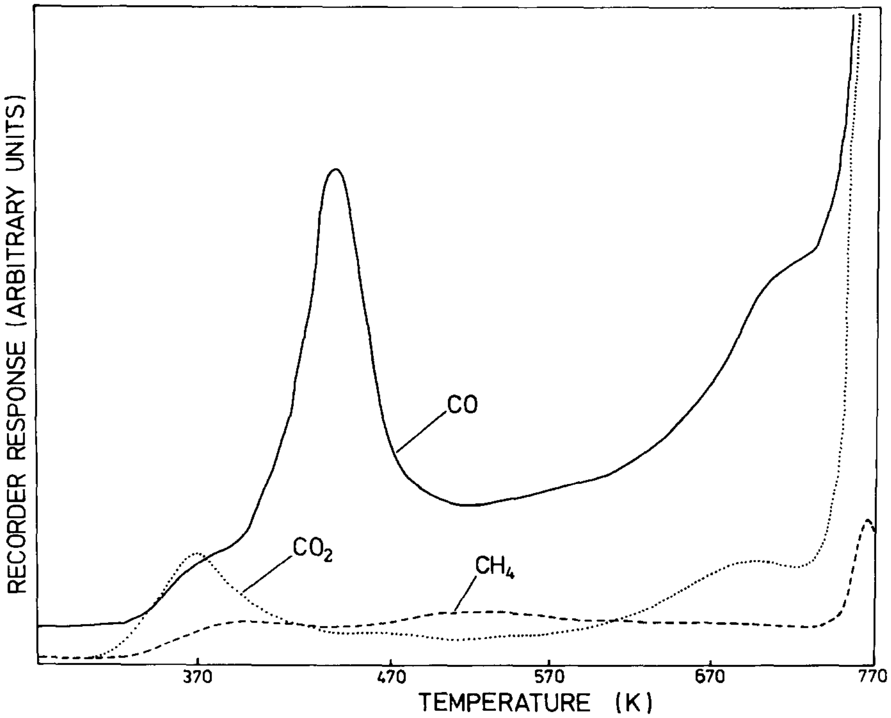


FIG. 1. Temperature-programmed decomposition of sample Ib.

high temperatures above 740 K. The full mass spectra taken at certain temperatures clearly indicate that C_2–C_4 hydrocarbons were also formed above approximately 400 K. These results compare well with those reported by Ugo *et al.* (*12*) and Smith *et al.* (*13*) for the SiO_2-supported system. A thermal degradation of the initially predominant structure A probably occurs below 470 K where the strong CO evolution occurs, the degradation products being further decarbonylated at increasing temperatures. Besides a simple decarbonylation of the surface osmium species, a water gas shift reaction (readsorbed H_2O was evolved over the entire temperature range) and CO hydrogenation must occur to account for the production of CO_2 and CH_4 and the higher hydrocarbons.

In a second experiment, CO was readsorbed at 370 K on the sample after the thermal decomposition under a pressure of 10^4 N m^{-2}. Figure 2 shows the subsequently recorded thermal desorption spectra (heating rate 15 K min^{-1}). CO, CO_2, and CH_4 are produced within the entire temperature range up to 770 K. CO_2 and CH_4 evolution traces show simultaneously occurring maxima at 440, 530, and 680 K and rise steeply above 730 K. CO evolution develops flat maxima at about 440 and 635 K and is strongly enhanced above 740 K. These desorption spectra are clearly distinct from the thermal decomposition traces. The experiments demonstrate that the degradation products of the supported trinuclear osmium cluster compound can be recarbonylated and that both the water gas shift reaction and CO hydrogenation must occur also on these new surface species.

The infrared carbonyl spectra of all Al_2O_3-supported samples undergo substantial changes during thermal treatment at temperatures above 370 K. The characteristic bands of the cluster structure A vanish and three carbonyl stretching bands near 2130, 2030–2050, and 1940–1970 cm^{-1} develop. This observation supports the con-

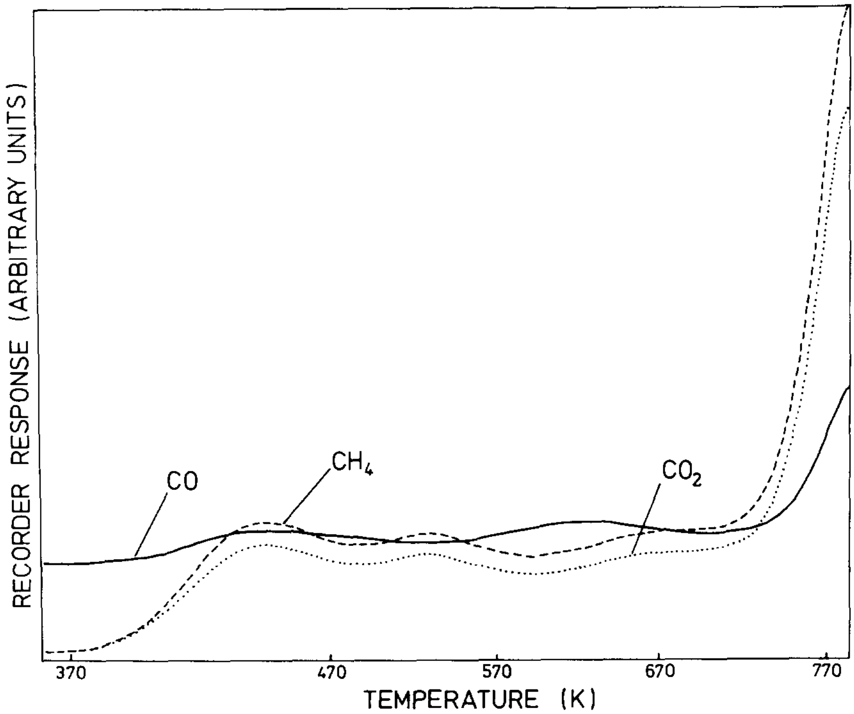


FIG. 2. Thermal desorption spectra from sample Ib after temperature-programmed decomposition and CO readsorption at 370 K.

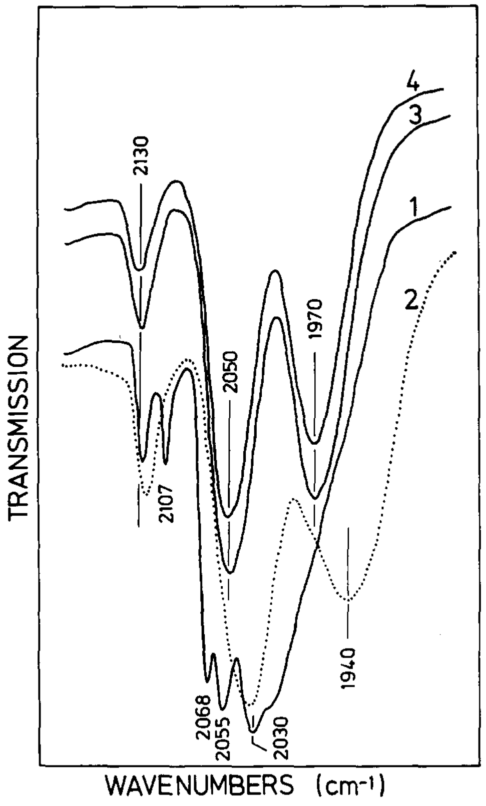


FIG. 3. Carbonyl infrared spectra of sample Ib during decarbonylation (evacuation $<10^{-2}$ N m^{-2}). (1) Room temperature, (2) 470 K, 6 h, (3) 620 K, 15 h, (4) 645 K, 15 h.

clusions from the thermal decomposition experiment, namely, the cluster degradation below 470 K. Figure 3 shows the development of these bands during decarbonylation of sample Ib. After heat treatment at 470 K *in vacuo* ($< 1.3 \times 10^{-2}$ N m^{-2}) three bands at 2125, 2031, and 1940 cm^{-1} are observed. These bands shift to higher wavenumbers at increased decarbonylation temperatures with final positions at 2130, 2050, and 1970 cm^{-1}. The intensity of the sharp high-frequency band at 2130 cm^{-1} is clearly reduced during decarbonylation, while that of the broad feature at 1970 cm^{-1} increases. These trends can be reversed on exposure to a CO atmosphere at elevated temperatures as evidenced in Fig. 4. On recarbonylation at 645 K the sharp band at 2130 cm^{-1} gradually increases in intensity at the expense of the broad feature at 1970 cm^{-1}, while the broad band in the center shifts from 2050 to 2040 cm^{-1}. The experiments therefore suggest an interconversion between at least two different osmium carbonyl species during decarbonylation–recarbonylation cycles after degradation of the originally formed cluster structure A.

This becomes still more evident on the basis of the spectra shown in Figs. 5 and 6 of sample IIa, which was prepared by room-temperature reaction of $Os_3(CO)_{12}$ with the Al_2O_3 surface. After treatment in a CO atmosphere (6.5×10^3 N m^{-2}) at 520 K the band at 1970 cm^{-1} has nearly vanished and two typical carbonyl stretching bands occur at 2128 and 2037 cm^{-1} (Fig. 5). The high-frequency band is relatively sharp (band half-width 20 cm^{-1}) as compared to the low-frequency band (band half-width 43

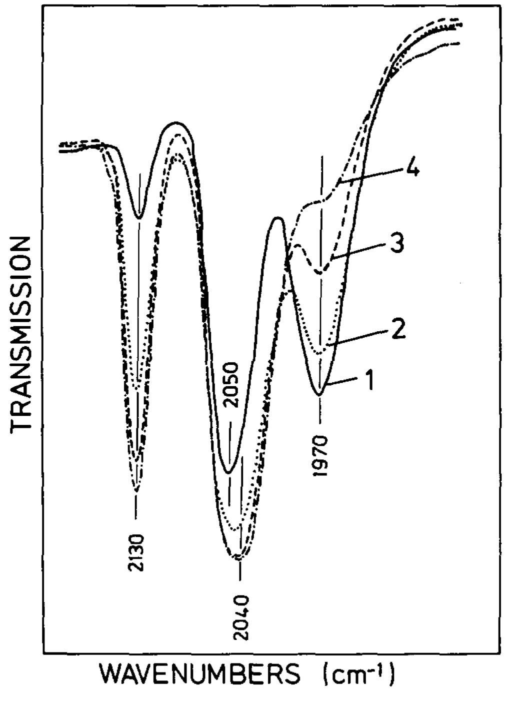


FIG. 4. Carbonyl infrared spectra of sample Ib during recarbonylation at 645 K: (1) sample evacuated $<10^{-2}$ N m^{-2} at 645 K, (2) 2.6×10^3 N m^{-2} CO for 1 h, (3) 2.6×10^3 N m^{-2} CO for 20 h, (4) 10^5 N m^{-2} CO for 20 h.

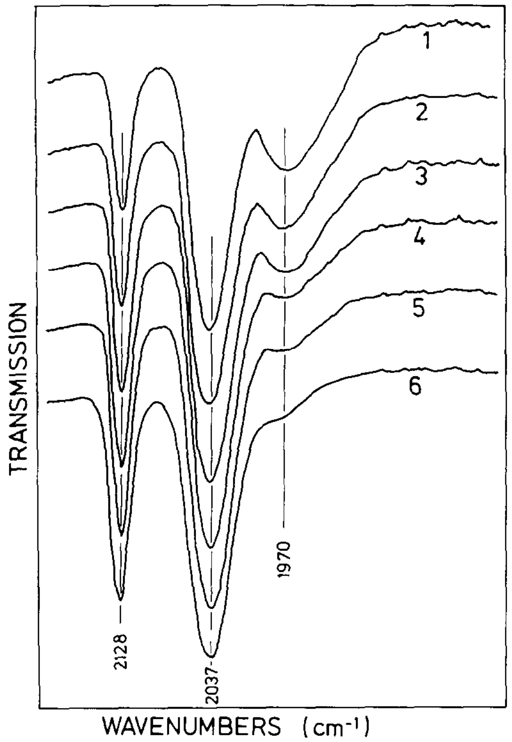


FIG. 5. Carbonyl infrared spectra of sample IIa during carbonylation: (1) after evacuation $<10^{-2}$ N m^{-2} for 16 h, (2) 6.7 × 10^3 N m^{-2} CO at 370 K for 4 h, (3) 6.7 × 10^3 N m^{-2} CO at 470 K for 4 h, (4) 6.7 × 10^3 N m^{-2} CO at 520 K for 3 h, (5) 6.7 × 10^3 N m^{-2} CO at 520 K for 15 h, (6) 6.7 × 10^3 N m^{-2} CO at 570 K for 3 h.

cm^{-1}). Subsequent decarbonylation leads to an intensity loss of the band at 2128 cm^{-1} and a shift of the band at 2037 cm^{-1} towards 2045 cm^{-1}, while the low-frequency band at 1970 cm^{-1} is being restored (Fig. 6). A linear correlation is obtained when the integrated intensity of the band at 2128 cm^{-1} is plotted against that of the band at 1970 cm^{-1} (Fig. 7), which clearly suggests the interconversion of two carbonyl species with characteristic stretching bands at 2128 and 2037 cm^{-1} for the carbonylated state and 2045 and 1970 cm^{-1} for the decarbonylated state. It is assumed that these two states can be described as mononuclear osmium tri- and dicarbonyl species, respectively:

$$Os(CO)_3 \rightleftharpoons Os(CO)_2 + CO;$$

the osmium being in the 2+ oxidation state as evidenced by quantitative gas analysis (*12, 13*) and XPS measurements (*30*). This assignment is based on the comparison of the observed infrared spectra with those of authentic mononuclear Os^{2+} carbonyl coordination compounds, which are summarized in Table 2. As in the molecular tricarbonyl compounds of the type $(Os(CO)_3X_2)_2$, the sharp high-frequency band at 2128 cm^{-1} and the broad band at 2037 cm^{-1} are assigned as the A_1 mode and the doubly degenerate $E(B_1)$ mode, respectively. These features are typical for tricarbonyls with C_{3v} symmetry (*26*). The second band doublet which is typical for the decarbonylated state, must then be assigned as the symmetric and antisymmetric carbonyl stretching modes of the dicarbonyl species (*26*).

An aggregation to metal particles obvi-

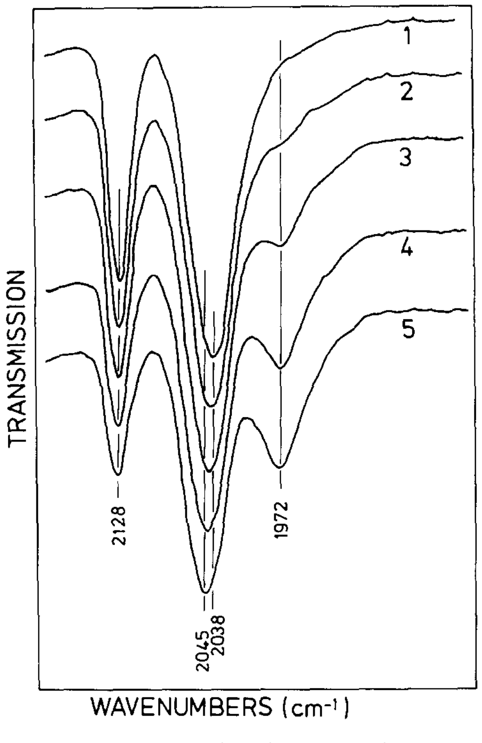


FIG. 6. Carbonyl infrared spectra of sample IIa during decarbonylation (evacuation $<10^{-2}$ N m^{-2}): (1) after treatment in 6.7 × 10^2 N m^{-2} CO at 670 K for 3 h, (2) evacuation at 570 K for 5 h, (3) 595 K for 5 h, (4) 620 K for 5 h, (5) 645 K for 8 h.

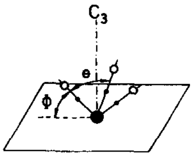
TABLE 2

Infrared Carbonyl Bands of Molecular Mononuclear Osmium Species

	Solvent	$\tilde{\nu}_{CO}$ (cm^{-1})	Ref.
$Os(CO)_3Cl_2$	CCl_4	2136, 2061	(*24*)
$Os(CO)_3Br_2$	CCl_4	2129, 2057	(*24*)
$Os(CO)_3I_2$	CCl_4	2119, 2051	(*24*)
$Os(CO)_2I_2$	Nujol mull	2119, 2045, 1988	(*24*)
$Os(CO)_2(PPh_3)_2Cl_2$	CH_2Cl_2	2040, 1975	(*24, 25*)
$Os(CO)_2(AsPh_3)_2Cl_2$	CH_2Cl_2	2038, 1971	(*24, 25*)
$Os(CO)_2(SbPh_3)_2Cl_2$	CH_2Cl_2	2031, 1966	(*24, 25*)
$Os(CO)_2(EtPh_2P)Cl_2$	CH_2Cl_2	2043, 1971	(*25*)

ously does not occur on heating the Al_2O_3-supported osmium species, in agreement with Ugo *et al.* (*12*) for SiO_2-supported catalysts. This suggests that a very strong osmium support interaction occurs. Moreover, the Os–CO bond must be extremely strong, since a complete decarbonylation was not possible on vacuum treatment at temperatures up to 770 K. Sample IIb showed the two strong bands at 2045 and 1970 cm^{-1} typical of the dicarbonyl species even after heating *in vacuo* at about 800 K. The stability of the surface carbonyl species and the strength of the metal–CO bond was also demonstrated by the fact that ^{13}CO exchange did not occur at low temperatures and was still extremely slow at temperatures around 650 K. It was therefore not possible to prove the above assignments by isotopic labelling experiments.

However, a more detailed analysis of the tricarbonyl spectra permits the estimation of some geometric structure parameters of the surface species. If a local C_{3v} symmetry is tentatively assumed for the surface tricarbonyl species with the C_3 axis perpendicular to the surface as shown below,



the angles Φ (between the Os–C bond and the surface) and Θ (between two Os–C bonds) can be estimated from the ratio of the integrated intensities $I(A_1)$ and $I(E)$ of the A_1, and E modes, respectively (*26*):

$$I(A_1)/I(E) = \tan^2\Phi = \tfrac{1}{4}\left[3\cot^2\left(\frac{\Theta}{2}\right) - 1\right].$$

As a result, the two angles were estimated to be $\Theta = 97°$ and $\Phi = 30°$. Together with the spatial requirements of the relatively bulky CO ligands and bond distances ($d_{C-O} = 1.15$ Å, $r_O = 1.50$–1.53 Å, $r_C = 1.25$–1.30 Å (*27*), $d_{Os-C} = 1.90$ Å), a tentative model for the closest approach of neighboring surface tricarbonyl complexes can be developed, which is shown in Fig. 8. The steric interaction of the CO ligands of neighboring tricarbonyl complexes is clearly evident and leads to a shortest possible Os–Os distance of about 5.9 Å which contrasts to 2.9 Å in the $Os_3(CO)_{12}$ cluster. Strong Os–Os interactions will thus not be possible in these systems and the surface species have to be considered as individual mononuclear complexes, which are apparently strongly bound to the support surface. As a matter of fact, osmium forms extremely strong bonds with oxygen. The bond dissociation

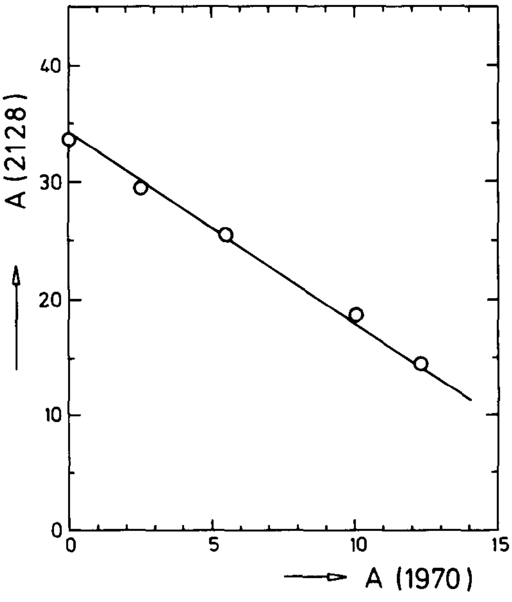


FIG. 7. Correlation between band intensities of bands at 2128 and 1970 cm^{-1} (data from Fig. 6).

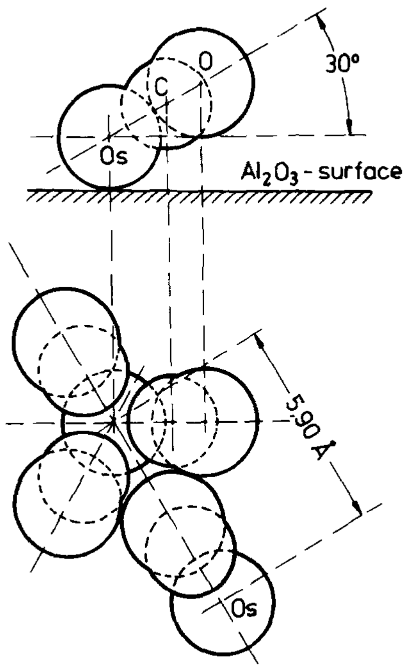


FIG. 8. Tentative model for nearest-neighbor approach of $Os(CO)_3$ species.

energy of the diatomic Os–O species was reported to be close to 590 kJ mol^{-1} (*31*). The strong osmium–support interaction *and* the steric interaction between CO ligands, which are very tightly bound to osmium atoms, must therefore be responsible jointly for the atomic dispersion of the osmium species.

This model is admittedly strongly oversimplified and ignores the structure of the Al_2O_3 surface; it is, however, a first approach towards a structural description of the surface species and explains some possible reasons for the high dispersion of osmium. Additional evidence for this comes from an electron microscopy study of the same sample which will be reported shortly (*30*). It is also interesting to note that the size of osmium very closely resembles that of the O^{2-} ions of the Al_2O_3 surface. Moreover, the distance between neighboring doubly or triply bridging sites on the low-index faces of the Al_2O_3 surface is approximately 2.85 Å (*20*). The predicted Os–Os distance of about 5.9 Å can thus be approached very closely if the osmium carbonyl complexes are being placed into every second site bridging either two or three O^{2-} ions on the surface.

The steric restrictions for the approach of the surface complexes become less stringent when the dicarbonyl species is being formed. Assuming a local C_{2v} symmetry for this complex, the angle Θ between the two Os–C bonds can be calculated (*26*) from

$$I_{sym}/I_{asym} = \cot^2\left(\frac{\Theta}{2}\right)$$

and turns out to be 92°. If a vertical orientation of the symmetry axis relative to the surface is assumed, two relative orientations of the dicarbonyl complexes would be possible with the planes containing the CO ligands either perpendicular or parallel to each other. In the first case, the steric repulsion of the CO ligands would allow for a shortest Os–Os distance of 4.2 Å, while in the second case rows of complexes with an Os–Os distance of only about 3.0 Å would be possible.

3. The Frequency Range 1900–1000 cm^{-1}

It is most interesting to mention that the formation of carbonate or bicarbonate species could not be detected after exposure of the samples to a CO atmosphere at elevated temperatures. This shows that the observed CO_2 evolution cannot be due simply to a thermal decomposition of surface carbonates or bicarbonates chemisorbed on the Al_2O_3 support. However, strong bands developed at 1595, 1395, and 1380 cm^{-1} on heating sample IIb at 648 K in CO. The band intensities were dependent on the CO pressure. This band pair must be assigned as the antisymmetric and symmetric stretching vibrations of a formate species (*28*). A formate species would certainly not form during CO adsorption on pure Al_2O_3 surfaces; it had, however, been detected as an intermediate of the water gas shift reaction by Amenomiya (*29*) when Al_2O_3 was exposed to CO_2 + H_2 mixtures between 570 and 770 K. The formation of the formate species on the present system is therefore not surprising since the water gas shift reaction with production of H_2 and CO_2 does occur, although it could still not be tested whether the formate acts as an intermediate or not.

IV. CONCLUSIONS

The reaction of $Os_3(CO)_{12}$ with the surface of Al_2O_3 leads initially to the formation of structure A which can be degraded by thermal treatments. Degradation products are tri- and dicarbonyl mononuclear osmium complexes which can be reversibly interconverted. Strong evidence has been found for very strong osmium–support interactions, which must be responsible for the atomic dispersion of the species. The raft-like structures observed by Prestridge *et al.* (*8*) for supported osmium catalysts may be due to this strong osmium–support interaction. However, for the present systems, the steric repulsion between CO ligands appears strongly to influence the Os–Os distance, too. This suggests that mononuclear carbonyl complexes may possibly play an important role for CO reactions at high pressures on supported osmium catalysts. These complexes could perhaps be formed from small particles or the raft-like structures, when coordination of CO ligands to metal atoms and the repulsive forces between them overcome attractive forces between the metal atoms. The "nuclearity" of the surface species present under working conditions may critically determine activity and selectivity of the catalysts.

ACKNOWLEDGMENTS

This work was financially supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Stiftung Volkswagenwerk. One of us (Y.Z.) gratefully acknowledges a grant given by the German Academic Exchange Service (DAAD). We also wish to thank Mr. R. Hierl for his assistance with the thermal decomposition experiments.

REFERENCES

1. Basset, J. M., and Ugo, R., *in* "Aspects of Homogeneous Catalysis" (R. Ugo, Ed.), Vol. 3, p. 137. Reidel, Boston, Mass., 1977.

2. Ichikawa, M., *Bull. Chem. Soc. Japan* **51**, 2268 (1978).

3. Ichikawa, M., and Shikakura, K., *in* "Proceedings, 7th International Congress on Catalysis, Tokyo, 1980," Part B, p. 925. Kodansha, Tokyo/Elsevier, Amsterdam, 1981.

4. Ichikawa, M., *J. Catal.* **59**, 67 (1979).

5. Hugues, F., Bussière, P., Basset, J. M., Commereuc, D., Chauvin, J., Bonneviot, L., and Olivier, D., *in* Proceedings, 7th International Congress on Catalysis, Tokyo, 1980," Part A, p. 418. Kodansha, Tokyo/Elsevier, Amsterdam, 1981.

6. Kavtaradze, N. N., and Sokolova, N. P., *Dokl. Phys. Chem.* **168**, 295 (1966).

7. Guerra, C. R., and Schulman, J. H., *Surface Sci.* **7**, 229 (1967).

8. Prestridge, E. B., Via, G. H., and Sinfelt, J. H., *J. Catal.* **50**, 115 (1977).

9. Via, G. H., Sinfelt, J. H., and Lytle, F. W., *J. Chem. Phys.* **71**, 690 (1979).

10. Brown, S. C., and Evans, J., *J. Chem. Soc. Chem. Commun.*, 1063 (1978).

11. Pierantozzi, R., McQuade, K. J., Gates, B. C., Wolf, M., Knözinger, H., and Ruhmann, W., *J. Amer. Chem. Soc.* **101**, 5436 (1979).

12. Ugo, R., Psaro, R., Zanderighi, G. M., Basset, J. M., Theolier, A., and Smith, A. K., *in* "Fundamental Research in Homogeneous Catalysis" (M. Tsutsui, Ed.), Vol. 3, p. 579, Plenum, New York/London, 1979.

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

14. Besson, B., Moraweck, B., Smith, A. K., Basset, J. M., Psaro, R., Fusi, A., and Ugo, R., *J. Chem. Soc. Chem. Commun.* 569 (1980).

15. Deeba, M., and Gates, B. C., *J. Catal.* **67**, 303 (1981).

16. Watson, P. L., and Schrader, G. L., *J. Mol. Catal.* **9**, 129 (1980).

17. Bryan, E. G., Johnson, B. F. G., and Lewis, J., *J. Chem. Soc. Dalton Trans.*, 1328 (1977).

18. Knox, S. A. R., Koepke, J. W., Andrews, M. A., and Kaesz, H. D., *J. Amer. Chem. Soc.* **97**, 3942 (1975).

19. Knözinger, H., Stolz, H., Bühl, H., Clement, G., and Meye, W., *Chem. Ing. Tech.* **42**, 548 (1970); Knözinger, H., *Acta Cient. Venez.* **24**, Suppl. 2, 76 (1973).

20. Knözinger, H., and Ratnasamy, P., *Catal. Rev. Sci. Eng.* **17**, 31 (1978).

21. Azam, K. A., Deeming, A. J., Kimber, R. E., and Shukla, P. R., *J. Chem. Soc. Dalton Trans.*, 1853 (1976).

22. Johnson, B. F. G., and Lewis, J., *J. Chem. Soc. A*, 2859 (1968).

23. Crooks, G. R., Johnson, B. F. G., Lewis, J., and Williams, I. G., *J. Chem. Soc. A,* 797 (1969).
24. Hales, L. A. W., and Irving, R. J., *J. Chem. Soc. A,* 1932 (1967).
25. Tripathi, S. C., Srivastava, S. C., Mani, R. P., and Shrimal, A. K., *Inorg. Chim. Acta* **15,** 249 (1975).
26. Braterman, P. S., "Metal Carbonyl Spectra." Academic Press, London/New York/San Francisco, 1975.
27. Chini, P., *Gazz. Chim. Ital.* **109,** 225 (1979).
28. Greenler, R. G., *J. Chem. Phys.* **37,** 2094 (1962).
29. Amenomiya, Y., *Appl. Spectrosc.* **32,** 484 (1978).
30. Knözinger, H., Zhao, Y., Tesche, B., Barth, R., Epstein, R., Gates, B. C., and Scott, J. P., *Faraday Discuss. Chem. Soc.*, **72,** in press.
31. Brewer, L., and Rosenblatt, G. M., *Advan. High Temp. Sci.* **2,** 1 (1969).