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Chemisorption and Catalysis by Metal Clusters

II. Chemisorption of Carbon Monoxide and of Oxygen by Supported Osmium Clusters Derived from $Os_3(CO)_{12}$ and from $Os_6(CO)_{18}$

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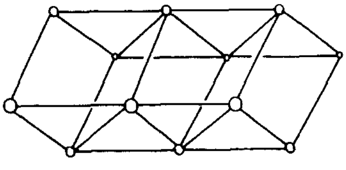
Carbon monoxide and oxygen have been chemisorbed at 293 K on the high-nuclearity carbonyl-protected clusters (the various "species A") obtained by heating *in vacuo* to 523 K $Os_3(CO)_{12}$ or $Os_6(CO)_{18}$ impregnated on silica, alumina, or titania. The adsorption isotherms have a conventional appearance, but most are composed of a primary and a secondary region. Material adsorbed in the secondary region is removed by evacuation at room temperature whereas that adsorbed in the primary region is removed by evacuation at elevated temperatures. For species A/alumina and species A/titania the primary region is complete and the secondary region commences when the pressure over the adsorbent is 0.2 Torr. Species A/silica gave no secondary region in oxygen adsorption. Adsorption and subsequent temperature-programmed desorption of $[^{18}O]CO$ occurred without any dilution by $[^{16}O]CO$, indicating that ligand-$[^{16}O]CO$ and adsorbed-$[^{18}O]CO$ do not exchange even at elevated temperatures. The two species A/aluminas catalyzed oxygen isotope exchange at 293 K. From the experimental evidence it is deduced that carbon monoxide and oxygen each adsorbs molecularly in both the primary and the secondary regions. In the primary region carbon monoxide adsorption occurs at osmium sites on the cluster framework, whereas in the secondary region it occurs at ligand-carbon bonded to osmium. For oxygen, adsorption in the primary region is again at osmium sites on the cluster framework but that in the secondary region is at osmium sites of the cluster framework suitably modified as a result of the support–cluster interaction.

INTRODUCTION

When $Os_3(CO)_{12}$ or $Os_6(CO)_{18}$ is impregnated onto silica, alumina, or titania in the manner described in Part I, and heated to 523 K *in vacuo* or in a stream of helium, coordinatively unsaturated osmium clusters of high nuclearity are obtained (*1*). These clusters appear to be a family of related species ("species A") formed by the dimerization or trimerization of Os_6-units and described by the empirical formula $Os_n(CO)_{an}C_{bn}$ where $2.0 < a < 2.9$, $0.1 < b < 0.4$, and n has the most likely value of 12. The variability of a and of b within these limits represents the differences between the compositions of this family of species A when supported on silica, alumina, and titania.

Two speculative structures were proposed in Part I (*1*) for the osmium framework of species A; one, (I), is a two-layer 3 × 2 × 2-atom structure containing equal numbers of osmium atoms in formal −1, 0, and +1 oxidation states, and the other, (II),



(I)

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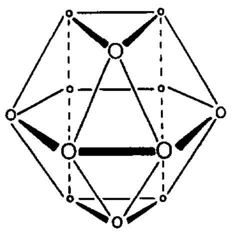


(II)

is a three-layer structure containing osmium atoms in the zero oxidation state only and having the symmetry of a unit of the close-packed hexagonal structure in which metallic osmium crystallizes. Part I presented evidence for the existence of chemical support–cluster interactions, but not for the distribution of CO-ligands or of C-ligands over the osmium framework.

These species A chemisorb both carbon monoxide and oxygen at room temperature. The character of the adsorption isotherms provides evidence concerning (i) the nature of the adsorbed states involved, (ii) the inert character of the CO-ligands that derive from the initial cluster compounds and which prevent sintering of clusters to give conventional polycrystalline metal, and (iii) the participation of C-ligands as adsorption sites in some circumstances. The catalytic properties of these materials have been the subject of a preliminary communication (*2*) and will be described in Part III.

EXPERIMENTAL

Chemisorption was measured by the volumetric method. The glass/steel adsorption vessel (volume 387.3 cm^3) was connected to (i) a stainless-steel vacuum system capable of attaining 10^{-8} Torr (1 Torr = 133.3 Nm^{-2}), (ii) a separately pumped, calibrated, glass dosing system, and (iii) a modified AEI MS3 mass spectrometer via a leak device. Gas pressures were measured by use of a calibrated thermal conductivity gauge (10^{-3} to 2 Torr) and a pressure transducer (2 to 10 Torr).

$Os_3(CO)_{12}$ and $Os_6(CO)_{18}$ were prepared by literature methods (*3, 4*). Supports used were alumina (Aluminium Oxid C, Degussa, 97 ± 5 m^2g^{-1}), silica (Cab-O-Sil, 110 ± 5 m^2g^{-1}), and titania (Tioxide, 43 ± 5 m^2g^{-1}). The titania was prepared from an organic titanate and contained <100 ppm silica.

CO (99.95%), $[^{18}O]CO$ (99% isotopic purity), O_2 and $[^{18}O]O_2$ (each 99.9%) were used as received after mass spectrometric validation.

The impregnation procedure has been described (*1*): loadings achieved were 2% by weight Os. Samples of freshly impregnated material (typically 0.30 g) were placed in the adsorption vessel, evacuated, heated to 523 K over a period of 0.75 h, maintained at that temperature for 0.5 h under dynamic pumping, and then cooled to room temperature. All chemisorptions and exchange reactions described in this paper were conducted at room temperature.

This procedure of heating the freshly impregnated materials to 523 K gives the species A described in the Introduction; *no evidence for the retention of osmium as the original cluster compounds remains* (*1*). Thus, all adsorbents used in this work were supported high-nuclearity clusters. It is, however, useful to keep in view the original cluster compound from which the various species A were formed; accordingly, we describe the adsorbents as, for example, "species A derived from $Os_3(CO)_{12}$/alumina."

RESULTS

The isotherm for carbon monoxide adsorption at 293 K on species A derived from $Os_3(CO)_2$/alumina is shown in Fig. 1. Adsorption was complete at a pressure of about 4 Torr.

Partial isotherms for carbon monoxide chemisorption at 293 K on species A derived from $Os_3(CO)_{12}$/titania and on $Os_6(CO)_{12}$/alumina are shown in Fig. 2*a* (curves A and B). After the measurement of isotherm A the adsorption vessel was evacuated at 293 K to 10^{-8} Torr for 24 h and the adsorption measurements repeated; curve

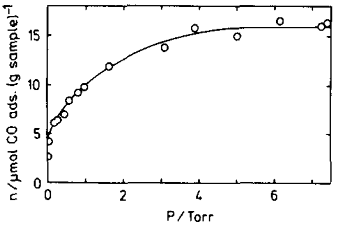


FIG. 1. Isotherm for the adsorption of carbon monoxide at 293 K on species A derived from $Os_3(CO)_{12}$/alumina.

C was thereby obtained. The displacement of C with respect to A shows that a considerable quantity of adsorbed-CO, in the region of 15–25 µmol (g sample)$^{-1}$, is too strongly adsorbed to be removed by this pumping procedure. After measurement of isotherm C, the sample was pumped briefly at 293 K, heated under vacuum to 523 K, and then cooled to 293 K. Further adsorption of carbon monoxide gave an isotherm identical to A, from which we conclude that the heat treatment caused the desorption of all the strongly adsorbed CO. These procedures of adsorption, partial or complete desorption, and regeneration of the sample in its initial state could be repeated time and again. It thus became clear that carbon monoxide was adsorbed in two states distinguishable by their strengths of adsorption; the region in which adsorption was strong we term the *primary region,* and that in which adsorption was relatively weak, the *secondary region.* The limits of these regions are defined in the Discussion.

In Part 1 it was established that ligand-CO/Os-atom ratios for freshly prepared species A (on which no carbon monoxide had been adsorbed) was >2.0. It was clearly important to establish whether exchange took place between ligand-CO and adsorbed-CO following carbon monoxide adsorption. Accordingly isotherm A was reproduced by adsorption of [^{18}O]CO in place of [^{16}O]CO; the sample was then pumped at 293 K and heated under vacuum to 523 K. Figure 3 shows the manner of [^{18}O]CO desorption as a function of temper-

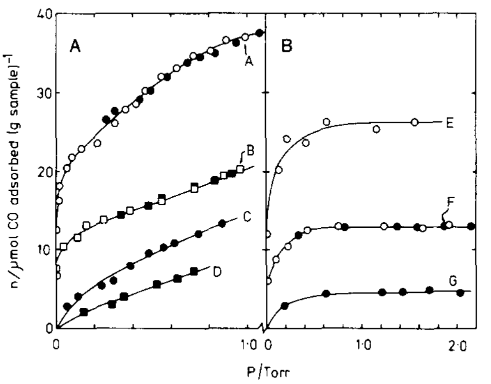


FIG. 2. (A) Partial isotherms for CO adsorption at 293 K. Curve A (open points), adsorption on $Os_3(CO)_{12}$/titania; curve B (open points), adsorption on $Os_6(CO)_{18}$/alumina; curve C, adsorption of CO on $Os_3(CO)_{12}$/titania after the measurement of isotherm A and thorough evacuation of the adsorbent at 293 K (for details see text); curve D, adsorption of CO on $Os_6(CO)_{18}$/alumina after measurement of an oxygen isotherm analogous to F and thorough evacuation. (B) Isotherms for O_2 adsorption at 293 K. Curve E, adsorption on $Os_3(CO)_{12}$/titania; curve F (open points), adsorption on $Os_6(CO)_{18}$/alumina; curve G, adsorption of O_2 on $Os_6(CO)_{18}$/alumina after measurement of isotherm F and thorough evacuation of the adsorbent at 293 K. Filled points on curves A, B, and F represent the translation of curves C, D, and G, respectively, to new coordinates as described under Discussion. Isotherms C, D, and G represent adsorption in secondary regions.

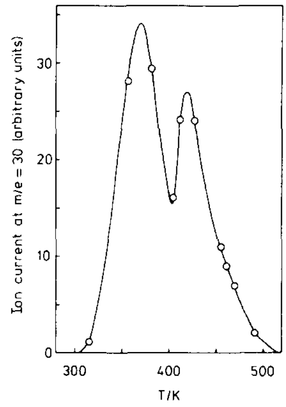


FIG. 3. Temperature-programmed desorption of [^{18}O]CO adsorbed in the primary region on species A derived from $Os_3(CO)_{12}$/titania; a small background ion current at *m/e* = 28 remained constant throughout the temperature scan. Duration of experiment = 0.74 h.

ature measured using the mass spectrometer linked to the adsorption vessel. No desorption of [^{16}O]CO was detected. Thus, no equilibration of ligand-CO with adsorbed-CO occurs even at elevated temperatures. Analogous information was also obtained for [^{18}O]CO adsorption on species A derived from $Os_6(CO)_{18}$/alumina.

Oxygen chemisorption at 293 K was examined on the same samples. Figure 2*b*, curves E and F, represents adsorption on species A derived from $Os_3(CO)_{12}$/titania and $Os_6(CO)_{18}$/alumina. Plateaus were achieved at pressures of about 0.6 Torr. Following the measurement of isotherm F, the sample was pumped at 293 K and further adsorption of oxygen gave curve G. About one-third of the adsorbed oxygen was removed by pumping at 293 K. The remaining two-thirds underwent desorption (mostly as molecular oxygen but accompanied by very small quantities of carbon dioxide) when the evacuated sample was heated to 523 K; subsequent oxygen adsorption at 293 K reproduced curve F exactly. Thus oxygen adsorption on these samples, like that of carbon monoxide, shows primary and secondary regions.

Oxygen adsorption on species A derived from $Os_6(CO)_{18}$/silica gave an isotherm similar to curve F, but after evacuation at 293 K no further oxygen could be adsorbed; thus it appears that there was no secondary region for oxygen adsorption in this case.

The oxygen isotope exchange reaction [Reaction (1)] occurred rapidly at 293 K when

$$[^{16}O]O_2 + [^{18}O]O_2 \rightleftharpoons 2[^{16}O,^{18}O]O_2 \quad (1)$$

10 Torr of a 1 : 1 mixture of reactants was adsorbed onto species A derived from $Os_3(CO)_{12}$/alumina and from $Os_6(CO)_{18}$/alumina; equilibrium was achieved after 0.3 h. No exchange occurred under these conditions in the presence of species A derived from $Os_3(CO)_{12}$/silica, $Os_6(CO)_{18}$/silica, $Os_3(CO)_{12}$/titania, or $Os_6(CO)_{18}$/titania.

In a further experiment, [^{16}O]O_2 was adsorbed onto species A derived from $Os_6(CO)_{18}$/alumina; material adsorbed in the secondary region was removed by evacuation at 293 K, and was then replaced by [^{18}O]O_2. No exchange resulting in the appearance of oxygen-16 in the gas phase occurred, which demonstrates that the exchange reactions described above involve only oxygen adsorbed in the secondary region.

Adsorption of carbon monoxide in the secondary region occurred on species A saturated by strongly adsorbed oxygen. Species A derived from $Os_6(CO)_{18}$/alumina was (i) characterized with respect to carbon monoxide adsorption (curve analogous to B, Fig. 2A), (ii) regenerated by heating to 523 K under vacuum, (iii) characterization with respect to oxygen adsorption (curve analogous to F), (iv) pumped at 293 K to remove reversibly adsorbed oxygen, and (v) exposed to CO at 293 K. Adsorption of carbon monoxide occurred on the sample thus saturated by oxygen (curve D, Fig. 2A); the isotherm, which is similar in type to that given in curve C, represents a secondary adsorption region occurring in the presence of oxygen adsorbed in a primary region.

Attempts to chemisorb oxygen at 293 K onto species A derived from $Os_6(CO)_{18}$/titania containing carbon monoxide adsorbed in a primary region failed.

The capacity of species A to chemisorb carbon monoxide at 293 K was enhanced by an oxygen adsorption/desorption cycle. After several cycles of carbon monoxide adsorption/desorption and oxygen adsorption/desorption, a limiting value for the extent of carbon monoxide was obtained. Figure 4 shows partial isotherms for carbon monoxide adsorption for all six cluster/support combinations. The results quoted in Table 3 of Part I (*1*) were obtained from this figure, reading off the extents of adsorption at P_{CO} = 0.2 Torr (for reasons discussed below).

DISCUSSION

Isotherms shown in Fig. 2 exhibit two regions, a secondary region in which adsor-

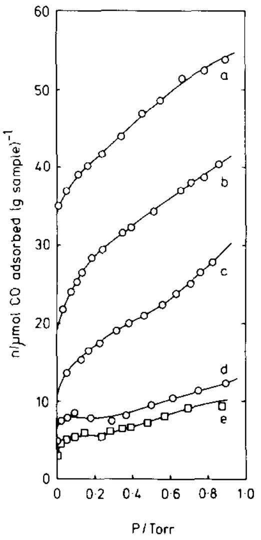


FIG. 4. Partial isotherms for carbon monoxide adsorption at 293 K after activation by oxygen (see text) for species A derived from various cluster support combinations: (a) $Os_3(CO)_{12}$/titania; (b) $Os_6(CO)_{18}$/alumina; (c) $Os_3(CO)_{12}$/silica; (d) $Os_6(CO)_{18}$/titania; (e) $Os_3(CO)_{12}$/alumina. The curve for $Os_6(CO)_{18}$/silica closely followed (e) and is not shown.

bate can be removed chemically unchanged by evacuation of the adsorbent at room temperature, and a primary region in which adsorbate undergoes desorption unchanged (carbon monoxide) or substantially unchanged (oxygen) but only at elevated temperatures.

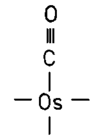
Figure 2 shows that curve C, which represents the secondary region of carbon monoxide adsorption on species A derived from $Os_3(CO)_{12}$/titania, lies on curve A if its origin is translated to the point (P/Torr = 0.2, n/μmol (g sample)$^{-1}$ = 22.5). Similarly, curve G, which represents the secondary region of oxygen adsorption on species A derived from $Os_6(CO)_{18}$/alumina, lies on curve F if its origin is translated to the point (P/Torr = 0.2, n/μmol (g sample)$^{-1}$ = 9.0). Furthermore, curve D which represents the secondary region of carbon monoxide adsorption on species A derived from $Os_6(CO)_{18}$/alumina lies exactly on curve B if its origin is translated to the point (P/Torr = 0.2, n/μmol (g sample)$^{-1}$ = 12.5) despite the fact that the adsorbate in the primary region in this instance was oxygen, not carbon monoxide. These observations demonstrate that the onset of the secondary region of adsorption occurs at P = 0.2 Torr and that the primary region is complete at that pressure.

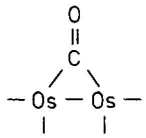
Material adsorbed in the primary region was not removed by pumping for 24 h, from which we conclude that these adsorbed species were not in equilibrium with those adsorbed in the secondary region.

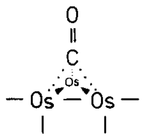
A threshold value of 0.2 Torr for regions of secondary adsorption on other clustered adsorbents involving ruthenium will be presented in a later paper; the effect may be quite general.

Carbon Monoxide and Oxygen Adsorptions in the Primary Region

When a given species A is prepared by the standard procedure of thermal activation, its adsorption capacity in respect of the primary adsorption region is similar whether the adsorptive is CO or O_2. For example, in Fig. 2, the terminations of the primary regions for $Os_3(CO)_{12}$/titania occur at n = 22.5 μmol (g sample)$^{-1}$ both for carbon monoxide adsorption and for oxygen adsorption. For $Os_6(CO)_{12}$/alumina, the comparable values are 12.5 μmol (g sample)$^{-1}$ for carbon monoxide adsorption and 9.0 μmol (g sample)$^{-1}$ for oxygen adsorption. Adsorption of carbon monoxide or of oxygen in the primary region occurs at the same sites, as witnessed by the observations (i) that no oxygen adsorption occurs on species A containing a completed primary region of adsorbed carbon monoxide, and (ii) that only carbon monoxide adsorption in a secondary region occurs on species A containing a completed primary region of adsorbed oxygen. We argued in Part I (*1*), from spectroscopic evidence (particularly the existence of an absorption band at 613 nm in the ultraviolet reflectance spectrum of species A exposed to CO and evacuated) that CO molecules chemisorbed on species A without dissociation in one or


(A)


(B1)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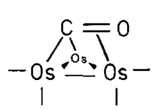
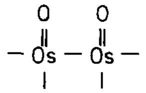
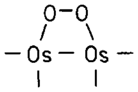

(B3)

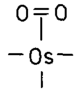
more configurations involving multiple bonding of the adsorbate to the adsorbent. Ligand-CO (structure A) and adsorbed-CO (structure B) are thus clearly distinguishable. Furthermore, the selective retrieval of [^{18}O]CO in the temperature-programmed desorption experiment (Fig. 3) demonstrates the absence of ligand-adsorbate exchange even at elevated temperatures.

The reproducibility of the CO adsorption isotherm after complete desorption of CO by heating to 523 K *in vacuo* indicates that the accommodation of adsorbed-CO by species A does not modify the environment of the CO adsorption sites.

The state of oxygen adsorbed in the primary region may in principle be represented by any of structures (C), (D), or (E).


(C)


(D)


(E)

The ultraviolet reflectance spectrum of species A containing oxygen adsorbed in the primary region gave a band at about 600 nm which suggests the presence of a nondissociatively adsorbed state of oxygen. No new charge transfer bands appeared such as might accompany the formation of structure (C). Furthermore, from measurements of the catalytic activity of various species A (*2*) we know that these materials exhibit catalytic activities that are not poisoned by air. In this sense they differ from conventional polycrystalline supported osmium catalysts which *are* poisoned by air. From these observations we conclude that electron availability at the osmium site in species A is insufficient to sustain the dissociative adsorption of oxygen (structure (C)) normally expected at Group 8 metal surfaces, and that adsorption occurs without dissociation (structures (D) or (E)). It must be recalled that the number of carbonyl and carbon ligands bonded to the osmium cluster framework of each species A is considerable and that on average, most osmium atoms which function as sites for carbon monoxide or oxygen adsorption will also be bonded to one or more CO-ligands. Thus, a proposition that reduced electron availability on the part of osmium atoms in species A enables adsorbed oxygen to achieve molecular adsorption but not structure (C) is not unreasonable. The bonding requirement for structure (D) would not differ greatly from that of (B2) or (B3).

Curiously, repetitive oxygen adsorptions increased the capacity of species A to adsorb carbon monoxide in the primary region, but the capacity to adsorb oxygen remained constant. The removal of oxygen at elevated temperatures caused some oxidation of ligand-CO to gaseous CO_2, but the amount of CO_2 produced was far too small to permit the increased carbon monoxide adsorption to be ascribed to an increased chemisorption site density. Moreover, such an effect would presumably have led to an increased capacity for oxygen adsorption in the primary region, which was not observed. We thus suppose that the processes that occur during oxygen desorption cause migration of CO-ligands over the cluster from the locations that they initially occupy (as a result of the thermal activation by which the species A are prepared) to other locations such that the groups of osmium atoms capable of sustaining structures (B) of adsorbed-CO are increased.

Such a migration of ligand-CO under the influence of an adsorbate other than carbon monoxide is comparable to behavior observed in infrared and temperature-programmed desorption studies of the interaction of CO with Pt/silica and with Pt/alumina (*5*, *6*). In those studies the presence of another gas, e.g., Ar (*5*) or N_2 (*5*, *6*) resulted in the removal of a fraction of a layer of adsorbed-CO, and this behavior was interpreted as the redistribution of adsorbed-CO over the platinum surface.

Carbon Monoxide Adsorption in the Secondary Region

Adsorption of carbon monoxide in the secondary region is comparatively weak, and the question immediately arises as to whether the adsorption sites utilized here are osmium atoms (as is the case for adsorption in the primary region) or some other reactive function of species A. We rule out the possibility that adsorption in the secondary region constitutes spillover onto the support on a combination of two grounds, viz., (i) no adsorption occurs on the supports in the absence of species A and (ii) the extent of the secondary region differs depending on whether, *for a given support*, species A has been derived from $Os_3(CO)_{12}$ or from $Os_6(CO)_{18}$. The latter point is the more powerful. If the secondary region represented spillover from the Os_{12}-cluster framework of species A to a given support, then it would not be expected that the extent of the spillover would vary by a factor of 5 depending on the parentage of species A. If we rule out both osmium atoms and the support as the sites for carbon monoxide adsorption in the secondary region, we are left with the carbon content of species A as the likely source of such sites. In Table 1 the number of carbon atoms present per gram of sample is compared with the number of carbon monoxide molecules adsorbed in the secondary region. In five of the six cases there is a fair correspondence between the number of carbon atoms present and the number of CO molecules adsorbed in the secondary region. This is *prima facie* evidence that carbon atoms provide the sites for CO adsorption in the secondary region. Evidence that carbon monoxide may coordinate to carbon in the cluster μ^4-carbido-μ^2-carbonyl-dodecacarbonyltetrairon ($Fe_4(CO)_{13}C$) during the conversion of $[Fe_6(CO)_{16}C]^{2-}$ to $Fe_4(CO)_{12}CCO_2Me$ has been presented by Bradley and coworkers (*7*, *8*), and this presents the closest analog from stoichiometric chemistry of which we are aware. It is to be expected that adsorption of CO on carbon would be weaker than on osmium, and hence a basis for a distinction between the primary and secondary regions becomes clear.

TABLE 1

Carbon Contents of the Various Species A and the Measured Extents of Carbon Monoxide Adsorption in the Secondary Region

Source of species A	Support	C present[a] [10^{18} atoms (g sample)$^{-1}$	CO adsorbed 10^{18} molecules (g sample)$^{-1}$
$Os_3(CO)_{12}$	Alumina	9.2	6.5
$Os_3(CO)_{12}$	Silica	5.5	16.3
$Os_3(CO)_{12}$	Titania	11.0	14.3
$Os_6(CO)_{18}$	Alumina	26.0	16.1
$Os_6(CO)_{18}$	Silica	9.5	6.7
$Os_6(CO)_{18}$	Titania	8.2	7.2

[a] Measured assuming that CO_2 evolved in the preparation of each species A arose solely from the reaction $2CO = C + CO_2$ (*1*).

Oxygen Adsorption in the Secondary Region, Support Effects, and Oxygen Isotope Exchange

Oxygen adsorption in the secondary region is different both in magnitude and kind from carbon monoxide adsorption in the secondary region. For oxygen, the secondary region is smaller than the primary (the reverse of the situation for CO); indeed, there was no adsorption in the secondary region on species A derived from $Os_6(CO)_{18}$/silica. The primary region of oxygen adsorption does not extend to coverage of ligand-C sites because a normal secondary region of carbon monoxide adsorption can be established on species A (derived from $Os_6(CO)_{18}$/alumina) which

TABLE 2

Support Effects and Related Phenomena

Source of species A	Support	Ligand-CO absorption frequency[a] (cm^{-1})	Z^b	Fraction of oxygen adsorption in the secondary region	Oxygen isotope exchange rate at 293 K
$Os_6(CO)_{18}$	Silica	1963	Zero	Zero	Zero
$Os_3(CO)_{12}$	Titania	1946	0.12	0.15	Zero
$Os_6(CO)_{18}$	Alumina	1944	0.24	0.25	Fast

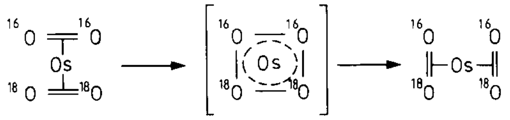
[a] The low frequency band of the three band spectrum (*1*) attributed to $Os^{-I}—C\equiv O$.

[b] The number of C_2-hydrocarbon molecules formed in the preparation of each species A cluster during temperature-programmed decompositions (*1*).

contains oxygen adsorbed in the primary region. However, the reverse of this experiment fails: no secondary region for oxygen adsorption occurs on species A (derived from $Os_6(CO)_{18}$/titania) which contains carbon monoxide adsorbed in the primary region, although a normal secondary region of carbon monoxide adsorption on ligand-C can be established (see above). Thus, carbon ligands of species A are not sites for oxygen adsorption in the secondary region.

A consideration of support-cluster interactions in these materials provides a more positive approach to an understanding of the nature of the sites for oxygen adsorption in the secondary region. Some relevant information is assembled in Table 2. First, in Part I (*1*), we argued that shifts in the carbonyl stretching frequency for CO-ligands bonded to osmium atoms in the formal −I oxidation state (column 3) provided evidence for electron donation from the supports to the species A clusters. On this basis, the extent of electron donation increases in the order silica < titania < alumina. Second, also in Part I (Table 2), we reported that C_2-hydrocarbons are produced when that support–cluster interaction is established in a temperature-programmed decomposition, the hydrogen for hydrocarbon formation coming from hydroxyl groups at the surface of the support. The column headed Z in Table 2 (this paper) contains values for the number of C_2-hydrocarbon molecules formed during the preparation of each species A cluster; again the sequence for the supports is silica < titania < alumina. Comparison of the values of *Z* with the fraction of the total oxygen adsorption at saturation that occurs in the secondary region (Table 2, columns 4 and 5) shows values that are closely similar. This demonstrates that the sites for oxygen adsorption in the secondary region occur on those species A clusters which experience the strongest support–cluster interaction.

The occurrence or otherwise of oxygen isotope exchange at 293 K can be viewed as another monitor of the support–cluster interaction because it occurred only when the interaction was strong, i.e., with species A derived from $Os_3(CO)_{12}$/alumina and $Os_6(CO)_{18}$/alumina. Exchange involves only molecules that are reversibly adsorbed in the secondary region (because no exchange occurred between $[^{16}O]O_2$ adsorbed in a primary region and $[^{18}O]O_2$ adsorbed in a secondary region). Since oxygen adsorption in the primary region appears to be nondissociative, that in the secondary region, which is weaker, must also be nondissociative. We thus distinguish structures (D) and (E) as the most likely structures for oxygen adsorbed in the primary and secondary regions, respectively, and propose that exchange occurs by the osmium-mediated molecular process shown in Eq. (2)



The absence of exchange over the species A/titanias which, nevertheless, show a secondary adsorption region and which may contain oxygen bonded as structure (E) is attributed either to a failure of pairs of oxygen molecules to achieve adsorption at the same (or possibly, cognate) sites, or to a special quality of the support-activated secondary-region adsorption site in the species A/aluminas.

Some Geometrical Implications

The empirical formulas of species A presented in Part I (*1*) indicate that the osmium cluster framework is highly protected by ligand-CO; moreover, the clusters interact with the support as discussed above. It follows, therefore, that sites for adsorption per cluster are few. The loading of osmium on our supports was 2% by weight, which is sufficient for the formation of 5.3×10^{18} species A of nuclearity 12 per gram of adsorbent. The adsorptions in the primary region presented in Fig. 2*a* correspond to 14.5×10^{18} molecules CO adsorbed per gram on species A derived from $Os_3(CO)_{12}$/titania, and 7.8×10^{18} on $Os_6(CO)_{18}$/alumina. The values for oxygen adsorption are similar. In each case, each cluster adsorbs 1, 2, or 3 molecules of adsorbate, providing all clusters of species A have an identical composition, and hence behave in an identical fashion. The number of molecules of oxygen involved in adsorption in the secondary region appears to be about 2.7×10^{18}, somewhat less than one per cluster on average. Since the proposed mechanism for oxygen exchange, Eq. (2), involves the coadsorption of pairs of oxygen molecules, it must be the case that only exceptionally will sites exist that permit oxygen adsorbed in the secondary region to undergo exchange.

Finally, we must emphasize that the geometrical presentations of the cluster frameworks of species A presented in Fig. 9 of Part I and reproduced in the Introduction of this paper are idealized structures. First, they take no account of the presence of ligand-C. Secondly, every addition to the molecular structure occasioned by the adsorption of CO or of O_2 will tend to lead to structural perturbations or relaxations, some of which may be so severe as to induce ligand-CO reorientations or modifications to the geometry of the metal cluster framework. The variability of structure may be of importance in the context of catalyzed reactions in which the configurations adopted by the species A clusters as a result of adsorption of reactants may be specially conducive to the chemical transformation of those adsorbates.

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