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Preliminary communication

SURFACE SUPPORTED METAL CLUSTER CARBONYLS. THE SURFACE ORGANOMETALLIC CHEMISTRY OF POLYMETALLIC AND MONOMETALLIC OSMIUM CARBONYL SPECIES FORMED BY DEPOSITING VARIOUS OSMIUM CLUSTERS ON SILICA AND ALUMINA

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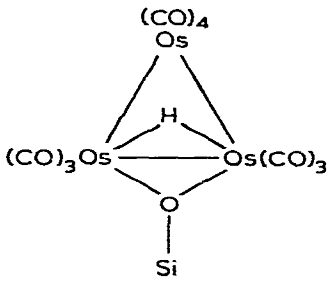
Summary

On highly hydroxylated silica, $Os_3(CO)_{12}$, $H_2Os_3(CO)_{10}$ or $Os_6(CO)_{18}$ are simply physisorbed at room temperature. At 150°C there is an oxidative addition of the surface Si—OH group to the Os—Os bond of $Os_3(CO)_{12}$ with formation of the surface species: $HOs_3(CO)_{10}(O—Si)$.
Such a structure was confirmed by the synthesis of the model compound $HOs_3(CO)_{10}(OSi\,Ph_3)$. When the physisorbed clusters $Os_3(CO)_{12}$, $H_2Os_3(CO)_{10}$, $Os_6(CO)_{18}$ or the chemisorbed clusters $HOs_3(CO)_{10}(O—Si\equiv)$, are heated at 200°C, a breakdown of the cluster frame occurs, with formation of osmium(II) carbonyl species of the type $[Os(CO)_2(O—Si\equiv)_2]_n$ or $[Os(CO)_3(O—Si\equiv)_2]_2$. Similar reactions are observed on alumina.

The use of transition metal cluster carbonyls to prepare highly dispersed metal catalysts on inorganic oxide supports is of considerable current interest [1,2]; it can also give direct experimental evidence about surface organometallic species and their chemistry [3]. Previous reports have dealt with the chemistry of $Rh_6(CO)_{16}$, [4,5], $Rh_4(CO)_{12}$ [6] or $Fe_3(CO)_{12}$ [7] supported on various inorganic oxides. The formation of hydrocarbons upon heating supported carbonyl clusters has been also observed [8]. A recent report [9] discussed the anchoring of osmium carbonyl clusters to silica via phosphine or vinyl groups. We report here new ways of anchoring $Os_3(CO)_{12}$ to a silica surface by direct reaction of the molecular cluster with surface silanol groups; depending on the experimental conditions, the formation of the neutral hydrido cluster $HOs_3(CO)_{10}(O—Si\equiv)$ and various osmium(II) carbonyl surface species is observed. Some similar molecular surface compounds are obtained on alumina. We also outline evidence for the very high stability of some of these surface organometallic molecular species, which was quite unexpected in the light of results reported for other metal carbonyl clusters (e.g. $Rh_6(CO)_{16}$ [4,5], $Rh_4(CO)_{12}$ [6], $Fe_3(CO)_{12}$ [7] and $Ir_4(CO)_{12}$ [2], which readily form metallic particles on thermal and (or) chemical treatment.

On highly hydroxylated silica degassed at 25°C (Aerosil Degussa 200 m^2/g, which we refer to as $silica_{25}$), the room temperature adsorption of $Os_3(CO)_{12}$, $H_2Os_3(CO)_{10}$ and $Os_6(CO)_{18}$ from CH_2Cl_2 solutions leads to a simple physisorption of the original clusters. This is shown not only by IR spectroscopy (see Table 1) but also by chemical analysis of the gas phase above the silica surface, which is found not to contain any gaseous CO, CO_2 or H_2.

When $Os_3(CO)_{12}$ physisorbed on $silica_{25}$ is heated at 150°C for 4 hours under argon, about 2 mol of CO per mol of supported cluster are evolved, without any significant H_2 or CO_2 evolution. Simultaneously, the IR spectrum in the $\nu(CO)$ region becomes rather similar in frequencies and intensities to that observed for $Os_3(CO)_{10}(H)(OR)$ [10] or $Os_3(CO)_{10}(OR)_2$ [11] clusters ($R = C_6H_5$, see Table 1). Although the $\nu(CO)$ stretching frequencies of this new surface species are more in agreement with a $Os_3(CO)_{10}(O{-}Si{\equiv})_2$ structure, the absence of hydrogen evolution suggests the occurrence of an oxidative addition of a surface silanol group to an Os—Os bond to form the surface species:



EXAFS measurements confirmed that the cluster frame was retained, and indicated that the average Os—Os distance in the grafted cluster was decreased to 2.68 Å compared with the value of 2.877 Å for the starting $Os_3(CO)_{12}$. These results will be published separately [13].

A model compound $Os_3(CO)_{10}(H)(OSiPh_3)$ was prepared by the reaction of $Os_3(CO)_{12}$ with $HOSiPh_3$ (high field ^1H signal at 21.00 ppm from TMS). The similarities between the IR spectra of the surface cluster species and the model compound are quite good (see Table 1).

On η-$alumina_{25}$ (with a specific area of 315 m^2/g) simple physisorption of $Os_3(CO)_{12}$ or $Os_6(CO)_{18}$ occurs at room temperature. Upon heating the physisorbed $Os_3(CO)_{12}$ under argon below 100°C, two moles of CO are evolved but no H_2 or CO_2; new IR absorption bands appear at 2109w and 2058s cm^{-1} which can be ascribed to a surface osmium cluster of the type $Os_3(CO)_{10}(H)$-$(OAl{\lessdot})$ although the IR spectrum is less clearly resolved than in the case of silica.

In contrast to $silica_{500}$, on $alumina_{400}$ physisorption of $Os_3(CO)_{12}$ and

TABLE 1

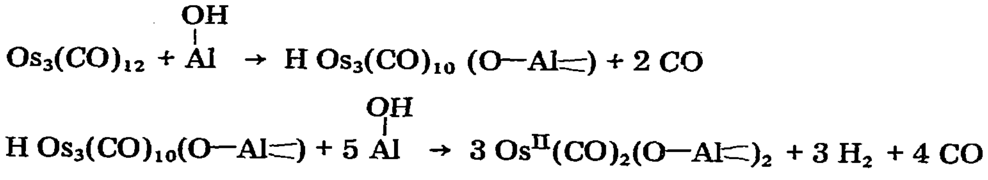
INFRARED DATA FOR OSMIUM POLYNUCLEAR AND MONONUCLEAR CARBONYLS

Compound	ν(CO) (cm^{-1})	Reference
$Os_3(CO)_{12}$ [a]	2135vw, 2076vs, 2068s, 2048m, 2035(sh), 2023s, 2003m, 1985m	this work
$Os_3(CO)_{12}/SiO_2$ [b] (25°C)	2135vw, 2070vs, 2048s, 2040s, 2025s, 2018(sh), 1980m	this work
$Os_3(CO)_{12}/\eta\text{-}Al_2O_3$ [c] (400°C)	2109vw, 2068vs, 2033s, 2020s, 2011(sh), 2000 (sh, br)	this work
$Os_3(CO)_{12}/\eta\text{-}Al_2O_3$ [c] (25°C)	2082w, 2066s, 2032s, 2020s, 2010—1998vs(br), 1980s, 1960(sh)	this work
$Os_6(CO)_{18}$ [g]	2107w, 2065—2078m, 2065—2049m, 2037s, 2018s, 1999m, 1971(sh), 1942m, 1955m	16
$Os_6(CO)_{18}/SiO_2$ [b] (25°C)	2116w, 2087s, 2072s, 2045s(br)	this work
$H_2Os_3(CO)_{10}$ [d]	2110vw, 2076vs, 2062s, 2025vs, 2009vs, 1987m, 1969vw, 1956vw	16
$H_2Os_3(CO)_{10}/SiO_2$ [b]	2112vw, 2078vs, 2064s, 2029vs, 2012s(br)	this work
$HOs_3(CO)_{10}(O{-}Si{\equiv})$ [b] (25°C)	2122w, 2088vs, 2075s, 2037vs(br), 1955w(sh)	this work
$HOs_3(CO)_{10}(O{-}Al{\sqsubset})$ [c] (25°C)	2109w, 2070m(sh), 2058s, 2030vs, 2018s, 2012s, 2000ms, 1990m(sh)	this work
$HOs_3(CO)_{10}(O{-}SiPh_3)$ [d]	2107w, 2069s, 2055s, 2017s, 1997m, 1980m	this work
$HOs_3(CO)_{10}(O{-}Ph)$ [d]	2112w, 2073vs, 2064ms, 2025vs, 2007ms, 1991w(sh), 1986mw	10
$Os_3(CO)_{10}(O{-}Ph)_2$ [d]	2109w, 2076s, 2060ms, 2019vs, 2002ms, 1955mw	11
$[Os(CO)_3Cl_2]_2$ [e]	2134s, 2059vs (isomer α), 2129s, 2050s, 2032s (isomer β)	15
$[Os(CO)_2I_2]_2$ [a]	2119s, 2045vs, 1988s	14
$[Os(CO)_2(O{-}Si{\equiv})_2]_n$ [b]	2135m, 2052vs(br), 1960m(sh)	this work
$[Os(CO)_3(O{-}Si{\equiv})_2]_2$ [b]	2135m, 2052vs(br)	this work
$[Os(CO)_2(O{-}Al{\sqsubset})_2]_2$ [c]	2125m, 2040s(br)	this work
$[Os(CO)_3(O{-}Al{\sqsubset})_2]_n$ [c]	2125m, 2040s(br), 1960(sh)	this work
$[Os(CO)_3Br_2]_2$ [e]	2126s, 2052vs	this work
$[Os(CO)_3Br_2]_2$ [f]	2128s, 2042vs, 2000w(sh)	this work
$[Os(CO)_3Br_2]_2/\eta\text{-}Al_2O_3$ [c] (400°C)	2124s, 2044vs, 1992(sh)	this work

[a] Nujol mull; [b] silica disc; [c] alumina disc; [d] cyclohexane; [e] CCl_4; [f] KBr disc.

$Os_6(CO)_{18}$ occurs at room temperature, in agreement with the low protonic acidity of this particular support [12]; upon heating below 100°C under vacuum (10^{-5} Torr) only partial decarbonylation is observed, and even above 100°C the IR absorption bands of the original cluster do not disappear completely.

On silica when the physisorbed clusters $Os_3(CO)_{12}$, $H_2Os_3(CO)_{10}$ and $Os_6(CO)_{18}$ or the anchored cluster $HOs_3(CO)_{10}(O{-}Si{\equiv})$ are heated for few hours at 200°C or above under vacuum or under argon, the final ν(CO) IR spectrum is the same in all cases. The IR spectrum of this new surface osmium carbonyl species show three bands in the ν(CO) region, at 2135s, 2052vs and 1960m(sh) cm^{-1}. Similar infrared changes in the ν(CO) absorption bands occur with osmium cluster carbonyls adsorbed on η-alumina at temperatures above 200°C (or more slowly at lower temperatures). With $Os_3(CO)_{12}$ the observed evolution of three moles of H_2 per mole of cluster is in agreement with a surface oxidation of the zerovalent osmium:



$$Os_3(CO)_{12} + \overset{\displaystyle OH}{\underset{|}{Al}} \rightarrow H\,Os_3(CO)_{10}\,(O{-}Al{\sqsubset}) + 2\,CO$$

$$H\,Os_3(CO)_{10}(O{-}Al{\sqsubset}) + 5\,\overset{\displaystyle OH}{\underset{|}{Al}} \rightarrow 3\,Os^{II}(CO)_2(O{-}Al{\sqsubset})_2 + 3\,H_2 + 4\,CO$$

The pattern of the infrared ν(CO) absorptions is also in agreement with such an oxidation since it is rather similar to that reported for $[Os(CO)_2I_2]_n$ (see Table 1). The breakdown of the original cluster is quicker in the presence of oxygen and the same infrared spectra are very easily obtained by thermal treatment of $[Os(CO)_3Br_2]_2$ physisorbed on η-Al_2O_3. The band at about 1960 cm^{-1} disappears both on silica and η-Al_2O_3 when the sample is heated for few hours at 100°C under one atmosphere of CO, while the other two bands remain nearly unchanged. Upon heating at 200—250°C for a few hours under vacuum the band at 1960 cm^{-1} reappears on both supports, in agreement with occurrence of reversible CO dissociation. (This kind of cycle can be repeated several times.) The above results and the formation of the same surface species independently from the nuclearity of the original cluster suggest a breakdown of the cluster cage; the surface osmium carbonyl species initially formed at 200°C may be a polymeric oxygen bridged complex of the type $[Os(CO)_2(O{-}Si{\equiv})_2]_n$, which reacts with CO to form the dimeric surface complex $[Os(CO)_3(O{-}Si{\equiv})_2]_2$, since the observed infrared changes are those expected for a change from $[Os(CO)_2X_2]_n$ to $[Os(CO)_3X_2]_2$ [14,15] (X = halogen, see Table 1).

The surface Os^{II} carbonyl species are stable on both SiO_2 and on η-Al_2O_3 up to temperatures of about 300°C; at higher temperatures (up to 400°C on η-Al_2O_3) we observed formation of no metallic particles, but only that of rather complex mixtures of other osmium surface molecular species whose nature is at present under investigation. Osmium metallic particles could be obtained either on silica or η-alumina only by very long treatment (more than 24 hours) of the surface Os^{II} carbonyl compounds with H_2 at 200°C or above.

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