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# Supported Transition Metal Compounds

## I. A New Method for the Preparation of Alumina-Supported Iridium and Osmium Carbonyls[1]

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An extraction technique for the preparation of alumina-supported iridium and osmium carbonyls from $Ir_4(CO)_{12}$ and $Os_3(CO)_{12}$ is reported. It is concluded that the metal carbonyl species produced are highly dispersed and of small particle size (less than 50 Å diameter) in contrast to the large crystallites of iridium and osmium carbonyls obtained by either the dry grinding or wet impregnation techniques. Partial decarbonylation of the metal carbonyl species can be effected by varying the conditions of the preparation and by heating the samples in air, the species $[Ir(CO)_2]^+$ and $[Os(CO)_n]^{2+}$, $n = 2,3$, have been identified from their infrared spectra. Strong interactions between the metal carbonyl species and the alumina support are present.

### INTRODUCTION

Catalysts containing supported metals are widely employed in a variety of chemical reactions; many of these catalysts are prepared by using transition metal salts and high surface area inorganic oxides as supports. The efficiency and selectivity of these catalysts are closely related to the dispersion and particle size of the metal component and to the nature of the interaction between the metal and the support. For a particular metal, catalytic activity may be varied by changing the metal dispersion and the support; thus the method of synthesis and any pretreatment of the catalyst are important in the overall process of catalyst evaluation. Several review articles have discussed different procedures for the synthesis of supported metal catalysts (*1–4*). In the most commonly employed procedure, usually referred to as the incipient wetness or wet impregnation technique, impregnation of the metal is achieved by treating the support with an aqueous solution of the metal salt in sufficient quantity to just wet the support. The water is then removed by drying; calcination and/or activation in hydrogen at higher temperatures usually follows the drying step. This procedure results in the deposition of small crystallites of the metal compound on the support surface. Often, particularly when higher metal loadings are achieved, the crystallite size is quite large and thus the dispersion is low. Incomplete or ineffective reduction of the metal may also result from the relatively large particle size and/or strong interactions between the oxidized form of the metal and the support.

Recently, metal cluster carbonyls, which consist of the metal in a low oxidation state, have been used for the preparation of materials containing supported metal species which may serve as potential Fischer–

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Tropsch catalysts (*5*). Metal cluster carbonyls were chosen as precursors for the supported metal catalysts for several reasons. First, some of these complexes are known to behave as homogeneous catalysts for a variety of reactions, including carbon monoxide hydrogenation, the Fischer–Tropsch reaction (*6–10*). Second, removal of some of the ligands, i.e., partial decarbonylation of the supported carbonyls, may lead to coordinative unsaturation. Third, low oxidation state metal clusters, which are highly dispersed on an inert metal oxide support, could be formed by removal of all the carbonyl ligands under a reducing atmosphere; this may produce materials which readily coordinate carbon monoxide, possibly through a bridging mode, leading to a reduction in the bond order of the carbon monoxide and a different mechanism for the $CO/H_2$ reaction than that postulated for the Fischer–Tropsch reaction (*11*). Fourth, these metal cluster carbonyls have been postulated to mimic metal aggregates that are present on conventionally used Fischer–Tropsch catalysts (*12–18*); thus, the materials prepared by using metal cluster carbonyls may serve as models for metal surfaces. And fifth, there is evidence that the use of metal cluster carbonyls to produce heterogeneous catalysts can lead to a higher degree of dispersion of the metal on the support than that which is obtained when aqueous solutions of metal salts are used (*19–24*).

Several metal cluster carbonyls, for example, $Fe_2(CO)_9$ (*19, 20, 25, 26*), $Fe_3(CO)_{12}$ (*19, 20, 25–30*), $Co_2(CO)_8$ (*19, 20, 31*), $Ru_3(CO)_{12}$ (*19–21, 32–35*), $Rh_6(CO)_{16}$ (*19, 20, 32, 36–45*), $Os_3(CO)_{12}$ (*19, 20, 32, 46–50*), and $Ir_4(CO)_{12}$ (*19, 20, 21–24, 32, 39, 40, 51*) have been used on simple oxide supports such as $Al_2O_3$, $SiO_2$, $TiO_2$, ZnO, MgO, and $La_2O_3$. The usual methods of preparation of these materials involve contact between a solution of the metal carbonyl and the support followed by removal of the solvent under reduced pressure, i.e., the wet impregnation technique (*19–28, 31, 33–51*) or sublimation of the metal cluster carbonyl onto the support (*25, 29, 30, 32*). Careful dry grinding of a metal carbonyl and support has also been used as a preparation method (*32, 52*) although Howe *et al.* (*52*) have noted that there are no significant differences between $Mo(CO)_6/Al_2O_3$ materials prepared by the wet impregnation technique and those prepared by dry grinding. Several authors have reported on the interaction of $Ir_4(CO)_{12}$ with alumina (*21–24, 51*). By using the wet impregnation technique the intact metal cluster carbonyl is deposited on the alumina surface, this species is decarbonylated by evacuation of the sample above room temperature. Extensive studies of the reaction between $Os_3(CO)_{12}$ and oxide supports such as $SiO_2$, $Al_2O_3$, ZnO, and MgO have been performed (*46–50*). Deeba *et al.* reported the initial formation of a surface bound hydridotriosmium cluster, $Os_3(H)(CO)_{10}(OM)$ where M represents Si, Al, Zn, or Mg from the support surface; the cluster can be decarbonylated upon heating to give atomically dispersed osmium (*46, 47, 50*). Knözinger and Zhao (*49*) reported the formation of the same hydridotriosmium species on alumina; this was shown to produce osmium(II) carbonyl species on heating in vacuum. Psaro *et al.*, however, reported that no change was seen in the carbonyl region of the infrared spectrum when $Os_3(CO)_{12}$ was supported on either $Al_2O_3$ or $SiO_2$, but that on heating at 150°C the hydridotriosmium species is formed (*32*). In addition, Psaro *et al.* report that on heating at 200°C two osmium(II) carbonyl species are formed, $[Os(CO)_3X_2]_2$ and $[Os(CO)_2X_2]_n$, where X is a surface oxygen atom.

As part of our overall program in the area of catalysis, we are investigating methods for the preparation of supported metal compounds. The initial goal of this program is to prepare, and subsequently to characterize, materials containing highly dispersed, small particle-sized supported metal species which may serve as potentially active heterogeneous catalysts. In this paper, we report a new method for the preparation of alumina-supported iridium and osmium carbonyls. The preparation of alumina-supported ruthenium and rhodium carbonyls will be discussed in a later paper (*53*).

## EXPERIMENTAL

### *Materials*

The metal cluster carbonyls, $Ir_4(CO)_{12}$ and $Os_3(CO)_{12}$, were obtained from Strem Chemicals (98% purity) and used as supplied. γ-Alumina, Harshaw Chemical Company, ~200 $m^2g^{-1}$, was obtained as $\frac{1}{8}$-in-diameter pellets and $\frac{1}{8}$-in-diameter extrudates; both pellets and extrudates were calcined in air at 500°C for 48 hr, cooled in an evacuated desiccator and stored under $N_2$ in a dry box, Vacuum Atmospheres Dri Lab, prior to use. The solvents, tetrahydrofuran (THF), or toluene (TOL), Fisher, certified grade, were degassed with $N_2$, stored over molecular sieves (Davison, 4 Å), and used without further purification.

### *General Preparation Methods*

*Extraction technique.* A weighed quantity of the metal carbonyl was placed in either a fritted glass or a cellulose extraction thimble in a Soxhlet extractor. The weighed alumina was placed in a reaction flask together with a known volume of solvent and connected to the extractor. The solution was stirred, heated, and maintained at reflux temperature; the refluxing solvent extracts the metal carbonyl into the flask where it is in contact with the alumina. The extraction process usually takes 2 to 4 h to complete, depending on the metal carbonyl and solvent used; however, the solution was allowed to reflux for varying amounts of time, up to 96 h, after the extraction is completed to ensure maximum interaction between the metal carbonyl and the alumina, and to prepare samples with differing extents of penetration of the metal carbonyl species into the alumina extrudates or pellets (*54*). After the extraction and refluxing were completed, the solution was filtered under $N_2$ in the dry box, and the residue washed several times with solvent. Any solvent remaining in the residue was removed under reduced pressure at room temperature in a vacuum desiccator by pumping for approximately 1 h. Final metal loadings for the prepared materials were in the range of 1 to 2 w%. Materials prepared by this technique from $Ir_4(CO)_{12}$ and $Os_3(CO)_{12}$ are designated $Ir/Al_2O_3/EX$ and $Os/Al_2O_3/EX$, respectively. Conditions for the extraction technique are summarized, where necessary, after the designation, e.g., $Ir/Al_2O_3/EX$(THF, 24 h) represents a sample prepared by using tetrahydrofuran as the solvent for a total reflux time of 24 h.

*Dry grinding and wet impregnation techniques.* For comparison purposes, two other methods for the preparation of metal carbonyl/alumina samples were employed, viz. dry grinding and wet impregnation. Dry grinding consists of pregrinding the alumina pellets or extrudates and then cogrinding a weighed amount of this alumina powder with a weighed amount of the metal carbonyl. Metal loadings are comparable to those used for the extraction technique. Materials prepared by the dry grinding technique are designated $Ir/Al_2O_3/DG$ and $Os/Al_2O_3/DG$. For the wet impregnation method, the procedure of Anderson *et al.* was followed (*21*) using tetrahydrofuran or toluene as the solvent. Excess solvent was removed under reduced pressure at room temperature in a vacuum desiccator as described above. Metal loadings are comparable to those used for the extraction technique. Materials prepared by the wet impregnation technique are designated $Ir/Al_2O_3/WI$ and $Os/Al_2O_3/WI$.

*Characterization.* Infrared spectra (4000–200 $cm^{-1}$) were obtained as Nujol mulls with CsBr plates by using a Perkin–Elmer Model 283 spectrometer, resolution ~3 $cm^{-1}$. X-Ray powder diffraction data were collected on a Rigaku horizontal goniometer using a copper X-ray tube operated at 40 kV and 35 mA. All measurements were made with a 1-degree divergent slit, 0.3-mm receiving slit, receiving graphite monochromator, and scintillation counter with pulse height discrimination. All samples were ground and then packed into a glass holder with an opening 16 × 8 × 0.5 mm, no binder or adhesive was needed. The weight percent of iridium was determined for the prepared materials by using a Siemens SRS-1 X-ray fluorescence spectrometer with standards prepared from carefully ground mixtures of $Ir_4(CO)_{12}$, alumina, and methyl cellulose (spectrographic grade, Chemplex Industries) as binder, and was in the range of 1 to 2 wt%. Raman spectra were obtained by using a Spex Ramalog IV Laser Raman spectrometer equipped with argon-ion and helium–neon lasers, Spectra Physics. Samples were used directly as extrudates or pellets, or they were ground and pressed into discs and mounted in a rotating sample holder (55).

## RESULTS AND DISCUSSION

The wet impregnation technique, employing a metal carbonyl and a nonpolar solvent, which has been used for the preparation of supported metal catalysts usually requires a large volume of the solvent due to the low solubility of the metal carbonyl. Following interaction in solution, removal of the solvent leads to crystallization of the metal carbonyl. Thus, by using this technique, materials with a low weight percent metal, containing crystals of the metal carbonyl are obtained. As noted earlier, Howe *et al.* (52) found that materials prepared by the impregnation technique are similar to those prepared by simple dry grinding.

The extraction technique, which we report in this paper, was developed in an attempt to circumvent the low solubility problems often encountered when using organometallic compounds and with the anticipation that by retaining a steady concentration of the compound in solution slow adsorption from this solution should lead to a high dispersion of the metal compound on the support, eliminate crystallization of the metal compound, and allow higher loadings of the metal compound to be obtained on the support.

Examination of the iridium and osmium samples prepared by the dry grinding or wet impregnation techniques shows the presence of small yellow crystals, similar to those of $Ir_4(CO)_{12}$ and $Os_3(CO)_{12}$, mixed in with the alumina. These crystals are more evident on examination under a stereoscopic microscope at 27× magnification. In contrast to the appearance of these samples, the iridium and osmium samples prepared by the extraction technique are uniformly beige, with no evidence for the presence of crystals under 27× magnification. The X-ray powder diffraction data obtained for the iridium and osmium samples prepared by the three different techniques are summarized in Table 1. For the samples prepared by the extraction technique, only the support was detected, whereas for the samples prepared by dry grinding and wet impregnation techniques additional bands due to $Ir_4(CO)_{12}$ or $Os_3(CO)_{12}$ were observed. The lack of an X-ray diffraction pattern for the iridium or osmium containing species in the $Ir/Al_2O_3/EX$ and $Os/Al_2O_3/EX$ samples may be explained by

TABLE 1

X-Ray Diffraction Data for $Ir_4(CO)_{12}$, $Os_3(CO)_{12}$, and Alumina-Supported Iridium and Osmium Carbonyl Samples, *d* spacings (Å) for the Major Bands

| | Metal carbonyl | Dry ground | Wet impregnation | Extraction[a] |
|---|---|---|---|---|
| $Ir_4(CO)_{12}$ | 7.07 | 7.07 | 7.07 | |
| | 6.65 | 6.60 | 6.60 | [b] |
| | | 1.97 | 1.97 | 1.97 |
| $Os_3(CO)_{12}$ | 7.13 | 7.10 | 7.13 | |
| | 6.96 | 6.96 | 6.96 | |
| | 6.70 | 6.70 | 6.55 | [b] |
| | 6.57 | 6.55 | 6.55 | |
| | 5.47 | 5.47 | 5.47 | |
| | | 1.97 | 1.97 | 1.97 |

[a] Designated (THF, 24 h).

[b] No pattern due to supported carbonyl observed.

concluding that these species are present in a highly dispersed state, with particle sizes less than approximately 50 Å diameter, the detection limit for the X-ray powder diffraction technique. This conclusion is consistent with data obtained for some supported iron and cobalt catalysts prepared by the extraction technique (56). Although no X-ray diffraction pattern is observed for the iron and cobalt species in these catalysts, other analytical methods have confirmed that the diameter of the metal species is approximately 50 Å. Thus, it is concluded that the extraction technique favors the formation of highly dispersed, small, less than approximately 50 Å diameter, particles of metal containing species on the supports.

Vibrational spectroscopy has been employed in an attempt to characterize the supported metal carbonyls in the prepared iridium and osmium samples and to detect any changes in these species that accompany changes in preparative conditions, solvent, reflux time, etc., or occur on exposure to or heating in air.

Raman spectra obtained for the iridium on alumina samples prepared by dry grinding and wet impregnation were identical to that obtained for the original $Ir_4(CO)_{12}$. For the samples prepared by the extraction technique fluorescence problems were so severe that no bands from carbonyl-containing species could be identified.

Infrared spectra were obtained for the metal carbonyls and for the prepared iridium and osmium samples. The $\nu$(CO) bands obtained for $Ir_4(CO)_{12}$ and $Os_3(CO)_{12}$ are listed in Table 2; good agreement with the previously reported solid state spectra was obtained. Infrared spectra, in the $\nu$(CO) region, for samples prepared by the dry grinding and wet impregnation techniques are identical. Bands for $Ir/Al_2O_3/DG$ and $Os/Al_2O_3/DG$ are listed in Table 3; the positions of the major $\nu$(CO) bands are the same as those observed for the original metal carbonyls. However, for the samples prepared by the extraction technique, the infrared

TABLE 2

Major $\nu$(CO) Bands in the Infrared Spectra for $Ir_4(CO)_{12}$ and $Os_3(CO)_{12}$

| Compound | $\nu$(CO) ($cm^{-1}$) | Reference |
|---|---|---|
| $Ir_4(CO)_{12}$[a] | 2073(sh), 2059(s), 2020(m), 2000(wsh) | This work |
| $Ir_4(CO)_{12}$[b] | 2075(sh), 2066(s), 2030(s), 2010(wsh), 2005(w) | [f] |
| $Ir_4(CO)_{12}$[c] | 2067(s), 2058(sh), 2027(m) | [g] |
| $Os_3(CO)_{12}$[a] | 2066(s), 2020(s), 2000(w), 1990(m) | This work |
| $Os_3(CO)_{12}$[d] | 2070(s), 2019(s), 1998(m), 1986(m) | [h] |
| $Os_3(CO)_{12}$[e] | 2068(s), 2034(s), 2014(m), 2002(m) | [i] |

[a] Nujol mull.

[b] Solid state.

[c] $CH_2Cl_2$ solution.

[d] KBr pellet.

[e] Cyclohexane solution.

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TABLE 3

Major $\nu$(CO) Bands in the Infrared Spectra for Alumina-Supported Iridium and Osmium Carbonyls ($cm^{-1}$)

| | $cm^{-1}$ | | | |
|---|---|---|---|---|
| | Dry ground | Extraction[a] | Exposed to air[b] | Heated[c] |
| $Ir_4(CO)_{12}$ | 2073(sh) | | | |
| | 2059(s) | 2060(m) | 2062(s) | 2060(m) |
| | 2020(m) | 2023(s) | 2022(m) | 2020(sh) |
| | 2000(wsh) | 1987(m) | 1987(s) | 1990(m) |
| $Os_3(CO)_{12}$ | | | | 2120(m) |
| | 2066(s) | 2060(m) | 2060(sh) | |
| | | 2046(m) | 2050(sh) | |
| | | | 2030(sh) | 2030(s) |
| | 2020(s) | 2013(s) | 2020(s) | |
| | 2000(m) | | | |
| | 1990(m) | 1990(sh) | | |
| | | | 1955(m) | 1955(s) |

[a] Designated (THF, 24 h).

[b] For 24 h.

[c] 120°C in air for 1.5 h after exposure to air for 24 h.

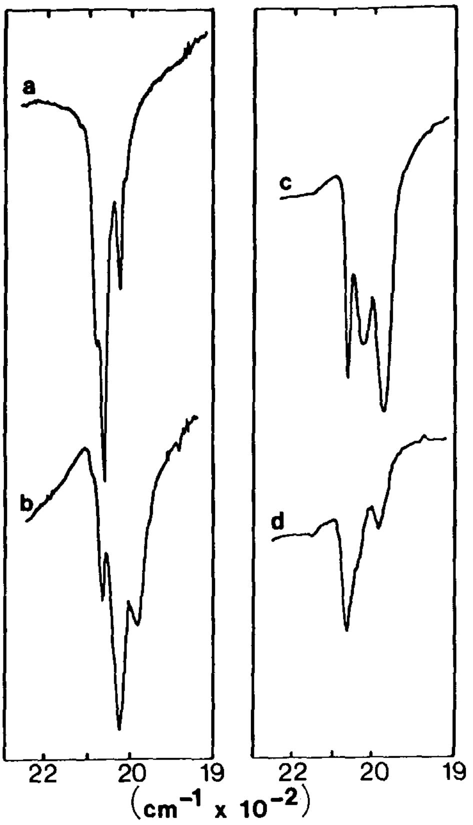

FIG. 1. $\nu$(CO) Region of the infrared spectra for alumina-supported iridium carbonyls. (a) Ir/$Al_2O_3$/DG, (b) Ir/$Al_2O_3$/EX(THF, 24 h), (c) (b) exposed to air for 24 h, and (d) (c) heated in air at 120°C for 1.5 h.

spectra are significantly different from the spectra for samples prepared by either the dry grinding or wet impregnation techniques, see Table 3, and Figs. 1 and 2. For Ir/$Al_2O_3$/EX(THF, 24 h) the shoulders at 2073 and 2000 cm$^{-1}$ observed for Ir/$Al_2O_3$/DG and Ir/$Al_2O_3$/WI samples are absent and a new band is observed at 1987 cm$^{-1}$. The three $\nu$(CO) bands present in the Ir/$Al_2O_3$/EX sample remain on exposure to air for 24 h and/or on heating at 120°C for 1.5 h; however, the relative intensity of these bands changes (see Table 3 and Fig. 1). For Os/$Al_2O_3$/EX(THF, 24 h), the band at 2000 cm$^{-1}$ observed for Os/$Al_2O_3$/DG and Os/$Al_2O_3$/WI samples is absent, and a new band at 2046 cm$^{-1}$ is observed. Exposure to air for 24 h leads to the loss of the shoulder at 1990 cm$^{-1}$, the appearance of an additional shoulder at 2030 cm$^{-1}$, and a new band at 1955 cm$^{-1}$. Subsequent heating in air at 120°C for 1.5 h leads to a spectrum containing bands at 2120, 2030, and 1955 cm$^{-1}$; none of these bands is in the same position found for $Os_3(CO)_{12}$ or for the original Os/$Al_2O_3$/EX sample.

The total reflux time and the solvent employed in the extraction technique affect the infrared spectrum of the product. For an iridium sample prepared by using tetrahydrofuran as solvent (boiling point 66°C) and a total reflux time of 96 h, Ir/$Al_2O_3$/EX(THF, 96 h), the $\nu$(CO) region of the infrared spectrum is the same as that for Ir/$Al_2O_3$/EX(THF, 24 h) which has been exposed to air for 24 h and for a sample prepared by using toluene as solvent (boil-

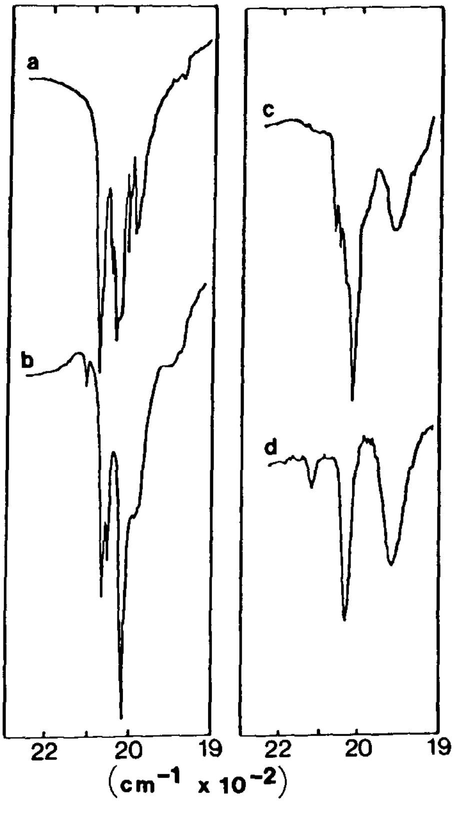

FIG. 2. $\nu$(CO) Region of the infrared spectra for alumina-supported osmium carbonyls. (a) Os/$Al_2O_3$/DG, (b) Os/$Al_2O_3$/EX(THF, 24 h), (c) (b) exposed to air for 24 h, and (d) (c) heated in air at 120°C for 1.5 h.

ing point 111°C) and a total reflux time of 24 h, $Ir/Al_2O_3$/EX(TOL, 24 h). Similarly, the infrared spectrum of $Os/Al_2O_3$/EX(THF, 96 h) is the same as the spectrum of an $Os/Al_2O_3$/EX(THF, 24 h) sample which had been exposed to air for 24 h. This suggests that supported metal carbonyls with differing degrees of decarbonylation or degradation of the metal carbonyl may be prepared by varying the conditions employed for the extraction technique without exposure of the samples to air.

Prolonged heating in air of the iridium and osmium samples prepared by the extraction technique leads to further decarbonylation of the supported metal carbonyl. If the samples which have been heated at 120°C for 1.5 h are subsequently heated at 150°C for 24 h in air, the $\nu$(CO) bands at 2020 and 2120 $cm^{-1}$, for the iridium and osmium samples, respectively, disappear. Further heating at 150°C for an additional 48 h reduces the intensity of the remaining two major bands, at 2060 and 1990 $cm^{-1}$ for the iridium sample and at 2030 and 1955 $cm^{-1}$ for the osmium sample. Complete removal of these $\nu$(CO) bands, i.e., complete decarbonylation of the samples, was achieved by heating in air for an additional 24 h at 240°C. It should be noted that for both the iridium and osmium samples prepared by the dry grinding or the wet impregnation technique, heating in air at 150°C for 1 h results in the formation of the same two bands that are detected for the samples prepared by the extraction technique which had been heated in air at 150°C for 24 h, viz. 2060 and 1990 $cm^{-1}$ (iridium) and 2030 and 1955 $cm^{-1}$ (osmium). Complete decarbonylation of the dry ground and wet impregnated samples is effected by heating at 150°C for only 24 h. The ease of decarbonylation of the samples prepared by the dry grinding or wet impregnation techniques is consistent with the conclusion reached earlier that in these samples the metal carbonyl is present in its original form with very little interaction between the carbonyl and the support. However, for the samples prepared by the extraction technique, the relatively harsh treatment required to effect decarbonylation suggests the presence of much stronger metal support interactions.

For the $Ir/Al_2O_3$/EX(THF, 24 h) sample, the positions of the $\nu$(CO) bands in the infrared spectrum (see Table 3) are not the same as those reported by Howe for iridium/alumina samples prepared by the wet impregnation technique (*23*). Howe suggested that in these samples $Ir_4(CO)_{12}$ is nondissociatively physiorbed onto the alumina and that evacuation of the samples above room temperature caused gradual decarbonylation with complete decarbonylation after 5 h at 350°C. Later studies by Tanaka *et al.* (*51*) showed that the $\nu$(CO) bands associated with the adsorbed $Ir_4(CO)_{12}$ remain on evacuation at room temperature or on heating at 50°C for 1 h. However, on heating at 100°C, three new bands appear at 2069(m), 2039(s), and 1997(m) $cm^{-1}$. The band at 2039 $cm^{-1}$ is removed after heating at 150°C for 1 h, and evacuation at higher temperatures causes a gradual reduction in intensity of the two remaining bands. The two bands were suggested to arise from a dicarbonyl iridium species.

Thus, we conclude that the extraction technique leads to partial degradation and decarbonylation of $Ir_4(CO)_{12}$ resulting in the formation of an oxidized iridium carbonyl species which interacts strongly with the support. This species is stable on exposure to air and on heating at 120°C for 1.5 h. Heating in air at higher temperatures results in the formation of the same species observed by Tanaka *et al.* (*51*). By analogy with similar rhodium carbonyl species adsorbed on alumina (*53*) and with the positions of the $\nu$(CO) bands reported by Whyman (*57*) for $[Ir(CO)_2Cl_2]^-$ at 2057 and 1970 $cm^{-1}$, we conclude that the species produced at these higher temperatures is $[Ir(CO)_2]^+$ which is then decarbonylated on further heating.

For the $Os/Al_2O_3$/EX(THF, 24 h) sample, the positions of the $\nu$(CO) bands in the infrared spectrum (see Table 3) do not correlate with those for $Os_3(CO)_{12}$ or for those reported by Deeba and Gates (*46*) and by Psaro *et al.* (*48*) for the species $Os_3(H)(CO)_{10}(O{-}Al)$. The position of the $\nu$(CO) bands reported for this surface bound hydridotriosmium complex are 2107(w), 2067(s), 2055(s), 2023–2027(vs), and 2005–2021(s and br) $cm^{-1}$. However, the spectra reported for the surface-bound hydridotriosmium species on alumina are very broad and not well resolved, thus the positions of the bands may not be exact. The infrared spectrum shown in Fig. 2(d) does correspond closely to those obtained by both Psaro *et al.* (*48*) and by Knözinger and Zhao (*49*) for osmium carbonyl/alumina samples that have been heated in vacuum. Psaro *et al.* (*48*) report the presence of three major bands in the $\nu$(CO) region of the infrared spectra for osmium carbonyl/alumina samples that were heated in vacuum at 150°C for 15 h or 200°C for 7 h, at 2127(m), 2034(s), and 1970(w and br) $cm^{-1}$. Knözinger and Zhao (*49*) also report three major bands in the $\nu$(CO) region of the infrared spectra for osmium carbonyl/alumina samples that were heated in vacuum at 200°C for 6 h, at 2125(m), 2031(s), and 1940(s) $cm^{-1}$; however, if the samples are heated at 372°C for 15 h, these bands shift to 2130(m), 2050(s), and 1970(s) $cm^{-1}$. Both Psaro *et al.* and Knözinger and Zhao interpret their spectra, by analogy to known divalent osmium carbonyl compounds, to be indicative of $[Os(CO)_n]^{2+}$, $n = 2, 3$, species which are covalently bound to the alumina surface.

Thus, we conclude that the osmium carbonyl species obtained from $Os_3(CO)_{12}$ by using the extraction technique is not adsorbed $Os_3(CO)_{12}$, nor is it the hydridotriosmium carbonyl complex reported by Deeba and Gates. Although we cannot unequivocally assign a structure to the osmium carbonyl species produced by the extraction technique, the experimental data suggest that a strong interaction between this species and the support is present. The osmium carbonyl species is stable to air, but heating at 120°C in air for 1.5 h leads to decarbonylation and degradation to produce the surface bound $[Os(CO)_n]^{2+}$, $n = 2, 3$ species.

The adsorption of metal cluster carbonyls on alumina and other simple oxides has been discussed by several workers. It is generally agreed that, unless the carbonyl is simply physisorbed onto the surface, reaction between surface hydroxyl groups and the metal carbonyl accompanies adsorption and is responsible for partial oxidation of the metal carbonyl. Studies by Hucul and Brenner (*26*) of the temperature programmed decomposition (TPDE) for alumina-supported metal carbonyls have shown that oxidation of the metal also occurs on decarbonylation. For $Ir_4(CO)_{12}/Al_2O_3$ samples prepared by impregnation or sublimation, the average oxidation number per Ir atom after TPDE is 1.8 whereas for $Os_3(CO)_{12}/Al_2O_3$ samples the oxidation number per Os atom is 3.6. Since the oxidation process occurs gradually upon decarbonylation, it is reasonable to assume the formation of species containing the metal in an intermediate oxidation state, such as Ir(I) and Os(II) in $[Ir(CO)_2]^+$ and $[Os(CO)_2]^{2+}$, respectively, for the samples prepared by using the extraction technique on degradation and partial decarbonylation of the metal carbonyl species.

## CONCLUSIONS

It can be concluded from the data presented that the samples prepared by the extraction technique are significantly different from those prepared by more conventional methods, i.e., dry grinding or wet impregnation. The samples prepared by the extraction technique consist of highly dispersed metal carbonyl species on the alumina support with particle sizes less than 50 Å in diameter. The infrared spectra of the samples prepared by the three methods indicate that there is strong interaction between the metal carbonyl species and the support in the samples prepared by the extraction technique, whereas for the samples prepared by the dry grinding and wet impregnation techniques this interaction is not as strong. Interaction of the metal cluster carbonyl with the support in the samples prepared by the extraction technique involves some decarbonylation of the metal cluster carbonyl accompanied by concomitant oxidation of the metal. Heating the samples in air results in the formation of species that can be identified as $[\mathrm{Os(CO)}_n]^{2+}$, $n = 2, 3$, as has been previously reported and $[\mathrm{Ir(CO)_2}]^+$.

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