JOURNAL OF Materials CHEMISTRY

Thermal decomposition of $[M_3(CO)_{12}]$ (M = Ru, Os) physisorbed onto porous Vycor glass: a route to a glass/RuO_2 nanocomposite

Aldo J. G. Zarbin,[a]† **Maria D. Vargas**[b]‡ **and Oswaldo L. Alves***[a]§

[a]*Laboratório de Química do Estado Sólido and* [b]*Laboratório de Organometálicos, Instituto de Química, Universidade Estadual de Campinas-UNICAMP, Caixa Postal 6154, CEP 13081-970, Campinas-SP, Brazil*

Received 1st June 1998, Accepted 23rd October 1998

This paper reports the preparation and characterization of oxide/glass nanocomposites, obtained by the impregnation and thermal decomposition of the trinuclear metal carbonyl clusters $[M_3(CO)_{12}]$ (M = Ru, Os) inside the pores of porous Vycor glass (PVG). The intermediate species formed during the thermal treatment of the $[M_3(CO)_{12}]$ adsorbed PVG materials were studied by UV–VIS–NIR and diffuse reflectance infrared (DR-IR) spectroscopy. At 65 °C (M = Ru) and 110 °C (M = Os), formation of surface bound $[HM_3(CO)_{10}(\mu\text{-OSi}\equiv)]$ species occurs, as a result of oxidative addition of a PVG surface silanol group to a cluster M–M bond. At $T > 130$ °C (M = Ru) and $T > 200$ °C (M = Os) cluster breakdown is observed, with formation of $[M(CO)_n(OSi\equiv)_2]$ ($n = 2$ and/or 3) species. When $[Ru_3(CO)_{12}]$ incorporated PVG is heated in air at $T > 250$ °C, decomposition of the cluster and formation of RuO_2 nanoparticles are observed. At 1200 °C, collapse of the glass pores leads to the formation of a transparent silica glass/RuO_2 nanocomposite of particle average size 45 Å.

Introduction

Recent years have seen a growing interest in the incorporation of organometallic compounds in porous glasses, with the purpose of obtaining new catalysts and materials for use in optical devices.[1–10] Photosensitive organometallic compounds such as $[Fe(CO)_5]$, $[(CH_3)_3SnI]$, $[M(CO)_6]$ (M = Cr, Mo, W), $[Co_2(CO)_8]$, $[M_2(CO)_{10}]$, among others, have been impregnated and photo-degraded, in attempts to obtain new vitreous materials that present significant refraction index variations.[1–10] Porous glasses have also been used as host matrices for the formation of nanoparticles of semiconductor materials.[11–20] In these cases, the pore size limits particle growth. The interest in semiconductor nanoparticles stems both from a desire to understand, at a fundamental level, the transition from molecular to bulk electronic properties,[21–25] and from the prospects of practical applications of these particles in areas such as non-linear optics,[26–28] photonics,[29] photocatalysis,[27,28,30,31] and information storage,[32] among others. The use of a host matrix to obtain nanoparticles offers the possibility of formation of new nanocomposite materials, with properties that differ from those of its individual components.[33–35] Semiconductor nanoparticles of CdS, ZnS, HgS, PbS, MoS_2, WS_2, and of the respective selenides, have been obtained from the reactions of chalcogenide sources (hydrogen chalcogenide or chalcogenide–urea) with metallic ions previously incorporated in the porous glass.[11,13] GaAs, GaP and InP nanoparticles with non-linear optical properties were also obtained in porous glass, by the chemical vapor deposition method.[14,16,17] Yamashita *et al* recently described the photo-catalytic degradation of octan-1-ol by TiO_2 nanoparticles formed inside porous glasses.[18]

One of the most commonly used glasses for these applications is Porous Vycor Glass, PVG (Corning 7930). This transparent porous material is obtained by acid leaching of a phase-separated alkaline borosilicate glass. The soluble borate phase is dissolved, leaving an open porous structure of essentially pure silica with interconnecting pores of narrow size distribution (between 20 and 200 Å), and a pore volume of nearly 28%.[36–38] The pore surface contains slightly acidic silanol groups. The structure of this porous glass can be consolidated upon heating at 1200 °C at which temperature the pores collapse to form a dense, high-silica content glass.[36–38] Chemically, PVG resembles silica gel as they both have hydroxylated surfaces. However, because of the method by which it is manufactured, PVG also possesses B_2O_3 Lewis acid sites,[39,40] although the influence of these sites on the surface chemistry of this material has not yet been described in the literature.

In recent years there has been a great deal of interest in the study of catalysts obtained from the decomposition of $[M_3(CO)_{12}]$ and other clusters supported on inorganic oxides.[41–45] This interest stems from the fact that these materials exhibit specific and unconventional catalytic properties.[41–43] Several reports have described the interaction and decomposition of clusters on Al_2O_3,[45–50] TiO_2[50] and SiO_2.[44–46,48–53] The incorporation of $[Ru_3(CO)_{12}]$ in PVG was recently reported by Gafney and Xu,[10] that described the photocatalytic isomerization of pent-1-ene using this material. However, the nature of the species formed at the different stages of thermal treatment of $[M_3(CO)_{12}]$ (M = Fe, Ru, Os) impregnated in PVG has, as yet, not been described in the literature. Incorporation, followed by thermal decomposition of these compounds in PVG, could be a good route to oxides and/or metals in nanometric dimensions, and to nanocomposites with interesting properties. In this paper we report a new method to obtain glass/metal oxide nanocomposites, based on the incorporation and thermal decomposition of trinuclear metal carbonyl clusters $[M_3(CO)_{12}]$ (M = Ru, Os) inside the pores of PVG, and the characterization of the intermediate species formed as the result of interactions between the cluster and the PVG pores surface, during the thermal decomposition process.

Experimental

Materials and methods

$[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{12}]$ (Aldrich), HCl (Merck), acetone (Merck), *n*-hexane (Merck) and acetonitrile (Merck) were

---

†Present address: Departamento de Química, Universidade Federal do Paraná-UFPR, CP 19081, CEP 81531-990, Curitiba-PR-Brazil. E-mail: aldo@quimica.ufpr.br

‡E-mail: mdvargas@iqm.unicamp.br

§E-mail: oalves@iqm.unicamp.br

used as received. Code 7930 Porous Vycor Glass was obtained from Corning Glass. Plates of PVG with dimensions of $10 \times 10 \times 1$ mm in size were dipped first in a 2 M HCl solution for 30 min, and then in acetone for the same period of time. The glass plates were then heated at 550 °C for 72 h, cooled to room temperature and stored in a desiccator.

Impregnation of $[M_3(CO)_{12}]$ in the PVG plates

Impregnation with $[Ru_3(CO)_{12}]$ was carried out by placing a PVG plate of known weight in a *n*-hexane solution of the cluster (20 mL, 10^{-3} M) for 4 h, at room temperature. After this period, the glass plate was removed from the solution and washed several times with *n*-hexane to remove any cluster absorbed on the plate external surface. This procedure did not lead to any colour change of the sample and the washings were not coloured. The solvent incorporated during the impregnation process was removed under vacuum ($P < 10^{-3}$ Torr). A similar procedure was employed for the impregnation with $[Os_3(CO)_{12}]$, except that the cluster was dissolved in acetonitrile and the solution was kept at 80 °C during impregnation.

The initial concentration of the cluster solution and the length of time the PVG plates were kept immersed were determining factors in the final amount of cluster incorporated in the glass. The conditions employed yielded samples which contained the clusters in adequate concentration for spectroscopic characterization. The amount of cluster incorporated in the PVG (<1 wt%) was estimated from the difference between the absorbance of the cluster solution before and after the impregnation step.

Thermal treatment

Thermal treatment of the samples was carried out in an oven, previously stabilized at the desired temperature (50–1000 °C). After heating for 1 h at a given temperature, the samples were removed and transferred to a desiccator, to reach room temperature. The uncertainty in the temperature measurements was 3 °C for $T < 300$ °C and 5 °C for $T > 300$ °C. The consolidation of the samples was carried out in an oven, coupled to a speed heating controller set to 10 °C min^{-1}, up to the temperature of 1200 °C which was kept for 30 min, after which time the oven was left to cool to room temperature at the approximate rate of 25 °C min^{-1}.

Materials characterization

Diffuse reflectance infrared spectra (DR-IR) were obtained using a Nicolet 520 spectrophotometer. The pure samples were crushed, and the spectra obtained using a DR-81 Japan spectroscopy accessory over the 4000–400 cm^{-1} region, with 256 scans and a resolution of 2 cm^{-1}. The Kubelka–Munk transformations and the spectral subtractions were done using the routine software of the equipment.

The UV–VIS–NIR absorption spectra of the glass plates were obtained on a Hitachi U-2000 spectrophotometer, in the 190–1100 nm region, with air as reference.

The Raman spectra of the glass plates were obtained on a Renishaw Raman imaging microscope, system 3000, with spatial resolution of 1 μm. A HeNe laser (632.8 nm) was used, with incidence power of 4 mW. The spectra were obtained over the 200–100 cm^{-1} region, with 28 scans. The transmission electron microscopy data were obtained from a Zeiss IN 902 microscope operating at 80 kV. The sample was crushed and a small amount of the powder was first suspended in water and allowed to settle for 15 min. A drop of the supernatant dispersion was then placed onto a Parlodion film supported by a copper grid (Parlodion is a 2% solution of Collodion in glass distilled amyl acetate). One layer of carbon was deposited on the samples by sputtering.

Results and discussion

Incorporation of $[M_3(CO)_{12}]$ in the PVG

When the PVG plate is introduced in a $[M_3(CO)_{12}]$ solution, diffusion of the cluster to the interior of the pores of the glass occurs through a capillary process.[54–56] The co-impregnated solvent is eliminated during the treatment of the material under low pressure.

During the incorporation process, the glass acquires the color of the solution, which remains after the elimination of the solvent. Thus, the $[Ru_3(CO)_{12}]$ incorporated PVG is dark yellow and the $[Os_3(CO)_{12}]$ incorporated material, light yellow. As previously reported for other PVG incorporated organometallic compounds,[3–5,7–9] the UV–VIS–NIR absorption spectra of the clusters in solution and inside the PVG pores are very similar. The amount of incorporated cluster was determined by the difference in the solution absorbance before and after the impregnation. The PVG was impregnated with a maximum of 2 to 5% (w/w) of $[M_3(CO)_{12}]$.

Owing to the low concentration of the incorporated material, the IR spectra of the samples in KBr disks and in Nujol dispersion are strongly dominated by the spectrum of the pure glass, and attempts at obtaining the spectra of the incorporated clusters in the ν_{CO} region were fruitless using this technique. To solve this problem the diffuse reflectance technique (DR-IR) was used. The spectra were obtained from crushed samples and corrected by the Kubelka–Munk function. The intensity and resolution of the ν_{CO} bands were increased by subtracting the spectrum of pure PVG from that of the impregnated PVG. All the DR-IR spectra presented in this work were obtained using this procedure. As is the case for their electronic spectra, the DR-IR spectra of $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{12}]$ PVG impregnated materials are similar to those of the clusters in solution. These results corroborate the idea that the impregnation is not accompanied by the formation of chemical bonds between the cluster and the glass surface. Furthermore, they also rule out any significant changes in the cluster molecular geometry as a result of the impregnation process.

Thermal decomposition of $[Ru_3(CO)_{12}]$ adsorbed on PVG

The $[Ru_3(CO)_{12}]$ impregnated PVG (referred to hereafter as PVG/Ru) is reasonably stable at room temperature for a few days at ambient atmosphere, and for months when stored under Ar. Fig. 1 and 2 show the evolution of the absorption and DR-IR spectra, respectively, of the PVG/Ru sample, as a function of heating.

The electronic spectrum of PVG/Ru [Fig. 1(a)] shows a band at 392 nm, previously attributed to the σ–σ* transition (associated to the presence of Ru–Ru chemical bonds), and two other bands at 270 and 238 nm, associated with the ligand-to-metal charge transfer.[57] Upon heating at 65 °C, the dark yellow PVG/Ru sample turns pale yellow. The only change observed in the absorption spectrum of this sample [Fig. 1(b)] is a decrease in the intensity of the band at 392 nm. In contrast, drastic changes in the DR-IR spectrum of the PVG/Ru sample were observed after it was heated at 65 °C [Fig. 2(b)], with the appearance of new bands at 2111, 2083, 2077, 2064, 2031 and 2017 cm^{-1}. These bands are due to the presence of the chemically absorbed $[HRu_3(CO)_{10}(\mu\text{-OSi}{\equiv})]$ species **1**, which is the product from the oxidative addition of a PVG surface silanol group to one of the Ru–Ru bonds of the cluster, and elimination of two CO. Similar species are formed from the thermal treatment of $[Ru_3(CO)_{12}]$ adsorbed on the silica surface.[41,51]

When the PVG/Ru sample is heated at 130 °C, the DR-IR spectrum still shows the bands due to compound **1**, in addition to a new band at 2082 cm^{-1} [Fig. 2(c)]. This band is also observed in the DR-IR spectrum of the sample heated at 170 °C, which also exhibits two new bands at 2143 and

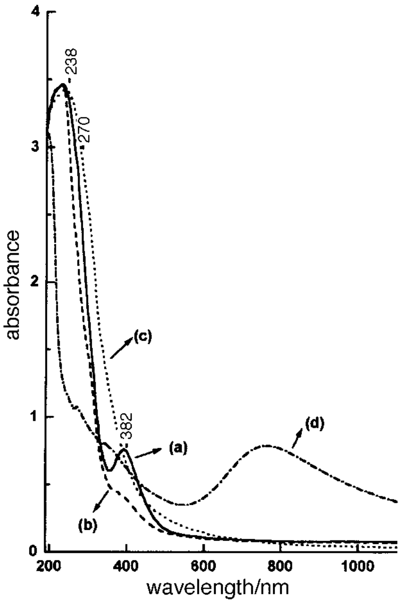

Fig. 1 UV–VIS absorption spectra of (a) PVG/Ru, (b) PVG/Ru heated at 65 °C, (c) PVG/Ru heated at 170 °C, (d) PVG/Ru heated at 1200 °C. Metal loading approximately 3 wt%.

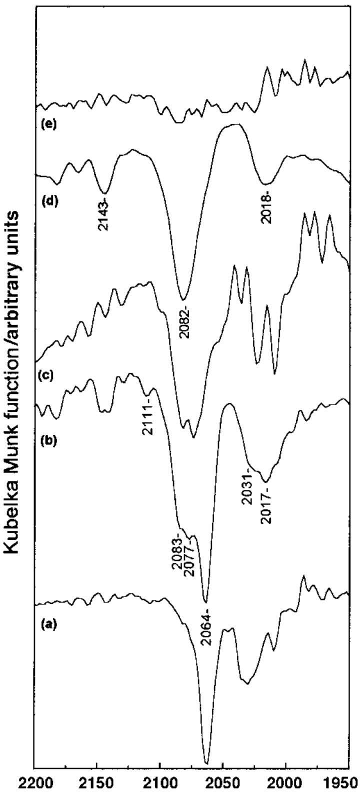

Fig. 2 DR-IR spectra of (a) PVG/Ru, (b) PVG/Ru heated at 65 °C, (c) PVG/Ru heated at 130 °C, (d) PVG/Ru heated at 170 °C and (e) PVG/Ru heated at 250 °C. Metal loading approximately 3 wt%.

2018 cm^{-1} [Fig. 2(d)]. These bands were attributed to the presence of Ru^{II} species, formed upon cluster breakdown. By analogy with the species characterized on the silica surface,[41,51] it is proposed that the species $[Ru(CO)_n(OSi\equiv)_2]$ ($n=2$ and/or 3) are chemically bonded to the PVG pores surface. This conclusion is corroborated by the UV–VIS spectrum of the material [Fig. 1(c)] which shows the disappearance of the band at 392 nm, indicating cleavage of the Ru–Ru bonds. Furthermore, the presence of Ru–CO bonds is evidenced both by the DR-IR and UV–VIS spectra.

The DR-IR spectrum of the green PVG/Ru sample which was heated at 250 °C does not show any bands that can be assigned to ν_{CO} [Fig. 2(e)]. The color remains the same up to 1200 °C, when the glass is consolidated. All through this wide temperature range, the absorption spectrum of the sample stays unchanged which indicates that the species formed at 250 °C is stable up to the glass consolidation temperature.

The final thermal decomposition product of $[Ru_3(CO)_{12}]$ adsorbed inside the pores of PVG was identified by Raman spectroscopy. Fig. 3 shows the Raman spectrum of consolidated PVG/Ru. It exhibits four well defined bands at 709, 642, 522 and 100 cm^{-1}, in addition to the bands of the glass (highlighted with asterisks). These bands were assigned to the B_{1g}, E_g, A_{1g} and B_{2g} modes of RuO_2, respectively.[58] The same bands are also observed in the Raman spectrum of the PVG/Ru sample heated at 250 °C, indicating that formation of the oxide had already occurred at this temperature.

A photomicrograph of consolidated PVG/Ru, obtained by transmission electron microscopy, is shown in Fig. 4. The material consists of small spherical particles of RuO_2, of average diameter 45 Å, suspended in the glassy matrix. A histogram of the size distribution of the RuO_2 particles in consolidated PVG/Ru is shown in Fig. 5.

The electron diffraction pattern of this material corresponds to reflections due the [210] and [211] planes of tetragonal RuO_2. The diffraction pattern was obtained from the area similar to that indicated in Fig. 4. It shows an amorphous

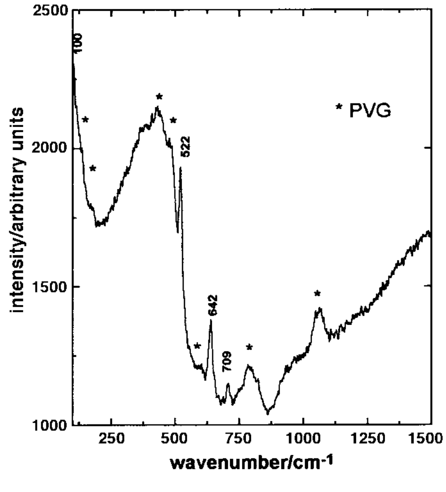

Fig. 3 Raman spectrum of the PVG/Ru sample heated at 1200 °C. Metal loading approximately 3 wt%.

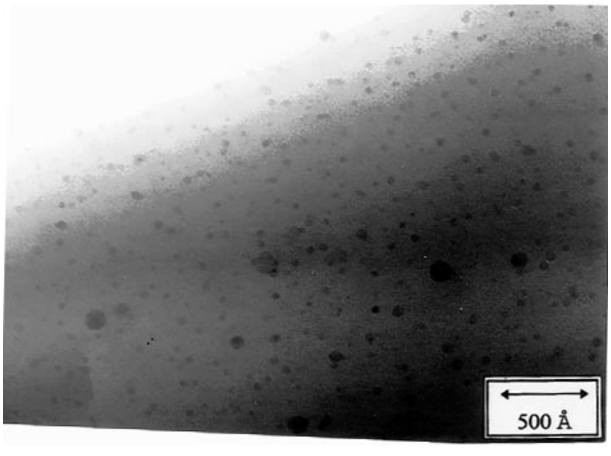

Fig. 4 Transmission electron micrograph of the PVG/Ru sample heated at 1200 °C. Metal loading approximately 3 wt%.

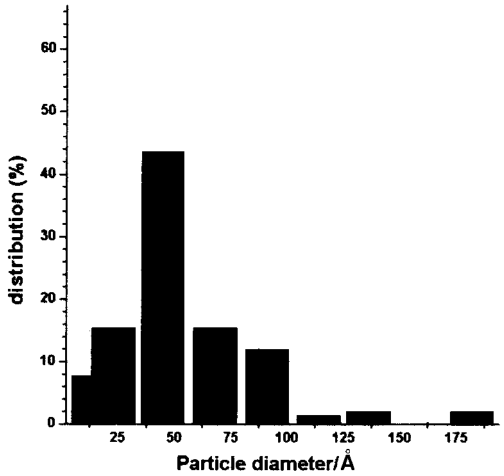

Fig. 5 Histogram showing the particle size of the RuO_2 species formed in the PVG/Ru sample heated at 1200 °C. Metal loading approximately 3 wt%.

halo, due to scattering from the vitreous matrix, which prevents the observation of the other RuO_2 reflections.

These results show that the incorporation and thermal decomposition of $[Ru_3(CO)_{12}]$ inside the PVG pores leads to a new vitreous material doped with RuO_2 nanoparticles. This extremely uniform and transparent nanocomposite exhibits a very small variation in the oxide particles size distribution and thus presents several potential applications in the optical field.

Thermal decomposition of $[Os_3(CO)_{12}]$ adsorbed on PVG

The PVG impregnation with $[Os_3(CO)_{12}]$ was carried out at 80 °C in order to increase the solubility of the cluster in acetonitrile. The resulting material is extremely stable at ambient conditions. The absorption and DR-IR spectra of the $[Os_3(CO)_{12}]$ impregnated PVG (referred to hereafter as PVG/Os) as a function of the heating temperature are illustrated in Fig. 6 and 7, respectively.

As in the case of the PVG/Ru material, the electronic absorption spectrum of the PVG/Os sample [Fig. 6(a)] exhibits bands due to $\sigma^{*\prime}$–σ^* and σ–σ^* transitions which appear at 385 and 328 nm, respectively, and to ligand-to-metal charge transfer, at 280 and 240 nm.[54] When the PVG/Os sample is heated at 80 °C, the absorption spectrum stays unchanged, as does the DR-IR spectrum, indicating that the cluster is stable inside the PVG at this temperature. Thermal treatment of the material at 110 °C, however, leads to a significant modification in the DR-IR spectrum with new bands appearing at 2132, 2110, 2089, 2079, 2066, 2031 and 2017 cm^{-1} [Fig. 7(c)]. These bands were attributed to the $[HOs_3(CO)_{10}(\mu\text{-OSi}\equiv)]$ species **2**,[44,45,48,50,52,53] analogous to the ruthenium species **1**, whose formation was discussed above.

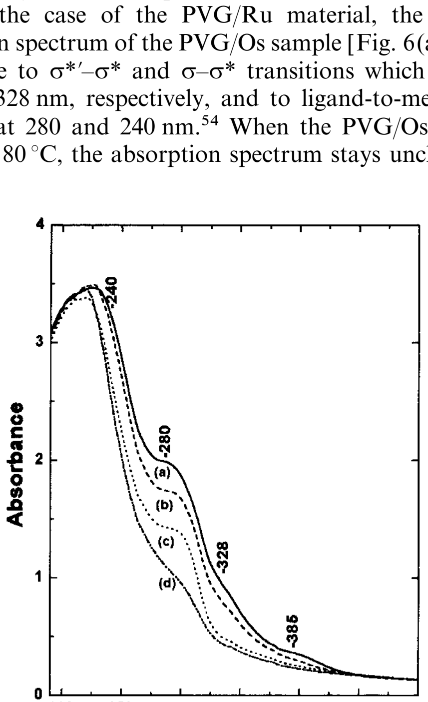

Fig. 6 UV–VIS absorption spectra of (a) PVG/Os, (b) PVG/Os heated at 110 °C, (c) PVG/Os heated at 200 °C, (d) PVG/Os heated at 300 °C. Metal loading approximately 2 wt%.

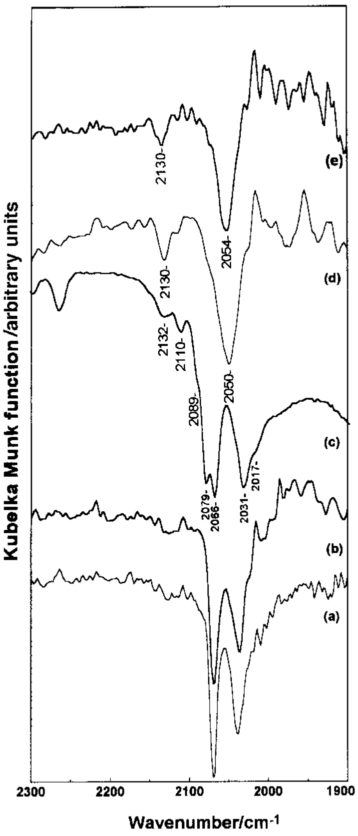

Fig. 7 DR-IR spectra of (a) PVG/Os, (b) PVG/Os heated at 80 °C, (c) PVG/Os heated at 110 °C, (d) PVG/Os heated at 200 °C and (e) PVG/Os heated at 300 °C. Metal loading approximately 2 wt%.

Heating the PVG/Os sample at 200–300 °C leads to a new modification in the profile of DR-IR spectrum [Fig. 7(d),(e)], with the appearance of a weak band at 2130 cm^{-1} and a broad intense band at around 2055 cm^{-1}. This spectral pattern is characteristic of Os^{II} carbonyls, such as $[Os(CO)_2(OSi\equiv)_2]$.[44,48,50,52] Thus, in both ruthenium and osmium, cluster oxidation and breakdown occurs. This process was confirmed by the absorption spectra of the PVG/Os samples heated at 200 and 300 °C [Fig. 7(c),(d)] that do not exhibit bands associated to Os–Os bonds. As in the case of the product from the PVG/Ru thermal decomposition, the new osmium species are chemically linked to the pore surface and may be represented as $[Os(CO)_n(OSi\equiv)_2]$ ($n=2$ or 3).

Heating the sample at $T=400$ °C leads to the disappearance of the ν_{CO} bands in the DR-IR spectrum. The sample becomes colorless, and the absorption spectrum is that of pure PVG. These results are evidence for the absence of any molecular species when the PVG/Os sample is heated above 400 °C. Thus, it appears that OsO_4 is formed and sublimes out of the glass, under these conditions.

Conclusions

The results presented herein reveal that thermal decomposition of PVG incorporated $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{12}]$ occurs *via* the intermediates $[HM_3(CO)_{10}(\mu\text{-OSi}\equiv)]$ and $[M(CO)_n(OSi\equiv)_2]$ ($n=2$ or 3), which are formed at low temperatures, in a similar fashion as previously described for the thermal decomposition of $[\mathrm{Ru_3(CO)_{12}}]$ and $[\mathrm{Os_3(CO)_{12}}]$ on silica and alumina surfaces. The different temperatures at which the formation of each species occurs, in the two cases, reflect the higher Os–Os and Os–CO than Ru–Ru and Ru–CO bond dissociation energies.[43] It is very likely that the $[\mathrm{HRu_3(CO)_{10}(\mu\text{-}OSi{\equiv})}]$ and $[\mathrm{Ru(CO)}_n\mathrm{(OSi{\equiv})_2}]$ species, formed upon decomposition of the PVG incorporated ruthenium carbonyl cluster, are responsible for the catalytic activity of Gafney's PVG/Ru material.[10] Similar fragments anchored on inorganic supports have been shown to exhibit good performance as catalysts for a large number of chemical transformations.[44,45,50]

Thermal decomposition of $[\mathrm{Ru_3(CO)_{12}}]$ impregnated PVG above 250 °C leads to the formation of $\mathrm{RuO_2}$ nanoparticles. The resulting material is a green, highly transparent and homogeneous nanocomposite, with a narrow oxide particle size distribution. These results suggest that the incorporation and thermal decomposition of organometallic compounds inside the pores of PVG might offer an excellent route to original nanocomposites.

Acknowledgement

The authors would like to thank Dr Daniel Ugarte for the electron diffraction micrography, CNPq and FAEP/UNICAMP (A. J. G. Z.) for a grant and FAPESP for research grants.

References

1 N. F. Borreli and D. L. Morse, *Appl. Phys. Lett.*, 1983, **43**, 1.
2 N. F. Borreli, D. L. Morse and J. W. H. Schreus, *J. Appl. Phys.*, 1983, **54**, 3344.
3 R. Simon and H. D. Gafney, *Inorg. Chem.*, 1983, **22**, 573.
4 M. S. Darsillo, H. D. Gafney and M. S. Paquete, *J. Am. Chem. Soc.*, 1987, **109**, 3275.
5 R. C. Simon, H. D. Gafney and D. L. Morse, *Inorg. Chem.*, 1985, **24**, 2565.
6 H. D. Gafney, *J. Macromol. Sci-Chem. A*, 1990, **27**, 1187.
7 D. Sunil, J. Sokolov, M. H. Rafailovich, X. Duan and H. D. Gafney, *Inorg. Chem.*, 1993, **32**, 4489.
8 E. A. Mendoza, E. Wolkow, D. Sunil, P. Wong, J. Sobokov, M. H. Rafailovich, M. DeuBoer and H. D. Gafney, *Langmuir*, 1991, **7**, 3046.
9 D. Sunil, J. Sokolov, M. H. Rafailovich, B. Kotyuzhanskii, H. D. Gafney, B. J. Wilkens and A. L. Harson, *J. Appl. Phys.*, 1993, **74**, 3768.
10 H. D. Gafney and S. P. Xu, *Inorg. Chim. Acta.*, 1995, **240**, 645.
11 J. C. Luong, *Superlatt. Microstruct.*, 1988, **4**, 385.
12 Y. Wang and N. Herron, *Res. Chem. Interm.*, 1991, **15**, 17.
13 R. D. Stramel, T. Nakamura and J. K. Thomas, *J. Chem. Soc., Faraday Trans. 1*, 1988, **84**, 1287.
14 D. G. Hendershot, D. K. Gaskill, B. L. Justus, M. Fatemi and A. D. Berry, *Appl. Phys. Lett.*, 1993, **63**, 3324.
15 J. C. Luong and N. F. Borreli, *Mater. Res. Soc. Symp. Proc.*, 1989, **114**, 695.
16 B. L. Justos, R. Tonucci and A. D. Berry, *Appl. Phys. Lett.*, 1992, **61**, 3151.
17 M. D. Dvorak, B. L. Justus, D. K. Gaskill and D. G. Hendershot, *Appl. Phys. Lett.*, 1995, **66**, 804.
18 H. Yamashita, Y. Ichihashi, M. Harada, G. Stewart, M. A. Fox and M. Anpo, *J. Catal.*, 1996, **158**, 97.
19 T. H. Elmer and H. J. Holland, *Am. Ceram. Soc. Bull.*, 1987, **66**, 1265.
20 A. L. Huston, B. L. Justus and T. L. Johnson, *Appl. Phys. Lett.*, 1996, **68**, 3327.
21 G. A. Ozin, *Adv. Mater.*, 1992, **4**, 612.
22 Y. Wang and N. Herron, *J. Phys. Chem.*, 1987, **91**, 5005.
23 L. Brus, *J. Phys. Chem.*, 1986, **90**, 2555.
24 M. L. Steigerwald and L. E. Brus, *Acc. Chem. Res.*, 1990, **23**, 183.
25 H. Weller, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1079.
26 Y. Wang, N. Herron, W. Mahler and A. Suna, *J. Opt. Soc. Am. B*, 1989, **6**, 4.
27 G. Cao, L. K. Rabenberg, C. M. Numm and T. E. Mallouk, *Chem. Mater.*, 1991, **3**, 149.
28 C. B. Murray, D. J. Norris and M. G. Bawendi, *J. Am. Chem. Soc.*, 1993, **115**, 8706.
29 J. P. Carpenter, C. M. Lukehart, D. O. Henderson, R. Mu, B. D. Jones, R. Glosser, S. R. Stock, J. E. Witting and J. G. Zhu, *Chem. Mater.*, 1996, **8**, 1268.
30 A. Hagfeldt and M. Gratzel, *Chem. Rev.*, 1995, **95**, 49.
31 J. E. MacDougall, H. Eckert, G. D. Stucky, N. Herron, Y. Wang, K. Moller, T. Bein and D. Cox, *J. Am. Chem. Soc.*, 1989, **111**, 8006.
32 H. J. Watzke and J. H. Fendler, *J. Phys. Chem.*, 1987, **91**, 854.
33 E. P. Giannelis, *Adv. Mater.*, 1996, **8**, 29.
34 R. J. Gehr and R. W. Boyd, *Chem. Mater.*, 1996, **8**, 1807.
35 P. Judeinstein and C. Sanchez, *J. Mater. Chem.*, 1996, **6**, 511.
36 Corning Glass Work, *Mater. Eng.*, 1979, **90**, 92.
37 P. Levitz, G. Ehret, S. K. Sinha and J. M. Drake, *J. Chem. Phys.*, 1991, **95**, 6151.
38 H. D. Gafney, *Coord. Chem. Rev.*, 1990, **104**, 113.
39 M. J. D. Law and N. Ramasubramanian, *J. Phys. Chem.*, 1966, **70**, 2740.
40 J. Fan and H. D. Gafney, *J. Phys. Chem.*, 1994, **98**,13058.
41 B. C. Gates, L. Guczi and H. Knözinger, *Metal Clusters in Catalysis*, Elsevier Science Publishing, New York, 1996.
42 M. Moskovits, *Metal Clusters*, Wiley-Interscience Publishing, New York, 1996.
43 D. M. P. Mingos and D. J. Wales, *Introduction to Cluster Chemistry*, Prentice Hall, Englewood Cliffs, NJ, 1990.
44 R. Barth, B. C. Gates, Y. Zhao, H. Knözinger and J. Hulse, *J. Catal.*, 1983, **82**, 147.
45 R. Psaro, R. Ugo, G. M. Zanderighi, B. Besson, A. K. Smith and J. M. Basset, *J. Organomet. Chem.*, 1981, **213**, 215.
46 K. Asakura, M. Yamada, Y. Iwasawa and H. Kuroda, *Chem. Lett.*, 1985, 511.
47 H. Knözinger and Y. Zhao, *J. Catal.*, 1981, **71**, 337.
48 A. K. Smith, B. Besson, J. M. Basset, R. Psaro, A. Fusi and R. Ugo, *J. Organomet. Chem.*, 1980, **192**, C31.
49 V. D. Alexiev, N. Binsted, J. Evans, G. N. Greaves and R. J. Price, *J. Chem. Soc., Chem. Commun.*, 1987, 395.
50 M. Deeba and B. C. Gates, *J. Catal.*, 1981, **67**, 303.
51 A. Theolier, A. Choplin, L. D'Ornelas and J.-M. Basset, *Polyhedron*, 1983, **2**, 119.
52 T. H. Walter, G. R. Frauenhoff, J. R. Shapley and E. Oldfield, *Inorg. Chem.*, 1991, **30**, 4732.
53 B. Besson, B. Moraweck, K. Smith and J. M. Basset, *J. Chem. Soc., Chem. Commun.*, 1980, 569.
54 W. H. Wade, *Soc. Petroleum Eng. J.*, 1974, 139.
55 C. Straley, A. Matteson, S. Feng, L. M. Schwartz, W. E. Kenyon and J. R. Banavar, *Appl. Phys. Lett.* 1989, **51**, 1146.
56 T. Okubo and H. Inoue, *J. Chem. Eng. Jpn.*, 1987, **20**, 590.
57 D. R. Tyler, R. A. Levenson and H. B. Gray, *J. Am. Chem. Soc.*, 1978, **100**, 7888.
58 Y. S. Huang and F. H. Pollak, *Solid State Commun.*, 1982, **43**, 921.

Paper 8/04066D