Thermolytic Transformation of Organometallic Polymers Containing the Cr(CO)$_5$ Precursor into Nanostructured Chromium Oxide

Carlos Díaz,[1,2] **Paola Castillo,**[1] **and Maria Luisa Valenzuela**[1]

Thermal treatment in air of the organometallic polymer$\{[NP(O_2C_{12}H_8)]_{0.8}$ $[NP(OC_6H_4CH_2CN \bullet [Cr(CO)_5]_{0.13})_2]_{0.18}\}_n$ (1) results in the formation of nanometer-size metal oxide particles. Cr particles in the 35–85 nm range, mostly 54 nm, immersed in an phosphorus oxides matrix were found. ATG studies in air suggest that the formation of the nanostructures occurs in four steps, the first involving loss of the carbonyl groups of the Cr(CO)$_5$ fragment. The following steps involve the oxidation of the organic matter and finally the oxidation of the chromium to give the pyrolytic product. The use of these kinds of organometallic polymers as precursors for a general and potential new route to materials having metal/metal oxide nanostructures is discussed.

KEY WORDS: Metallic nanoclusters; organometallic polyphosphazenes; chromium nanoparticles; pyrolysis.

INTRODUCTION

The development of synthetic methods that allow fine control of solid-state structures at the atomic level is a fundamental goal in materials science. In this context there has been significant interest in routes to nanostructured metal and metal oxide materials [1]. Although chemical and physical methods for preparing these kinds of materials from solution have been widely used, solid state methods are scarce. In particular, the methods for

[1]Departamento de Química, Facultad de Ciencias, Universidad de Chile, 653, Casilla, Santiago, Chile.
[2]To whom correspondence should be addressed. E-mail: cdiaz@uchile.cl

synthesizing metal oxides are only slightly controllable and they are generally physical, starting from the metal oxide prepared and ground to the nano-level [1, 2]. An alternative approach for the preparation of nano-structured metal oxides could be the use of polymeric organometallic precursors [3]. The advantages of the single polymeric precursor routes include the efficient incorporation of metals and the *in situ* formation of the corresponding oxides by oxidation in air. Burning of the organic matter may produce "holes" which serve as templates for producing the aggregates. On the other hand, the inorganic polymer backbone could serve as a matrix to stabilize the metallic cluster.

Transition metal oxides form a large family of materials which find use in areas of catalysis, superconductivity, large magnetoresistances, piezo-electricity, etc. Their nanosize form differs greatly in many properties from the bulk materials [1]. The most common nanosize materials are nonopar-ticles. Among the metal oxides, chromium oxide is used commercially as catalyst in the polymerization of ethylene and in the dehydrogenation of light paraffins [4]. Nanostructured chromium oxide may exhibit enhanced catalytic activity; however, to the best of our knowledge, few examples have been reported. Most of them refer to chromium oxide nanoparticles supported on another metal oxide (SiO_2 [4b], Al_2O_3 [4a], or others [2a]). We have already reported the preparation of the chromium organometallic polymer$\{[NP(O_2C_{12}H_8)]_{0.8}[NP(OC_6H_4CH_2CN \bullet [Cr(CO)_5]_{0.13})_2]_{0.18}\}_n$ (1), and found high pyrolytic residues in TGA studies in N_2 [5]. This encouraged us to study the pyrolysis of organometallic polymer (1) in air and the characterization of the pyrolytic residues. In this paper we report the thermolytic conversion of (1) to nanoclusters of Cr_2O_3 in a P_4O_7 matrix.

EXPERIMENTAL

Reagents and Methods

Reactions were performed under nitrogen. Organometallic polymer (1) was prepared as described previously [5]. Thermal treatment of polymer (1) was carried out in a Lindberg Blue programmable furnace. The pyrolysis experiments were performed by pouring a weighed portion (0.05–0.15 g) of the organometallic polymers into an aluminium oxide boat that was placed in a furnace under a flow of air using a temperature program. The pyrolytic residues were characterized by IR, XRD, scanning electron microscopy, and transmission electron microscopy. IR spectra were recorded on a Bruker Vector 22 spectrophotometer. Thermogravimetric analyses were performed on a Mettler TA 4000 instrument. The samples were heated at a rate of 10°C/min from ambient temperature to 800°C under a constant flow of air

(200 mL/min). X-ray diffraction (XRD) was made on a Siemens D-5000 diffractometer with θ-2θ geometry working at room temperature. The XRD data were collected using Cu–kα radiation (40 kV and 30 mA) wave.

SEM micrographs were performed on a Philips EM 300 apparatus. Elemental analyses of the pyrolytic products were made by energy dispersive X-ray analysis using a NORAN Instruments micro-probe attached to a JEOL 5410 scanning electron microscope. Satisfactory data according to the proposed structure for the pyrolytic residues were obtained. TEM images were made on a JEOL SX 100 transmission electron Microscope. The finely powdered samples were dispersed in water and dropped on a conventional carbon-coated copper grid, Particle size distribution was obtained by manual measurements of particle diameters from the bright-field TEM micrographs.

RESULTS AND DISCUSSION

The solid state thermolytic conversion of (1) to nanostructured materials in an air atmosphere was examined. At a preparative scale the experiments were performed in the furnace in an air atmosphere (see Experimental section) and details of the processes were obtained from a thermogravimetric study. Pyrolysis of the polymer (1) affords a green powder in ca. 11% yield. The material was characterized by IR, XRD, SEM-EDAX and TEM microscopy (see below). The TGA of the sample (see Fig. 1) in air shows a small initial weight loss that can be attributed to the loss of four CO groups from the $Cr(CO)_5$ organometallic fragment (calculated weight loss 5.59%, found 5.66%).
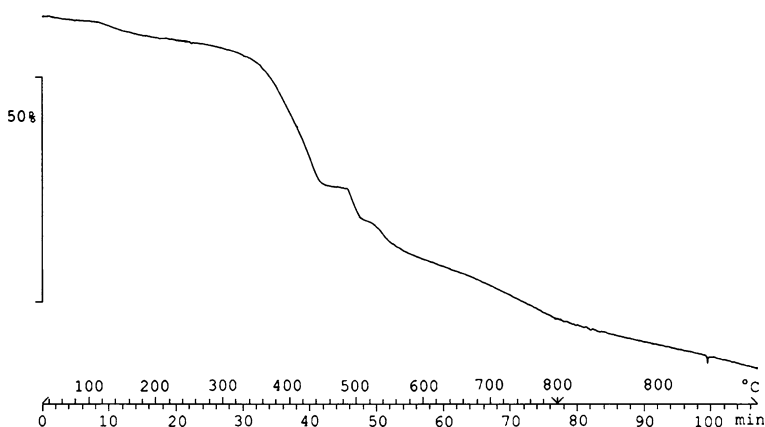

Fig. 1. TGA curve for polymer (1) in air.

The second sudden weight loss, starting at ca. 300°C, can be assigned to the transformation of the carbon-bispiro groups to CO_2 (calculated weight loss 43.6%, found 39.23%).

The final smooth decrease of the weight loss curve – which can be divided into two steps – may be ascribed to the formation of CO_2 from the carbon phenyl groups together with the formation of nitrogen oxides in the first step (calculated weight loss 23.3%, found 22.7%). The second step can be attributed to the formation of Cr_2O_3/P_4O_7, the final residue (calculated weight loss for a mixture of 30.74% Cr_2O_3 and 69.265% P_4O_7: 25.18, found: 22.84).

These results are consistent with the formulation of the pyrolysis product as nanostructured Cr_2O_3 immersed in a P_4O_7 matrix. On the other hand, the SEM-EDAX analysis was consistent with a mixture of 30.7% Cr_2O_3 and 69% P_4O_7. These results suggest that the main Cr species present in the pyrolysis is the thermodynamically favoured chromium oxide Cr_2O_3. In agreement with this, the IR spectrum showed bands at 632, 562 and 483 cm^{-1}, typical of Cr_2O_3 [4b]. It is well known that the thermolysis in air of substrates containing the $Cr(CO)_5$ moiety yields chromium oxides as Cr_2O_3 [6, 7]. On the other hand, Intense IR bands around 1100 and 1000 cm^{-1}, assigned to the ν (P=O) vibrations of the phosphorus oxides [8], confirm their presence as a matrix in the pyrolysis product. The transmission electron microscopy (TEM) image of a typical organometallic pyrolytic residue is shown in Fig. 2.

These particles have a broad size distribution, as seen in the histogram of Fig. 3. The size distribution ranges from 33 at 86 nm, with 54 nm being the most abundant.

As shown in the inset of Fig. 1, EDAX analysis of the materials confirmed the presence of chromium, phosphorus, oxygen, and traces of
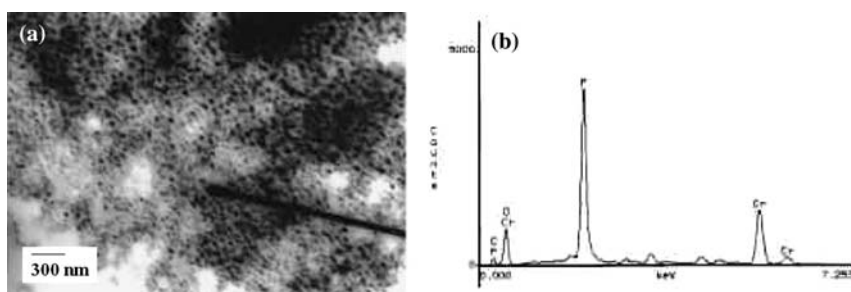

Fig. 2. (a) TEM image of the product of the pyrolysis of the polymer (1) on a holes copper grid. The darker circular region is made of chromium oxide nanoparticles. (b) EDAX analysis of a portion of the material.

carbon. EDAX analysis carried out on several zones of the material showed that it was homogeneous.

The morphology observed on calcination of the sample was investigated by scanning electron microscopy. The material both before and after calcination is porous, with a evident 3D assemblies networks (after pyrolysis) as shown in Fig. 4.

The X-Ray patterns of the pyrolytic material (see Fig. 5) exhibits the diffraction peaks expected (W 15406) for P_4O_7 at $2\theta = 18.62°$, $18.93°$ and $19.34°$. The signals for Cr_2O_3 were not observed due to either broadening of the expected signals [2a, 4a, b] or masking by the phosphorus oxide matrix. The intense peak in the low-angle diffraction regime at $2.17°$ not observed in the XRD patterns of P_4O_7 can due to a typical secondary reflections presumably arising from the nanoparticles of Cr_2O_3.

The pyrolysis experiments showed that the product was etched on the ceramic crucible, and therefore chemical treatment of the crucible with concentrated acid (HNO_3/H_2SO_4), alkali (NaOH) or an HCl/HNO_3 mixture did not dissolve the chromium materials.

Possible Mechanism for the Formation of Cr_2O_3/P_4O_7 from Polymer (1)

A mechanism for the formation of the nanostructurated Cr_2O_3 immersed in a matrix of phosphorus oxides can be proposed considering the results discussed above. The polyphosphazene polymer backbone affords the matrix that initially keeps the metal centres separated. Release
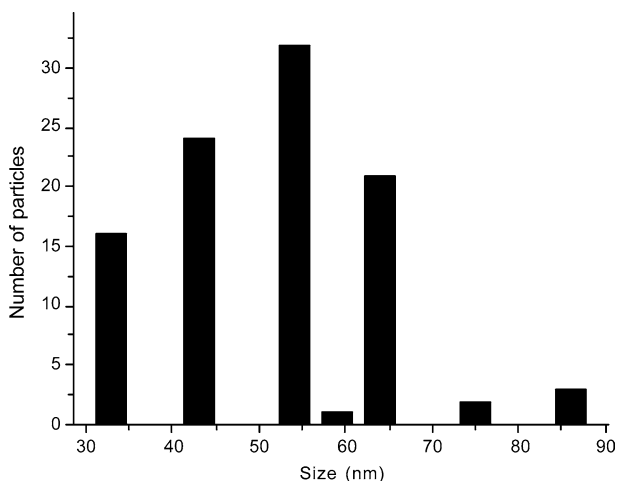

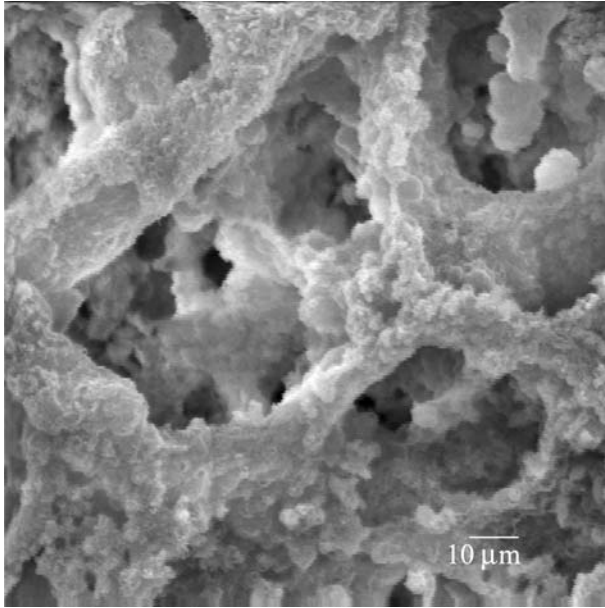**Fig. 3.**   Histogram of Cr particles from the pyrolytic residue.

Fig. 4.   SEM of the preceramic product formed at 800°C via pyrolysis in air.
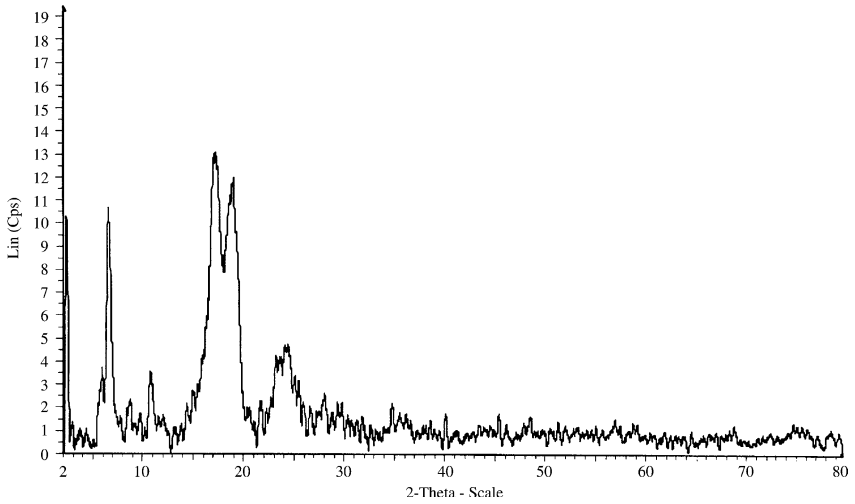

Fig. 5.   XRD patterns of the pyrolytic product.

of the carbonyl groups detected in the first step of the TGA study affords the Cr atoms necessary for the later formation of the oxide. Calcination of the organic matter, the following step in the TGA study, produces holes in the polymeric matrix which allow the agglomeration of the previously formed Cr_2O_3 particles (probably by oxidation of the Cr atoms formed earlier). Finally, the formation of the phosphorus oxides yields the matrix that stabilizes the nanoclusters of Cr_2O_3.

The experiments described above open a potential way for imprinting metals or metal oxides on ceramic surfaces, with possible applications in advanced ceramic technologies. Of greater interest yet, if the ceramic precursor is incorporated in the polymer precursor (i.e. as an aluminium or silicon organometallic fragment anchored to the polyphosphazene backbone) together with the organometallic fragment containing the metal precursors of the nanostructures (i.e. $Cr(CO)_5$, $W(CO)_5$, etc.), and then the polymer is pyrolyzed in air, a product containing the metallic nanostructures (Cr_2O_3, WO_3, etc.) immersed in a ceramic matrix (Al_2O_3, $(SiO_2)_n$) may be obtained. Experiments to confirm this are being performed.

The finding that incorporation of chromium organometallic fragments anchored to polyphosphazene polymers affords nanostructured pre-ceramic materials encouraged us to investigate the pyrolysis of polyphosphazenes containing other anchored organometallic fragments, such as $W(CO)_5$ [9a], $(\pi\text{-}CH_3C_5H_4)Mn(CO)_2$ [9b], $CpFe(dppe)^+$ [9c], and $CpRu(PPh_3)_2^+$ [9c], whose results can become the basis for a new solid state method for preparing nanostructured metal oxide materials.

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