GENERAL GROUP VI TRANSITION NANOSTRUCTURED METAL OXIDES AND THEIR INCLUSION INTO SOLID MATRICES BY A SOLUTION-SOLID APPROACH

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ABSTRACT

A facile and general solution/solid-state (SSS) approach to the synthesis of nanostructured metal oxides Cr2O3, MoO3 and WO3 was investigated. They are made from solid-state pyrolysis of the metal- macromolecular precursors PS-co-4-PVP•MCln and Chitosan•MCln with M= Cr, Mo and W, which were easily prepared by direct reaction of the salts CrCl3, MoCl5 and WCl6 with the respective polymer. The size and morphology of the products, the nanostructured oxides Cr2O3, MoO3 and WO3 depend on the polymer and on the coordination degree of the precursor, Cr2O3 as well as WO3, prepared from this method were included in silica and Titania matrix using an also solution/solid-state approximation. The nanoparticles of Cr2O3 and WO3 are in general distributed with uniformity within the amorphous silica. A probable formation mechanism of the Cr2O3 and MoO3 nanoparticles was proposed. The nanocomposites Cr2O3/SiO2 and WO3/SiO2 could be useful materials in catalysis.

Keywords: Solid-state, pyrolysis, nanostructured, metal oxide

INTRODUCTION

Among the metal-ligand coordination compounds, the macromolecular complexes [1] can be considered as a special case, where the ligand has multiple coordination sites. The preparation of such metal multi-sites ligands is usually difficult because of metal ions must coordinate hundreds and sometimes thousands of coordination sites. This process is often a slow kinetics, being the products usually insoluble and of poor characterization. Thus, these macromolecular complexes rarely reach the 100%-degree coordination [2-5]. In spite of this, this particular type of multi-coordination compounds have attracted much attention due to their interesting applications in the materials science. For instance the metallic derivate from polyphosphazenes affords, after pyrolysis at 800 °C under air, nanostructured materials of the type M’ and M0/Mx(PO4)2 [6-9]. The metallic phosphate phases normally appear due to the presence of phosphorus atoms in the polymeric chain.

Metal oxides have attracted great interest for their applications as anode materials for lithium batteries [10,11], catalysis [12,13], sensors [14], solar cells [15], solid-state transistors [16] and metal ion removal [17]. Although several solution methods to prepare metal oxides have been reported [18-22] few solid-state routes have appeared [23,24]. The aim of developing solid-state methods to prepare nanoparticles stems mainly from their possible application in solid-state materials and powder-oriented applications, from thin film metal deposition to noble metal nanoparticle-carbon catalysts, oxide growth, photonic and dielectric materials, to new materials for Li-ion rechargeable batteries. The ability to rationally prepare metallic and metal oxide nanoparticles stems from the exploring methods for alternative nanoscale metal deposition in solid-state nanoelectronics and nanotechnology [25-28] and the benefit of being able to deposit both metals and dielectric or semiconducting oxides, both from the same base route. Issues including limitations on good mechanical and thermal stability of nanoscale metal have been found related to certain deposition methods for these metals. Most of this application requires pure phase metal oxides.

For group VI metal oxides there not a general method to prepare these nanostructured materials. For instance, using W(CO)6 as precursors the W13O49 nanostructured molybdenum oxide was obtained [29]. On the other hand the Cr2O3 nanostructured nanoparticles was obtained from the thermal treatment of the carbene Fischer (CO)5Cr(Ph)(OMe)3. The nanostructured MoO3 was obtained from a hydrothermal method using (NH4)6Mo7O24•4H2O as source of Mo [31]. Alternatively other methods have also been used to obtain the nanostructured Cr2O3, MoO3 and WO3 [32-38]. On the other hand, the thermal treatment [(NP(OCH2CH2CN)3Cr(CO)3]x, (NP(OCH2CH2CN)3Mo(CO)3]x, (NP(OCH2CH2CN)3W(CO)3]x results in the formation of nanometer-size metal oxide particles [38].

We have developed a new solid-state method to prepare phase pure metal oxide nanoparticles from the macromolecular complexes Chitosan•Mx and PS-co-4-PVP•Mxn (PS-co-4-PVP = Poly(styrene-co-4-vinylpyridine)) see scheme 1. In this paper the phase pure Cr2O3, MoO3 and WO3 were prepared using this synthetic approach. We have chosen Chitosan because of it is a cheap commercial product and by their effective coordinative properties to ion metal. Chitosan [39-41] is a polysaccharide obtained by deacetylation of natural chitin, which is one of the important natural polymers constituting the shells of crustaceans and the cell wall of many fungi. Due to its available from the NH2 groups and the OH moieties present in the polysaccharide chains; it can bind metal ions -in solution- forming macromolecular metal complexes [42-44]. Although the ability to retain metal ions in solution, Chitosan has been widely studied and previously reported, solid-state-macromolecular complexes have been not well characterized. Particularly for several some Cu /Chitosan complexes, some X-ray and ESR studies have been performed [45-47]. Chitosan can act as solution template/stabilizer for the formation of nanoparticles [47-55]. Some biological applications [54-55] including biosensors for glucose have been reported [58]. In addition, Chitosan as support for catalysis processes have been also described [56].

On the other hand, Poly(styrene-co-4-vinylpyridine) is useful functional copolymer due to the vinylpyridine block which binds metal ions and the styrene groups to facilitate stable macromolecular complexes 1, [53-56]. It has also been used in an selective facet growth in noble metal nanoparticle. PS-b-4-PVP has been used in solution as a template/stabilizer of metals and other nanoparticles [57-58].

Although several solution methods to prepare nanostructured Cr2O3, MoO3 and WO3 oxides few solid-state routes have been informed [61-67]. Using a solid state approach with precursors having the organometallic fragment W(CO)6 linked to oligo and poly-phosphazene mixtures of W/WO3 linked to oligo and poly-phosphazene mixtures of W/WO3/PS has been obtained [68] while that using the organometallic derivatives of poly(styrene-co-4-vinylpyridine), (CH2=CH(CH2)3)0.10(CH2=CH(CH2)16NMLa)0.50, MLa = W(CO)6, as precursors pure WO3 obtained [69]. On the other hand from the N5P5[OC(2H5)CH2CH2CN-Mo(CO)3]8 (I) and N5P5[OC(2H5)CH2CH2CN-Mo(CO)3]8 (II) precursors pure phase MoO3 was obtained [69].

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SEM images were acquired with a Philips EM 300 scanning electron microscope. Energy dispersive X-ray analysis (EDAX) was performed on a NORAN Instrument micro-probe attached to a JEOL 5410 scanning electron microscope. Transmission electron microscopy (TEM) experiments were performed using a FEI Tecnai T20 microscope, operated at 200 kV, in order to analyse the average size, distribution and morphology of the particles. High-resolution transmission electron microscopy (HRTEM) was performed using a JEOL 2000FX microscope at 200 kV. Interplanar distances were measured using the Gatan Digital Micrograph software. The TEM samples were prepared by dispersing pyrolyzed material onto copper grids, previously sonicated under ethanol media and then dried at room temperature. For high-resolution examination of graphic carbons, flakes of sonicated carbons were dispersed on grids and examined under SEM to determine their thickness. X-ray diffraction (XRD) was conducted at room temperature on a Siemens D-500 diffractometer with 0-20 geometry. The XRD data was collected using Cu-Kα radiation (40 kV, 30 mA). FTIR measurements were performed on a Perkin Elmer FTIR spectrophotometer model Spectrum BXII.

RESULTS AND DISCUSSION

Macromolecular complexes

The direct reaction of the metallic salts CrCl\(_2\), MoCl\(_4\) and WCl\(_4\) with the respective polymer Chitosan or PS-co-4-PVP in CH\(_2\)Cl\(_2\) as solvent affords very stable insoluble solids with colors stemming from the coordination of the metal ion to the polymer. For instance, precursors, green from the (Chitosan)(CrCl\(_2\))\(_n\), and PS-co-4-PVP(4CrCl\(_3\)), see S1 Supplementary data.

Coordination of the metal ions to the coordinating groups of both polymers was achieved by IR spectroscopy. For Chitosan-metal complexes, the coordination was evident from the broad ν(OH) in Chitosan [44,46,70] which becomes unfolded upon coordination, appearing a new band around 3100 cm\(^{-1}\). On the other hand for poly(styrene-co-4-vinylpyridine) the coordination was confirmed by the emergence of a new band centered at 1600 cm\(^{-1}\) characteristic of pyridine coordination [69,70]. Selected data for the precursor PS-co-4-PVP(4MoCl\(_4\))\(_n\) and Chitosan(MoCl\(_4\))\(_n\) are shown in Supplementary data, S2.

Pyrolysis of Macromolecular complexes

The pyrolytic products were characterized by XRD powers. Illustrative XDR the pyrolytic products CrO\(_2\), MoO\(_3\) and WO\(_3\) from the respective precursors PS-co-4-PVP(4MoCl\(_4\))\(_n\) are shown in supplementary data S3, figure A. For precursors (2) sharp peaks – among other less intense – were obtained corresponding to the planes (012), (104), (110), (113), (024) and (116) indicating the rhombohedral CrO\(_2\)[32]. Fig. B of S3 shows the XRD peaks which can be indexed to orthorhombic crystal MoO\(_3\) (ICPDS card N° 00-005-0508). Main peak was observed at (020), (110), (040) (021) (111), (112), (060), see Fig S3. Thus the crystal phase is somewhat different to that obtained from precursors N\(_2\)P\(_2\)(OCH\(_2\)CH\(_2\)CN-Mo(CO)\(_3\))\(_6\) (I) and N\(_2\)P\(_2\)(OCH\(_2\)CH\(_2\)CH\(_2\)Mo(CO)\(_3\))\(_n\) (II) precursors [69] were some fraction of lamellar was also observed. The observed XRD pattern is similar to that of MoO\(_3\) obtained by another solution method. [33].

Figure C of S3 shows the XRD peaks which can be indexed to monoclinic crystal WO\(_3\) (ICPDS card N° 01-083-0950). Main peak was observed at (002), (020), (200) (120) (-120), (112), (022), (220) (-202) and (400) see Fig S3. The observed XRD pattern is similar to that of pyrolytic residue from the organometallic precursors [CH\(_2\)CH\(_2\)CH\(_3\)]\(_3\)[CH\(_2\)CH\(_2\)CH\(_2\)H\(_N\)(W(CO))\(_3\)]\(_n\) [68].

As is usually observed for nanoparticles produced by thermal methods the size and shapes exhibits wide distributions being usually rather big sizes and with a variety of shapes [23]. TEM images for the Cr precursors show a clear dependence of the size with the molar ratio as shown in figure 2. There is no clear explanation for this finding, although it could be related with the form of how the metallic centers are distributed along the polymeric chain. HRTEM images show different morphologies for the pyrolytic products from the chromium oxide. Figure 2 (f) confirms the formation of CrO\(_2\) as the interplanar distance of 0.25 nm (110) was measured. EDS analysis see figure 2d shows as expected the presence of Cr and O (also Cu arising from the copper grid).
On the other hand, the TEM image shows a no relationship of the size with the molar ratios for the Mo precursors. For the pyrolytic product from the precursors 1:1 Chitosan●MoCl₃, somewhat big bars nanostructures were observed see figure 3. The SAED image, figure 3 d, exhibits the presence of some planes characteristic of MoO₃ as (1 3 0), (1 4 0), (1 5 0), (0 0 2), (2 1 1), y (1 8 0). In figure 3 e, the EDS of the sample exhibits the presence of the O and Mo elements expected for MoO₃. HRTEM image (figure 3d) confirmed the structure of WO₃. The inset shows a SAE of the area with the zone axis [010].

For WO₃ particles, as shown in figure 4, big agglomerates were observed. HRTEM images (figure 3d) confirmed the structure of WO₃, as the interplanar distance of 0.37 nm (020) was measured in both images. EDS analysis see figure 4e, as expected confirms the presence of W and O elements.
Figure 4. TEM a) and b) and HRTEM image c) d) and EDS e) of WO₃ from PS-co-4-PVP●WCl₄ precursors.

Inclusion of Cr₂O₃ and WO₃ inside silica

Owing the most applications of nanostructured Cr₂O₃ and WO₃ involves the use of these metal oxides inside SiO₂ (for instance catalysis) we attempted the inclusion of Cr₂O₃ and WO₃ inside silica using the here described solution-solid state method. SiO₂ was generated by the sol-gel method and added over the solution were the precursor PS-co-4-PVP●MXn and Chitosan●MXn with M= Cr and W was forming [71]. Then the PS-co-4-PVP●MXn/SiO₂ and Chitosan●MXn/SiO₂ precursors were pyrolyzed forming the Cr₂O₃/SiO₂, MoCl₃/SiO₂ and WO₃/SiO₂ composites. The X-ray analysis of the respective materials are shows in supplementary materials see figure S4.

The composite Cr₂O₃/SiO₂ and WO₃/SiO₂ obtained both, from the Chitosan●CrCl●SiO₂ as well as from PS-co-4-PVP●WCl₄/SiO₂ precursors exhibit the typical diffraction peaks of Cr₂O₃ or WO₃ discussed already, as well as a broad peak between 2θ = 15-20 ° for the Cr₂O₃/SiO₂ composite and a broad peak between 2θ = 5-20 ° for the WO₃/SiO₂ typical of amorphous silica [71-74].

The distribution of the metal oxides Cr₂O₃ and WO₃ was investigated using the SEM-EDS mapping technique. For both composites Cr₂O₃/SiO₂ and WO₃/SiO₂, a uniform distribution of the Cr₂O₃ and WO₃ of the nanoparticles inside SiO₂ was observed as is shows in figure 5 a) and 5b) and 6a) and b).
Figure 5. EDX-elemental mapping of a) Cr$_2$O$_3$ nanoparticles inside silica from PS-co-4-PVP●(CrCl$_3$)$_3$//SiO$_2$ precursor and of b) Cr$_2$O$_3$ nanoparticles inside silica from precursor Chitosan●(CrCl$_3$)$_3$//SiO$_2$. 

a) 

b)
Formation Mechanism of the CrO₃, MoO₃ and WO₃ nanoparticles.

In order to give some insight about the formation mechanism of the nanostructured CrO₃, MoO₃ and WO₃, we believe that materials from both precursors can be proposed using the mechanism of formation of nanostructured metallic materials from the oligomer precursor [NP(OC₃H₇Cl)₉OC₃H₇)PPh₃-Mn(OC₃H₇)(η₃-C₆H₅Me)]ₙ [9,75]. A schematic representation of this process is provided in figure 7. Briefly, the first step on heating involves the formation of a 3D network to produce a thermally stable matrix. This step is crucial because it offsets the sublimation. The first heating step could involve a cross linking of the chitosan or PSP-4-PVP polymer giving a 3D matrix containing the CrO₃, MoO₃ and WO₃ compounds linked to the polymeric chain.

The following steps could involve the starting of the organic carbonization, producing holes where the nanoparticles begin to nucleate. As it was confirmed in earlier studies [9,75], the CrO₃, MoO₃ and WO₃ could grow over layered graphitic carbon host which is lost near to the final annealing temperature ie. 800 °C.

CONCLUSIONS

The series of nanostructured CrO₃, MoO₃ and WO₃ oxides can be in pure phase obtained from the solid-state method using as precursors the macromolecular complexes PS-co-4-PVP●MCl₃ and Chitosan●MCl₃ with M= Cr, Mo and W by thermal treatment. Similarly, the composites CrO₃/SiO², MoCl₃/SiO² and WO₃/SiO² were prepared from thermal treatment of the PS-co-4-PVP●MCl₃ and Chitosan●MCl₃. In these materials, the CrO₃, MoO₃ and WO₃ oxides exhibited, in general, a uniform dispersion inside the silica matrix, which suggests a possible catalytic activity of these materials. The investigation of the optical properties of CrO₃, MoO₃ and WO₃ and the effect on the inclusion inside the SiO² are in course.

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COMPLIANCE WITH ETHICAL STANDARDS

Competing interests, the authors declare that they have no competing interests.

REFERENCES

1. D. Worle, A.D. Pomaglio (2003). “Metal Complexes and Metals in Macromolecules” Wiley-VCH
2. C. Díaz and M.L. Valenzuela (2006) in Polymer Research Developments, “Coordination of Organometallic Fragments to Polyphosphazenes Containing Side Groups with Donor Atoms”. R.K. Bregg Ed. Nova Science Publishers, New York Pp 1-22.
3. G.A. Carriedo, F.J. Garcia-Alonso, J.L. García Alvarez, C. Díaz, N. Yutronic (2002) Polyhedron 21, 2587-2592.
4. G.A. Carriedo, F.J. Garcia-Alonso, P. A. González, C. Díaz, N. Yutronic (2002) Polyhedron 21, 2579-2586.
5. C. Díaz, P. Castillo, G.A. Carriedo, P. Gomez-Elipe, F.J. Garcia-Alonso (2002). Macromolec. Phys. and Chem. 203, 1918-1925.
6. C. Díaz, M.L. Valenzuela (2006). Macromolecules 39, 103-111.
7. C. Díaz, M.L. Valenzuela (2006). Journal Inorganic and Organometallic Polymer and Materials 16, 419-435.
8. C. Díaz, M.L. Valenzuela, L. Zuliaga, C. O’Dwyer (2009). Journal Inorganic and Organometallic Polymer and Materials, 19, 507-520.
9. C Díaz, M.L. Valenzuela, V. Lavayen, C. O’Dwyer (2012). Inorganic Chem. 51, 6228-6236.
