

SOL-GEL INCORPORATION OF ORGANOMETALLIC COMPOUNDS INTO SILICA: USEFUL PRECURSORS TO METALLIC NANOSTRUCTURED MATERIALS

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ABSTRACT

Inclusion of the organometallic $ML_n = [HOC_5H_4N \cdot Cp_2TiCl][PF_6]$ (1), $HOC_5H_4N \cdot W(CO)_5$ (2), $HOC_5H_4N \cdot Mo(CO)_5$ (3), $[HOC_6H_4CH_2CN \cdot Cp_2TiCl][PF_6]$ (4), $HOC_6H_4CH_2CN \cdot W(CO)_5$ (5) and $HOC_6H_4CH_2CN \cdot Mo(CO)_5$ (6) into amorphous silica using the gelator precursor TEOS and $N_3P_3\{NH[CH_2]_3Si[OEt]_3\}_6$ afford the gels $(ML_n)(SiO_2)_n$. The inorganic-organic hybrid nanocomposites were pyrolyzed under air at 800 °C to give nanostructured metal oxides and/or metal pyrophosphates (phosphates) included in the silica matrices. The morphology of the monolithic nanocomposites exhibited a strong dependence on the gel precursor used being mainly laminar for those prepared using $N_3P_3\{NH[CH_2]_3Si[OEt]_3\}_6$ as gelator. TEM images show different shape and size such as circular nanoparticles, nanocables and agglomerates in some cases with sizes of 20 nm for the circular nanostructures, and diameter about 25 nm for the nanocables.

Keywords Sol-gel, Nanostructured, Nanocomposites, Pyrophosphates.

INTRODUCTION

Since the Ebelmen discovery of the polymerization of TEOS (tetraethoxysilane)¹ to give amorphous SiO_2 , great amounts of the material glasses and other have appeared^{2,3}. When an organic moiety was attached to the $Si(OR)_3$ moiety as $R-Si(OR)_3$ or $(OR)_2Si-R$, $Si(OR)_3$ interesting "hybrid organic-inorganic" materials emerged^{4,5}. It was found that the organic groups are capable of modifying the properties of the bulk materials. Also inclusion of some inorganic substrates gives rise to metallic structures included inside the SiO_2 matrix^{6,7}. Owing to the discovery of the ordered mesoporous SiO_2 assisted by surfactants, a new field emerged^{8,9}. Actually several organic and inorganic substrates have been included in ordered mesoporous giving rise to interesting materials^{10,11}. Organometallic compounds included in periodic mesoporous silica have been also discussed¹². Although ordered mesoporous silica with substrate included, are the most studied, amorphous form and its inclusion compounds could have also interesting an unforeseen reactivity pattern¹². Some examples of metal and metal oxides included in amorphous silica have been reported¹³⁻²⁴.

The most used method within this type of materials is the hydrolysis of TEOS in presence of metal salts (usually metal nitrate). By this method for instance metal oxide/ SiO_2 as Fe_2O_3/SiO_2 ^{13,14}, Cr_2O_3/SiO_2 ¹⁵ and metal/ SiO_2 as Au/SiO_2 , Ag/SiO_2 , Cu/SiO_2 , Pt/SiO_2 and Pd/SiO_2 ^{16,17} have been prepared. Another related approximation uses TEOS with metal salts in presence of citric acid for the reduction. Ni, Co, Ag, Fe/ SiO_2 composites were obtained¹⁸. Hydrolysis of the metal/alkoxy as $Cr(O^iBu)_4$ in presence of $HOSi(O^iBu)_3$ affords nanostructured chromium oxides inside amorphous silica¹⁹. Impregnation of $Cu(NO_3)_2$ salts in a SiO_2 xerogel gives Cu_xO ²⁰. Another different approximation to metal oxide/ SiO_2 is the use of precursor of the type $MX_n \cdot H_2N(CH_2)_3Si(OEt)_3$ with a co-condensation with TEOS to give $MO \cdot nSiO_2$ nanocomposites²¹. Xia²² in another way use a novel procedure to obtain nanocables of Ag covered with amorphous silica. The preformed Ag nanocables were covered with SiO_2 generated using the Stöber procedure.

Only two ways to include organometallic compounds inside amorphous silica have been reported^{23,24}. One used the precursor²³ $ML_n \cdot R_2P(CH_2)_2Si(OEt)_3$, $ML_n = Fe(CO)_5$, $RuCl_2(\eta^6\text{-cymene})$, $Co_2(CO)_8$, and hydrolyzing in presence of $Si(OCH_3)_3$. The another approximation uses the precursor $cis-Ru(Cl((CO)_2P(R)(R')(CH_2)_xSi(OCH_3)_3$ in presence of TEOS²⁴. Here we report a new simple way to include the organometallics $[HOC_5H_4N \cdot Cp_2TiCl][PF_6]$, $HOC_5H_4N \cdot W(CO)_5$, $HOC_5H_4N \cdot Mo(CO)_5$, $[HOC_6H_4CH_2CN \cdot Cp_2TiCl][PF_6]$, $HOC_6H_4CH_2CN \cdot W(CO)_5$ and $HOC_6H_4CH_2CN \cdot Mo(CO)_5$ inside amorphous silica. The inclusion was performed by Sol-gel method using TEOS and $N_3P_3\{NH[CH_2]_3Si[OEt]_3\}_6$ as agent gelant and in presence of the respective organometallic dissolved in the adequate solvent. $N_3P_3\{NH[CH_2]_3Si[OEt]_3\}_6$ was, for the first time used as gelator.

Pyrolysis of these gels at 800 °C under air affords nanostructured metal oxides and metal phosphates inside the silica. To the best our knowledge the organometallic complexes (1-6) included in amorphous silica have been not reported. The organometallic (1-6) were select with the aim to obtain

nanostructured with Ti, W and Mo containing nanostructured materials inside SiO_2 . Here we report a simple, suitable and general way to prepare metallic nanostructured nanoparticles as metal oxides and phosphates, inside amorphous silica from organometallic precursors see figure 1. We have previously shown the preparation of nanostructured materials from pyrolysis of molecular and macromolecular precursors²⁵⁻²⁹.

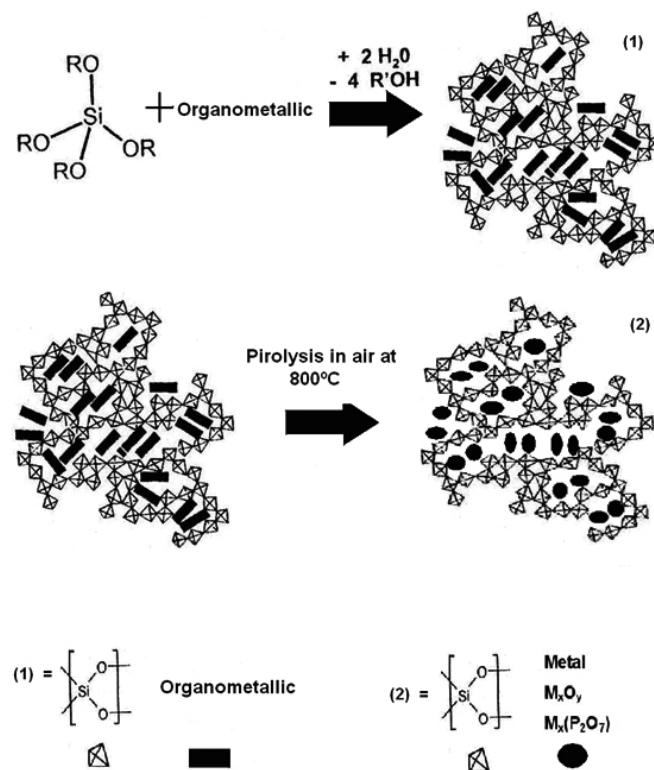


Fig. 1 Schematic representation of the Sol-gel/pyrolysis method to obtain nanostructured metallic materials inside amorphous silica.

EXPERIMENTAL

Organometallic precursor preparation

All reactions were run under dry argon using standard Schlenk techniques unless otherwise noted. 4- HOC_5H_4N , 4- $HOC_6H_4CH_2CN$, $Mo(CO)_6$, $W(CO)_6$,

Si(OEt)₄ and NH₄F were purchased from Aldrich. The complexes (1), (2) and (4) were prepared as previously reported^{25, 28}.

Preparation of (3) HOC₅H₄N•Mo(CO)₅: 0.51 g, 1.93 mmol, of Mo(CO)₆ in methanol (130 ml) was irradiated under a UV- lamp for 45 min. After this the solution was transferred and 0.18 g, 1.8 mmol, of HOC₅H₄N was added under inert atmosphere and stirred for 2 h. Then, the solvent was eliminated under vacuum and the solid washed with diethylether and dried under reduced pressure. IR (KBr) 3225 cm⁻¹ (νOH), 1974 cm⁻¹ (νCO), 1635 cm⁻¹, 1508 cm⁻¹, 1152 cm⁻¹, 1189 cm⁻¹, 835 cm⁻¹. Elemental analysis: Calc. C 39.09; H 1.62; N 4.62. Found C 38.53; H 2.03; N 4.69.

Preparation of (5) HOC₆H₄CH₂CN•W(CO)₆: 0.65 g, 1.84 mmol of W(CO)₆ in methanol was irradiated under a UV- lamp for 45 min. After this the solution was transferred and 0.26 g, 1.95 mmol, of HOC₆H₄CH₂CN was added under inert atmosphere and stirred for 2 h. The solvent was then eliminated under vacuum and the solid washed with diethylether and dried under reduced pressure. IR (KBr) 3422 cm⁻¹ (νOH), 2345 cm⁻¹ (νCN), 1936 cm⁻¹ (νCO), 1635 cm⁻¹, 1511 cm⁻¹, 1241 cm⁻¹, 1061 cm⁻¹, 1002 cm⁻¹, 942 cm⁻¹, 578 cm⁻¹. Elemental analysis: Calc. C 36.04; H 1.61; N 3.23. Found C 35.53; H 1.75; N 3.45.

Preparation of (6) HOC₆H₄CH₂CN•Mo(CO)₅: 0.51 g, 1.93mmol, of Mo(CO)₆ in methanol (130 ml) was irradiated under a UV- lamp for 45 min. After this, the solution was transferred and 0.25 g, 1.87 mmol, of HOC₆H₄CH₂CN was added under inert atmosphere and stirred for 2 h. Then, the solvent was eliminated under vacuum and the solid washed with diethylether and dried under reduced pressure. IR (KBr) 3367 cm⁻¹ (νOH), 2267 cm⁻¹ (νCN), 1987 cm⁻¹, 1940 cm⁻¹ (νCO), 1631 cm⁻¹, 1516 cm⁻¹, 1440 cm⁻¹, 1216 cm⁻¹, 1175 cm⁻¹, 814 cm⁻¹. Elemental analysis: Calc. C 45.22; H 2.0; N 4.00. Found: C 45.91; H 2.2; N 3.8

Gelations

Using TEOS

General procedure: The organometallic (see table 1 for details) was dissolved in 50 ml of ethanol and then Si(OEt)₄ (0.41g-0.81g) followed by 0.141g-0.745 g of nanopure water and NH₄F 0.0197 g as catalyst. The beaker was covered with Parafilm and the reaction mixture was left at room temperature until dryness. Photographs were taken at this stage. Further details for all the organometallic are shown in table 1.

Table 1 Preparative detail of the gels.

Gelant agent	Si(OC ₂ H ₅) ₄			N ₃ P ₃ {NH[CH ₂] ₃ Si[OEt] ₃ } ₆		
	Organometallic	g complex	g Gelant	g H ₂ O ^a	g complex	g Gelant
{HOC ₅ H ₃ N•Ti[Cp] ₂ Cl}PF ₆ (1)	0.096	0.408	0.141	0.1	2.253	0.71
{HOC ₆ H ₄ CH ₂ CN•Ti[Cp] ₂ Cl}PF ₆ (4)	0.149	0.894	0.309	0.25	5.099	1.61
{HOC ₅ H ₃ N•W(CO) ₅ }(2)	0.438	2.182	0.754	0.1	2.448	0.77
{HOC ₆ H ₄ CH ₂ CN•W(CO) ₅ }(5)	0.175	0.811	0.276	0.1	2.239	0.71
{HOC ₅ H ₃ N•Mo(CO) ₅ }(3)	0.342	2.122	0.726	0.1	3.092	0.98
{HOC ₆ H ₄ CH ₂ CN•Mo(CO) ₅ }(6)	0.142	0.821	0.276	0.07	1.988	0.628

^aH₂O Nanopure.

Using N₃P₃{NH[CH₂]₃Si[OEt]₃}

To the respective organometallic (see details in table 1) dissolved in ethanol, in a beaker, N₃P₃{NH[CH₂]₃Si[OEt]₃}₆ was added followed by water and NH₄F according to amounts given in table 1. The mixture was stirred until dryness after which photographs of the gels were taken.

Pyrolysis of the gels

Solid samples of the as prepared gels were ground to a powder and then placed into an alumina crucible. The alumina crucible containing the sample was inserted into the furnace. (Thermolyne 1400 oven) The temperature of the system was ramped to 300°C and then to 800 °C. Following thermal treatment, the samples were cooled to room temperatures over ca. 2h.

Characterization

IR spectra were recorded on an FT-IR Perkin-Elmer Spectrum BX II spectrophotometer. Magic Angle Spinning (MAS) Nuclear Magnetic Resonance (NMR) spectra were obtained using an Oxford wide bore 9.4 T magnet equipped with a Bruker Avance II console and employing a 4 mm H/X-CPMAS probe. For all samples, ¹H-X Cross Polarization (CP) experiments were acquired using a CP mixing time of 2 ms (X being ¹³C, ²⁹Si and ³¹P). A strong ¹H decoupling during acquisition time was applied by using the two-pulse phase modulation (TPPM) scheme. Spectra were acquired at 20°C temperature controlled by a BRUKER BCU unit.

For ¹³C experiments the spectral frequency was 100.577 MHz and the NMR chemical shifts are externally referenced to adamantane (major peak positioned at 38.6 ppm). For ²⁹Si experiments spectral frequency was 79.46 MHz and the NMR chemical shifts are externally referenced to DSS. For ³¹P experiments spectral frequency was 161.923 MHz and the NMR chemical shifts are externally referenced to ADP. X-ray diffraction (XRD) was carried out at room temperature on a Siemens D-5000 diffractometer with 0-2θ geometry. The

XRD data was collected using Cu-Kα radiation (40 kV and 30 mA). Scanning electron microscopy (SEM) was performed on a SEM LEO 1420 VP, Oxford Instruments equipped with EDS. Transmission electron microscopy (TEM) was carried out on a JEOL SX100 TEM, on the finely powered samples were dispersed in isopropanol and dropped on a conventional carbon-coated copper grid dried under a lamp. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed on a Mettler TA 4000 instrument and Mettler DSC 300 differential scanning calorimeter, respectively.

RESULTS AND DISCUSSIONS

Preparations of the organometallic precursors

The complexes (1), (2) and (4) have been reported previously^{25,28}. The complexes (3), (5) and (6) were prepared using standard method (see experimental part). The new compounds are brown or yellow solid insoluble in common organic solvent. IR spectra exhibits clearly the presence of the M(CO)₅ moiety, M = Mo and W moiety. IR bands at 1974 cm⁻¹ and 1951 cm⁻¹ for (3), a broad absorption between 1987-1880 cm⁻¹ for (6) and a broad band at 1936 cm⁻¹ for (5) corresponding to ν(CO) vibrations were observed for the Mo and W derivatives. Additionally the expected ν(CN) band was observed for the complexes (5) and (6)³¹. For the pyridine complex (3) the emergence of a band at 1635 cm⁻¹ typical of coordination of pyridine ligand, was also observed³⁰. The n(OH) band for (3), (5) and (6) was observed normally at 3435 cm⁻¹, 3422 cm⁻¹ and 3367 cm⁻¹ although slightly shifted respect to that of free ligand.

Preparations of the Gels

Table 2 summarizes all the gels formed. In the symbol G⁽ⁱ⁾(x), (i) means the gelator used ie. TEOS (1) or N₃P₃{NH[CH₂]₃Si[OEt]₃}₆ (2) and (x) represent the organometallic precursor used ie. 1 - 6.

Table 2 Gels, $G^{(x)}$ prepared using the sol-gel/pyrolysis method.

Organometallic	$\text{Si}(\text{OEt})_4$	$\text{N}_3\text{P}_3\{\text{NH}[\text{CH}_2\text{Si}(\text{OEt})_3]\}_6$
$[\text{HOC}_5\text{H}_4\text{N}\cdot\text{Cp}_2\text{TiCl}][\text{PF}_6]$	$G^{(1)}$ (1)	$G^{(2)}$ (1)
$\text{HOC}_5\text{H}_4\text{N}\cdot\text{W}(\text{CO})_5$	$G^{(1)}$ (2)	$G^{(2)}$ (2)
$\text{HOC}_5\text{H}_4\text{N}\cdot\text{Mo}(\text{CO})_5$	$G^{(1)}$ (3)	$G^{(2)}$ (3)
$[\text{HOC}_6\text{H}_4\text{CH}_2\text{CN}\cdot\text{Cp}_2\text{TiCl}][\text{PF}_6]$	$G^{(1)}$ (4)	$G^{(2)}$ (4)
$\text{HOC}_6\text{H}_4\text{CH}_2\text{CN}\cdot\text{W}(\text{CO})_5$	$G^{(1)}$ (5)	$G^{(2)}$ (5)
$\text{HOC}_6\text{H}_4\text{CH}_2\text{CN}\cdot\text{Mo}(\text{CO})_5$	$G^{(1)}$ (6)	$G^{(2)}$ (6)

Experimental details are given in experimental section. The gels adopt approximately the color of the organometallic precursor i.e. orange for $G^{(1)}$ (1), $G^{(2)}$ (1) and $G^{(2)}$ (4), yellow for $G^{(1)}$ (2), $G^{(1)}$ (5), $G^{(2)}$ (2) and $G^{(2)}$ (5) and white for $G^{(1)}$ (4) and $G^{(1)}$ (1) and see electronic supplementary materials (S_1). Additionally the ^{29}Si MAS NMR spectroscopy confirms the presence of T^1 (-59.2 ppm for $G^{(2)}$ (4)) and T^2 (-68.38 ppm for $G^{(2)}$ (1)) structures corresponding to R-Si(OSi)₂OH and R-Si(OSi)(OH)₂ links in the gels typical of condensation of TEOS⁴. The presence of the organometallic inside the corresponding gel is evidenced by their ^{13}C MAS NMR which exhibits signals at 44ppm, 26.4 ppm, 23 ppm and 17 ppm for $G^{(2)}$ (1). Thus, a signal observed at 64 ppm can be assigned to some uncondensed Si-O-CH₂CH₃ arising from TEOS. For the gelation with $\{\text{N}_3\text{P}_3\{\text{NH}[\text{CH}_2\text{Si}(\text{OEt})_3]\}_6\}$ a ^{31}P NMR signal at 22.89 ppm typical of the N_3P_3 evidenced the presence the phosphazene ring in the matrix³¹. Further MAS NMR data for another representative compounds are given in supplementary materials S_2 .

Pyrolysis of the gels under air at 800 °C affords solids with pyrolytic yields in the range of 14- 64 %. XRD of the solids exhibits a broad peak around $2\theta = 23^\circ$ which is characteristic of amorphous silica¹³. A representative XRD is showed for $G^{(1)}$ (1) in figure 2a. At the left the peaks values tabulated and present in the sample are also given.

In another case, the broad peak around $2\theta = 23^\circ$ masks the possible peaks corresponding to the presence of metal oxide or metal phosphate inside the silica matrix. However, in some cases some peaks characteristic of the titanium oxides mixtures $\text{TiO}_2/\text{Ti}_3\text{O}_5$ were observed as shown in figure 2a, for the product from $G^{(1)}$ (1). In some cases the typical peak at $2\theta = 6^\circ$ typical of lamellar silica was observed as shown in figure 2b for the pyrolytic product from $G^{(2)}$ (2). Table 3 summarizes the pyrolytic products identified by XRD.

Table 3 Summary of the pyrolytic products from precursors gels $G^{(x)}$.

$G^{(x)}$	Pyrolytic products	$G^{(y)}$	Pyrolytic products
$G^{(1)}$	Ti_3O_5 (ortorrómbico) TiO_2 (anatasa)	$G^{(2)}$	SiP_2O_7 (monoclinic) SiO_2 (tetragonal) $\text{Ti}(\text{PO}_3)_3$ (monoclinic)
$G^{(2)}$	PW_6O (monoclinic) SiO_2 (tetragonal) WO_3 (tetragonal)	$G^{(2)}$	P_4O_7 (monoclinic) SiO_2 (monoclinic) SiP_2O_7 (monoclinic) $\text{W}_{32}\text{O}_{84}$ (monoclinic)
$G^{(3)}$		$G^{(2)}$	Mo_4O_{11} (monoclinic) SiP_2O_7 (monoclinic) SiO_2 (monoclinic)
$G^{(4)}$	$\text{Ti}_{0.784}\text{O}_2$ (tetragonal) $\text{Si}_{0.98}\text{O}_2$ (cubic)	$G^{(2)}$	SiO_2 (rómico) TiO_2 (anatasa)
$G^{(5)}$	SiO_2 (tetragonal) WO_3 (tetragonal)	$G^{(2)}$	SiP_2O_7 (monoclinic) SiO_2 (triclinic) P_4O_7 (monoclinic) $\text{W}_{32}\text{O}_{84}$ (ortorrómbico)
$G^{(6)}$	SiO_2 (tetragonal) Mo_9O_{26} (monoclinic)	$G^{(2)}$	Mo_9O_{26} (monoclinic) SiP_2O_7 (monoclinic) P_4O_7 (monoclinic) $\text{Mo}_2(\text{P}_4\text{Si}_4\text{O}_{23})$ (triclinic)

Clearly when the gelator is $\{\text{N}_3\text{P}_3\{\text{NH}[\text{CH}_2\text{Si}(\text{OEt})_3]\}_6\}$ appears the respective metal phosphate and pyrophosphates as pyrolytic products, which

are absent when the gelator is TEOS ; in this case only the metal oxides are obtained. An exception is for $G^{(1)}$ (2) where the PW_6O product can arise from the PF_6 anion of the precursor (1).

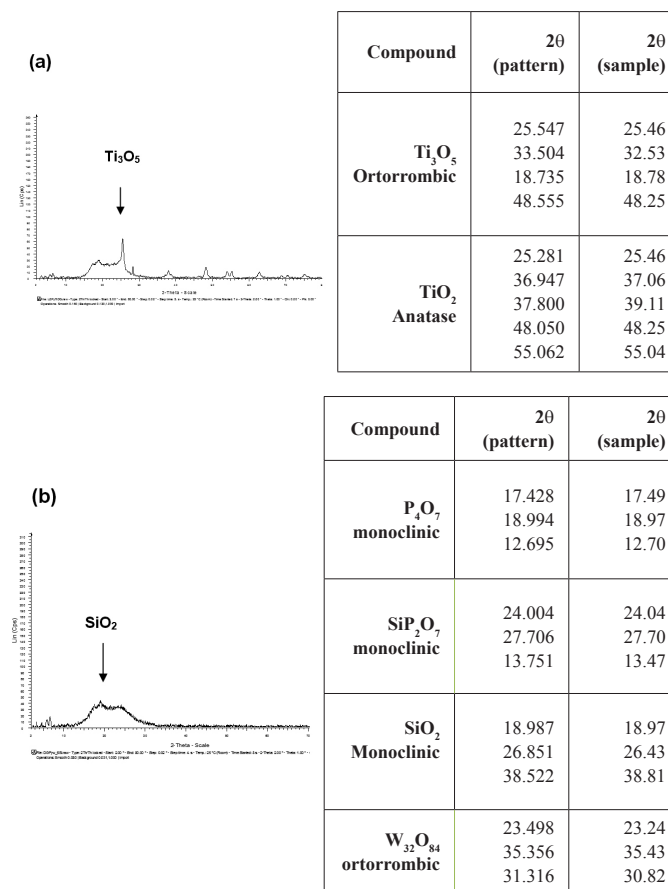
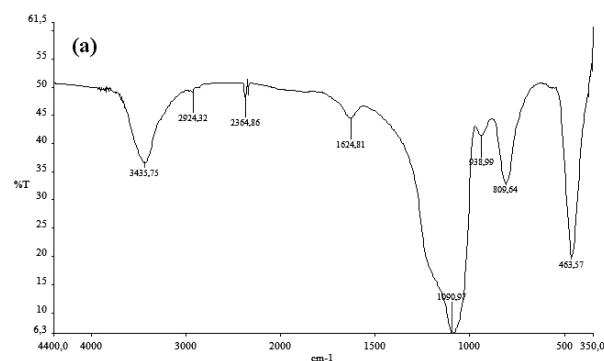


Fig. 2 Representative X-Ray diffraction pattern powder of the pyrolytic product from the gel $G^{(1)}$ (1), (a) and from $G^{(2)}$ (2) (b). On the right of each pattern, a detailed comparison of the observed lines with those of the reported are showed.

IR spectra of the pyrolyzed gels exhibits a very simple pattern with an intense band around 1100 cm^{-1} and a less intense one at 800 cm^{-1} , which can be assigned to Si-O, Si-O-Si vibrations of the silica³³⁻³⁵. A medium intensity band around 470 cm^{-1} is assigned to a Si-O-Si rocking modes. In the spectra of gels derived from the gelator $\text{N}_3\text{P}_3\{\text{NH}[\text{CH}_2\text{Si}(\text{OEt})_3]\}_6$ the band around 1100 cm^{-1} appears broad due to the presence of P=O bands arising from metal pyrophosphates and phosphates³⁶. Additionally, a weak band around 1640 cm^{-1} was assigned to an overtone of the O-H stretching band of the residual Si-OH bonds³³⁻³⁵. This appears in the range of $4320\text{-}3420\text{ cm}^{-1}$. A representative IR spectrum is given in figure 3 for $G^{(1)}$ (5) and $G^{(2)}$ (1).



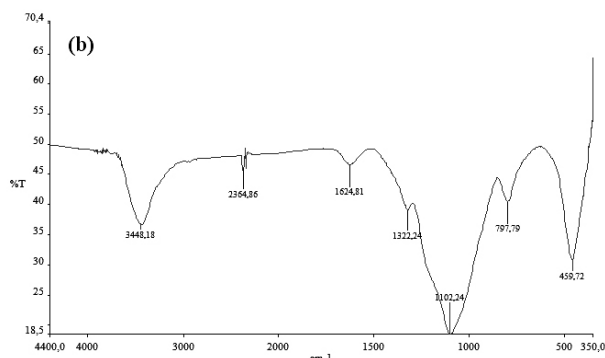


Fig. 3 Representative IR spectra (KBr) of the pyrolytic power product from precursor for G⁽¹⁾(5) (a) and G⁽²⁾(1) (b).

The morphology of the products observed by SEM is summarized in table 4.

Table 4 Main morphology of the products obtained by SEM.

Organometallic	Si(OEt) ₄	N ₃ P ₃ {NH[CH ₂] ₃ Si[OEt] ₃ } ₆
[HOC ₅ H ₄ N·CpTiCl][PF ₆]	Porous	Foam
HOC ₅ H ₄ N·W(CO) ₅	Laminar	Laminar/Inner, porous
HOC ₅ H ₄ N·Mo(CO) ₅	-----	Laminar
[HOC ₆ H ₄ CH ₂ CNCpTiCl][PF ₆]	Dense	Laminar
HOC ₆ H ₄ CH ₂ CN·W(CO) ₅	Dense	Laminar
HOC ₆ H ₄ CH ₂ CN·Mo(CO) ₅	Porous	Laminar

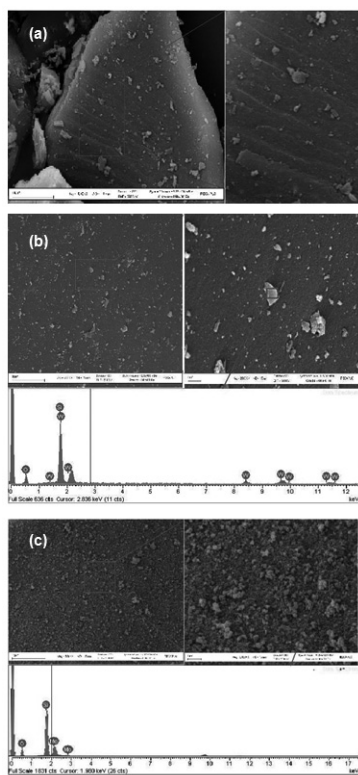


Fig. 4. SEM image of the pyrolytics products from from G⁽²⁾(2) (a), G⁽¹⁾(5) (b) and G⁽¹⁾(6) (c) illustrating the morphologies laminar, dense and porous, respectively. For G⁽¹⁾(5) below fig. (b) and for G⁽¹⁾(6) below fig.(c) their respective EDX are also showed.

The laminar morphology in silica has been observed in other sol-gel products³². In the laminar morphologies, almost always the typical peak at $2\theta = 6^\circ$ typical of lamellar silica was observed. It is interesting to observe that the laminar morphology is obtained mainly when the precursor N₃P₃{NH[CH₂]₃Si[OEt]₃}₆ is used as gelator, see figure 4. This can be owing to the self-organization induced by the N₃P₃ moiety. EDS analysis showing the expected presence of the corresponding elements are displayed on top of figure 5b, 5c for G⁽¹⁾(5) and G⁽¹⁾(6) respectively.

TEM images exhibited different shapes and sizes. For G⁽¹⁾(1) the typical nearly circular nanoparticles of mainly Ti₃O₅ were observed as shown in figure 5a. The most gray back corresponds to SiO₂.

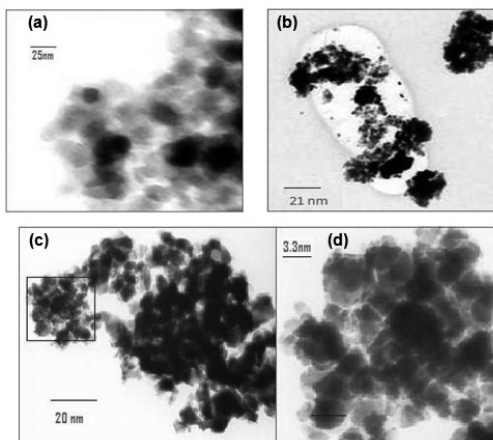


Fig. 5 TEM image of the pyrolytic products from precursors G⁽¹⁾(1) (a), G⁽¹⁾(4) (b) and G⁽¹⁾(6) (c).The image (d) is a magnification of the squared marked zone of (c).

Similar TEM of metallic nanoparticles inside SiO₂ have been reported^{13,16,21,23}. Some more irregular shapes were observed for G⁽¹⁾(4), figure 5b (titanium oxides tetragonal phase mainly) and for G⁽¹⁾(6) (two mainly phases, molybdenum oxides and SiP₂O₇), see figure 5c. Similar image TEM have been reported for other metallic nanoparticles included inside SiO₂^{6,14}. Figure 5d show a magnification of the square zone exhibited in figure 5c. The line below the image of figure 5d show a particle with a mean size of 3.5nm.

Interestingly for the pyrolytic product from G⁽²⁾(5) (tungsten oxides and SiP₂O₇ phases mainly) a nanocable was observed as shown in figure 6. Comparing with similar TEM of nanocables of metallic, metal oxides nanowires coated with amorphous silica^{37,38}, the TEM observed for G⁽²⁾(5) can be suggested to be nanowires of WO_x/SiP₂O₇ coated with amorphous silica. Also metal nanotubes encapsulated in ZrO₂ exhibit similar TEM images³⁹.

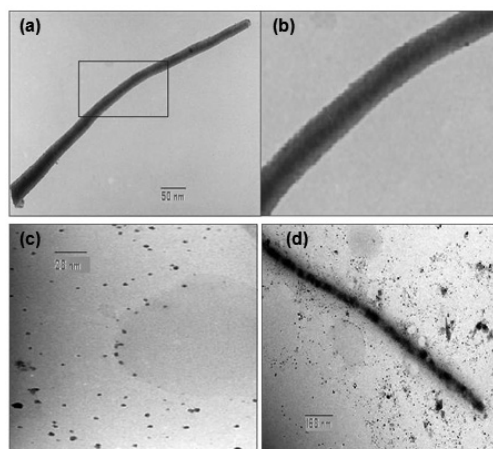


Fig. 6 Nanocables observed from pyrolysis of G⁽²⁾(5) (a), (b) and G⁽²⁾(1) c, d. The image (b) is a magnification of (a). Images (c) and (d) are two different zones of the same sample, see text.

For G⁽²⁾(1) two different zones were observed, one with small nearly circular nanoparticles and another with nanotubes. The most dark structures probably are Ti(PO₃)₃. The observed TEM image 6d is similar to the one decorated in nanowires nanostructures³⁹⁻⁴¹. For instance, iron oxides nanoparticles inside carbon nanotubes^{39,40} and SiO₂-coated CdTe nanowires exhibit similar TEM images⁴¹. For another pyrolyzed gel and as observed normally in metal inside, SiO₂ gels¹⁹, agglomerates were observed by TEM see supplementary materials S₃.

Evidence of the mechanism of formation of the metallic nanostructures in the silica matrix, from gels precursors, was obtained by TG/DSC analysis. Important differences were observed in the TG patterns either being the gel either was obtained by using TEOS or N₃P₃{NH[CH₂]₃Si[OEt]₃}₆ as gel precursor. For the former two main weight losses in contrast to when using the phosphazene-Si precursor, four weight losses were observed. In Supplementary material S₄ representative curves TG/DSC for G⁽¹⁾(1), and G⁽²⁾(1) are shown. For the G⁽¹⁾(i) series the first weight loss was attributed to the residual water molecules and/or removal of solvent molecules. The second weight may be assigned to a loss of water from condensation of residual Si-OH units. An appreciable mass loss is detectable between 300 and 600 °C, which correspond to strong exothermic peaks in the DTA curves. This is due to the combustion of organic which arises from another residual CH₃CH₂ of TEOS and/or the organic groups of the organometallic compound included in the silica.

For the series G⁽²⁾(i) a first weight loss around 100 °C can be attributed to a loss of solvent and/or water molecules consistently with the endothermic peak around this temperature observed in their DSC curve. The expected combustion of the organic matter was observed in several steps starting around 300 °C with strong loss around 400 °C and 500 °C in agreement with their DSC showing exothermic peaks at these temperatures. This thermogravimetric behavior is similar and typical of those of another metal/organometallic/SiO₂ system^{14,19,42,43}.

4.-General discussion

As discussed previously (see introduction section) few examples of organometallic compounds included into SiO₂ have been reported. Also few report of metallic oxides incorporated inside amorphous SiO₂ have appeared. The most of these last type of compounds arise from catalyst system of the type metal oxide/SiO₂⁴⁴⁻⁴⁶ or mixture of metal oxides systems (metal oxide)²(metal oxide)²/SiO₂^{47,48}.

In comparing TEOS and N₃P₃{NH[CH₂]₃Si[OEt]₃}₆ as gelators some conclusion emerge. As can be expected in agreement with our previous results²⁵⁻²⁹ when the gelator was N₃P₃{NH[CH₂]₃Si[OEt]₃}₆ metal phosphates and pyrophosphates were obtained. Also this latter as a new gelator agent⁴⁹ induce materials with mainly laminar morphologies.

The actual technological application usually requires the use of metallic nanoparticles⁵⁰⁻⁵² in solid-state devices. This in turn, requires the development of adequate methods for the solid-state preparation of nanoparticles. Thus this is one of the main challenges of the nanochemistry. Then, the here presented method, can be a useful and general method to obtain metal phosphates, pyrophosphate and metal oxide inside amorphous silica, materials with potential technological application in solid-state device⁵⁰⁻⁵².

5. CONCLUSIONS

The organometallic MLn = [HOC₅H₄N•Cp₂TiCl][PF₆] (1), HOC₅H₄N•W(CO)₅ (2), HOC₅H₄N•Mo(CO)₅ (3), [HOC₆H₄CH₂CN•Cp₂TiCl][PF₆] (4), HOC₆H₄CH₂CN•W(CO)₅ (5) and HOC₆H₄CH₂CN•Mo(CO)₅ (6) were successfully included into amorphous SiO₂ using the gelator precursor TEOS and N₃P₃{NH[CH₂]₃Si[OEt]₃}₆. The products, gels of composition (MLn)(SiO₂)_n, after pyrolysis afford mainly laminar products using the N₃P₃{NH[CH₂]₃Si[OEt]₃}₆ as gelator and either dense or porous using TEOS as gelator. Diverse shapes as nanocables and nanowires of WO₃/SiO₂ and Ti(PO₃)₃ probably coated with amorphous silica were observed. The method can be a new easy and simple way to obtain nanostructured metallic containing inside amorphous SiO₂. In contrast when the gelator was TEOS and the organometallic does not contain any phosphorus atoms, the metal oxide inside silica was obtained. The silylated cyclotriphosphazene N₃P₃{NH[CH₂]₃Si[OEt]₃}₆ as a new gelator, induce the formation of mainly laminar SiO₂ matrix.

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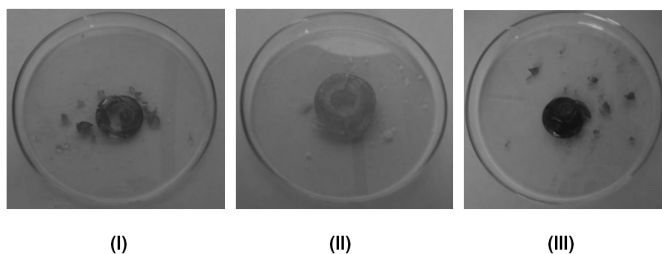
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SUPPLEMENTARY MATERIALS TO:
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Incorporation of Organometallic compounds into silica: useful precursors to metallic nanostructured materials

S₁
 Photographie showing the color of some of the as synthesized gels : (I) G⁽¹⁾
 (2) , (II) G⁽²⁾(6) and (III) G⁽²⁾(5)

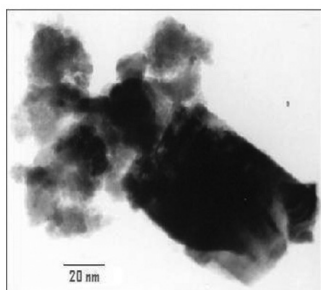


S₂
²⁹Si- MAS-NMR for some representative G⁽¹⁾(x) gels

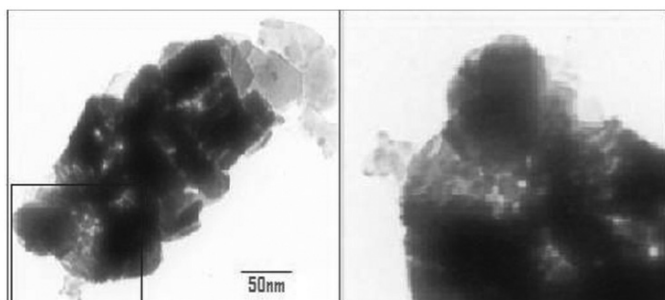
Gel	²⁹ Si (ppm)
G ⁽¹⁾ (5)	59.2 68.38
G ⁽²⁾ (4)	59.74 68.17
G ⁽¹⁾ (2)	59.62 69.56
G ⁽²⁾ (1)	59.52 68.10
G ⁽²⁾ (6)	59.54 68.35

S₃ TEM images for another pyrolytic products

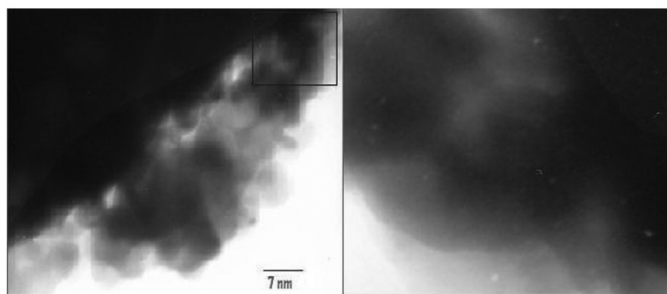
1) TEM from precursor G⁽¹⁾(2).



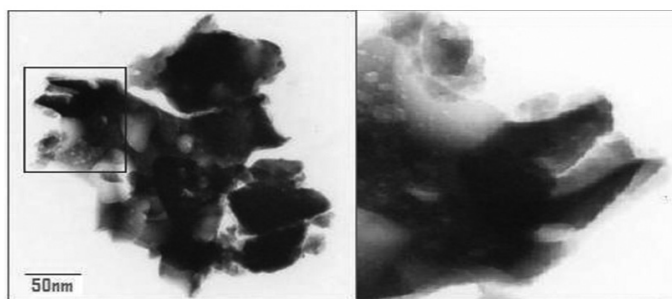
2) TEM from precursor de G⁽²⁾(2).



3) TEM from precursor G⁽²⁾(3).

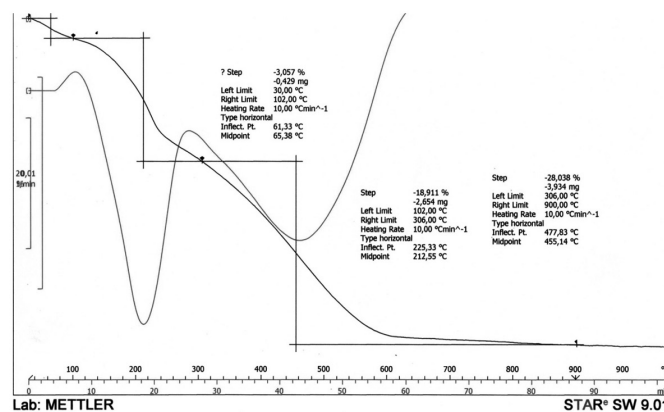


4) TEM from precursor G⁽²⁾(4).

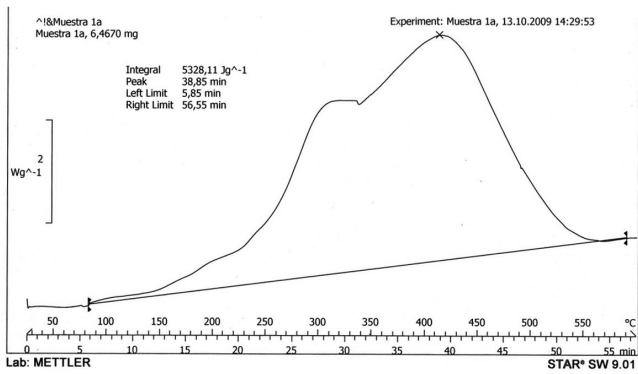


S₄ Some TG and DSC data for some representative G⁽¹⁾(x) gels
 TG and DSC curves of G⁽¹⁾(1) and G⁽²⁾(1)

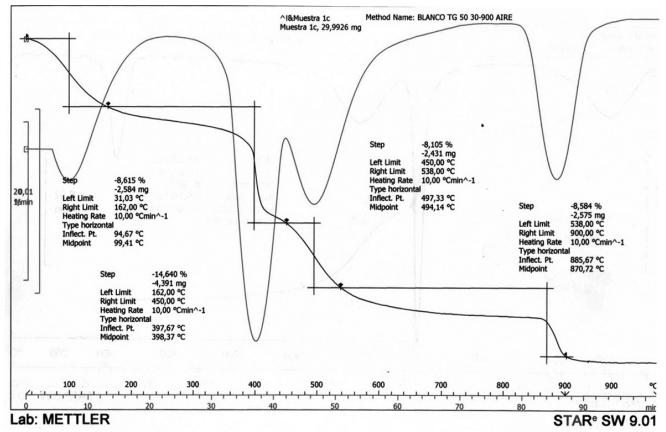
TG of G⁽¹⁾(1)



DSC of G⁽¹⁾(1)



TG of G⁽²⁾(1)



DSC G⁽²⁾(1)

