

# Organic-inorganic hybrids containing phosphonate groups obtained by sol-gel process

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Organophosphorus acids and their derivatives are highly promising coupling molecules that allow the anchoring of organic groups to inorganic solids. In this paper we present the synthesis, by sol-gel method, of organic-inorganic hybrids containing organic phosphonic groups. The obtained hybrid materials were characterized by N<sub>2</sub> adsorption/desorption, IR Spectroscopy, Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). IR spectra of the obtained samples show in the 900-1300 region the presence of the vibration typical of phosphonates group. These results suggest the formation of the hybrid network containing Si-O-Si and Si-O-P bonds. TEM, SEM micrographs show mezzomacroporous materials with high surface area. A low ordered mesoporous structure was evidenced by TEM images.

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## 1. Introduction

Looking forward to the 21st century, nanosciences will be one of the fields that will contribute at a high level to scientific and technological developments. Hybrid organic-(bio)-inorganic materials will play a major role in the development of advanced functional nanomaterials.

Research in functional hybrid organic-inorganic materials is supported by the growing interest of chemists, physicists, biologists and materials scientists who are looking to fully exploit this opportunity for creating smart materials that benefit from the best of the three realms: inorganic, organic and biological.[1]

Organophosphorus compounds represent a particular class for synthesis of organic – inorganic hybrids. Thanks to the versatile phosphorus chemistry, a wide range of functional organic groups is available are presented by many authors in different papers like.[2-4]

Organophosphorus acids and their derivatives (salts, esters) are quite complementary of organosilicon coupling molecules for the preparation of hybrid organic-inorganic materials, by sol-gel processing or surface modification.

The different reactivity of organophosphorus coupling molecules leads to different structures and stabilities of the final hybrid materials and may provide decisive advantages in the sol-gel synthesis of homogeneous hybrids, the preparation of surface monolayer or the selective surface modification of nanopatterned supports.

The condensation between organophosphorus acids and metal alkoxides is quite general and has been used to prepare layered metal phosphates and phosphonates as well as molecular metal phosphates, phosphonates, and phosphinates.[5,6]

Surface modification using organophosphorus coupling molecules has been applied by to a large variety of metal oxide supports, including the native oxide layer at

the surface of metals such as titanium, aluminium, iron, steel, copper, and brass.[7,8] Applications have been reported in various fields, such as separation[9], in catalysis[10], as optical devices or bio-sensors.[11]

In this paper we present the synthesis, by sol-gel method, of new organic-inorganic hybrids containing organic phosphonic groups having double bond.

## 2. Experimental

### 2.1 Reagents

The reagents tetraethylorthosilicate, absolute ethanol, 3-aminopropyltrimethoxysilane and hydrochloric acid 1 N were purchased from Merck Company. Styryl, 1-phenyl phosphonic acids and vinylphosphonic acid, di-2-chloroethylester and diethylester were synthesized in our laboratory.

### 2.2 Analysis

The obtained materials were characterized by Fourier transform infrared spectroscopy (FTIR-Jasco), scanning electron microscopy (SEM) with a Philips XL-20 microscope, transmission electron microscopy (TEM) with Philips Tecnai microscope and N<sub>2</sub> adsorption-desorption (Micromeritics).

#### 2.2.1 One step sol-gel process

Tetraethylorthosilicate (0.1 mol) was added dropwise to a solution of phosphorus derivative (usually 0.1 mol) in 10 ml absolute ethanol at room temperature under stirring. The mixture is maintained under stirring for one hour then 10 ml of deionized water and 5 ml HCl 1N are

added under stirring and the mixture is maintained three hours under stirring, then the mixture is aged three days at room temperature, dried at 60°C and analyzed.

### 2.2.2. Two steps sol-gel process

Tetrahydroxysilicate (0.1 mol) was added dropwise to a solution of phosphorus derivative (usually 0.1 mol) in 10 ml absolute ethanol at room temperature under stirring. The mixture is maintained under stirring for 5 hours at 50°C, the mixture is cooled then 10 ml of deionized water and 5 ml HCl 1N are added under stirring and the mixture is maintained under stirring one hour at room temperature, then the mixture is aged three days at room temperature, dried at 60°C and analyzed.

### 2.2.3. Three component process

Tetrahydroxysilicate (0.1 mol) was added dropwise to a solution of phosphorus derivative (0.1 mol) in 10 ml absolute ethanol at room temperature under stirring. The mixture is maintained under stirring for five hours at 50°C, the mixture is cooled, then 3-aminopropyltrimethoxysilane (0.1 or 0.5 mol) is added, the mixture is stirred another hour then 10 ml of deionized water is added under stirring and the mixture is maintained two hours under stirring, then the mixture is aged three days at room temperature, dried at 60°C and analyzed.

## 3. Results and discussion

Phosphorus derivatives are much less sensitive to nucleophilic substitution than the silicon parent derivatives, with two important consequences: P–O–C bonds are quite stable toward hydrolysis, and homocondensation of P–O–H bonds with formation of P–O–P bonds takes place only under high temperature

dehydrating conditions. Accordingly, organophosphorus coupling molecules are usually organophosphorus acids (alkyl - phosphoric, phosphonic and phosphinic acids) or, as P–O–C bonds are quite stable, mono and diesters of phosphoric acid.

An important advantage of these phosphorus-coupling molecules is that the formation of P–O–P bonds by homocondensation should not occur in sol-gel processing. On the other hand, the formation of M–O–P bonds by heterocondensation is kinetically favored, owing to the protonation of the leaving alkoxy group by the acidic P–OH groups. Heterocondensation is also thermodynamically favored, as reflected by the huge number of reported crystalline metal phosphate and metal phosphonate phases built of M–O–P bonds. In addition to heterocondensation, M–O–P bonds may also result from the coordination of the phosphoryl oxygen to the metal (as in metal phosphates and phosphonates).

Bonding of the organophosphorus molecules to the inorganic phase should result from the formation of strong M–O–P bonds only, through heterocondensation and coordination. Synthesis of organic-inorganic hybrids by sol-gel processing offers many possibilities: control of the organic content, of the surface area and porosity, and shaping of the final material before the liquid-to-gel transition (film coating for instance). Recently the incorporation of organophosphorus groups within zirconium, titanium and aluminium oxides by a two step sol-gel process has been reported.[12,13]

In first step, the metal alkoxide precursor was mixed with a solution of a phosphonic or phosphinic acid in an organic solvent. P–O–M bonds form at this stage, in the absence of water, by heterocondensation between P–OH and M–OR groups, with release of alcohol. In the second step, water (neutral) was added, leading to the formation of the M–O–M bonds of the oxide network by hydrolysis/condensation of the residual alkoxide groups.

Table 1. The obtained hybrid by sol-gel method.

Reagents			Molar ratio	Code	Type of synthesis
Si(OEt) <sub>4</sub>	CH <sub>2</sub> =CH-P(O)(OEt) <sub>2</sub>	-	1:1	P1	one steps
Si(OEt) <sub>4</sub>	C <sub>6</sub> H <sub>5</sub> -CH=CH-P(O)(OH) <sub>2</sub>	-	1:0.5	P2	two step
Si(OEt) <sub>4</sub>	C <sub>6</sub> H <sub>5</sub> -CH=CH-P(O)(OH) <sub>2</sub>	-	1:1	P3	two step
Si(OEt) <sub>4</sub>	CH <sub>2</sub> =CH-P(O)(OCH <sub>2</sub> CH <sub>2</sub> Cl) <sub>2</sub>	-	1:1	P4	one steps
Si(OEt) <sub>4</sub>	CH <sub>2</sub> =CH(C <sub>6</sub> H <sub>5</sub> )-P(O)(OH) <sub>2</sub>	-	1:1	P5	two step
Si(OEt) <sub>4</sub>	C <sub>6</sub> H <sub>5</sub> -CH=CH-P(O)(OH) <sub>2</sub>	NH <sub>2</sub> -C <sub>3</sub> H <sub>7</sub> -Si-(MeO) <sub>3</sub>	1:1:1	P6	three component process

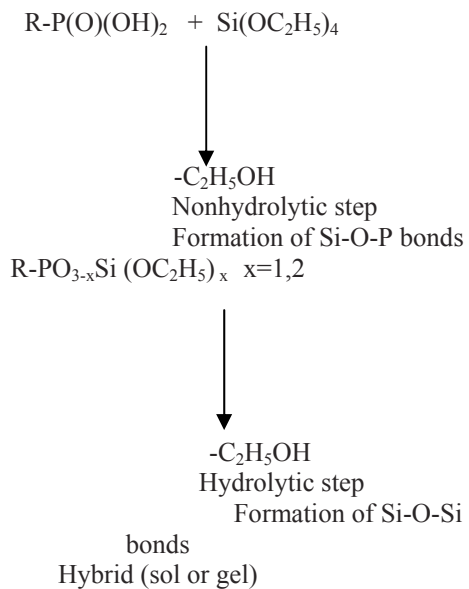
Alternatively, the acid precursors may be replaced by their silyl ester derivatives, which are more soluble in organic solvents. Depending on the P/Ti and H<sub>2</sub>O/Ti ratios, and on the nature of the organophosphorus acids, molecular species, sols, gels, or precipitates were obtained.

We used for synthesis of organic inorganic hybrids both methods one step condensation and two steps condensation. Synthesized compounds are presented in Table 1.

In one step synthesis the Si-O-P and Si-O-Si bond are formed concomitant while in two step process first are formed Si-O-P then Si-O-Si (Scheme 1)

The FTIR spectra for synthesized hybrids show no bands around 900–950 cm<sup>-1</sup> (the region of P–O(H) stretching bands) and characteristic bands for phosphonates around 1000–1300 cm<sup>-1</sup>.

SEM pictures of the P1-P6 samples, given in Fig. 2 show a mesoporous structure. Dimension of particles and dimension of the pores are higher from P1 sample to P5.



Scheme 1

These results were been confirmed by  $\text{N}_2$  adsorption-desorption results (Fig. 3). The nitrogen adsorption-desorption isotherms and pore size distributions show increasing of porosity and pore diameter with dimensions the organic groups.

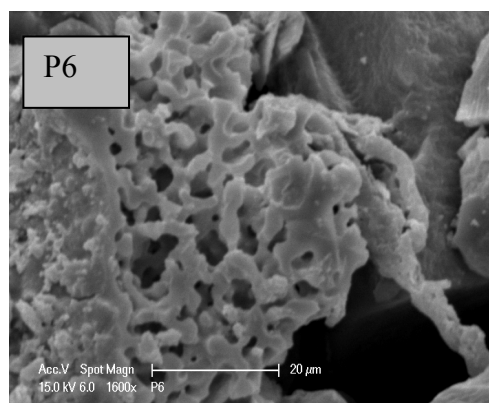
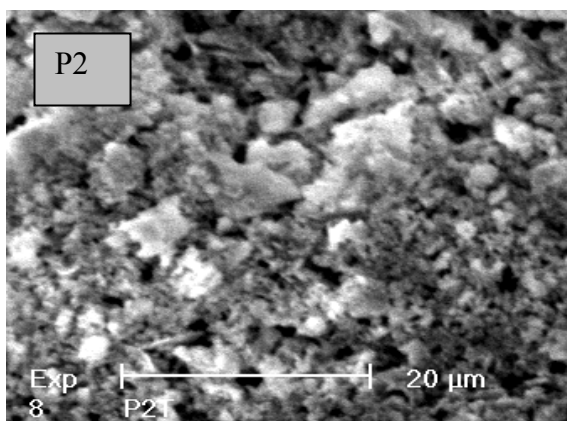
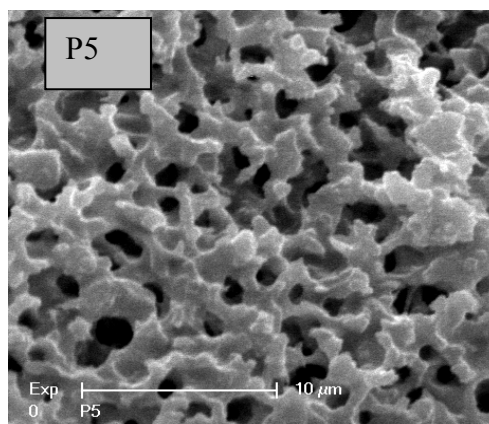
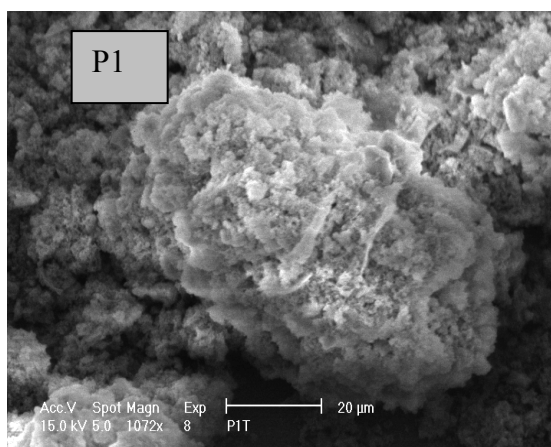
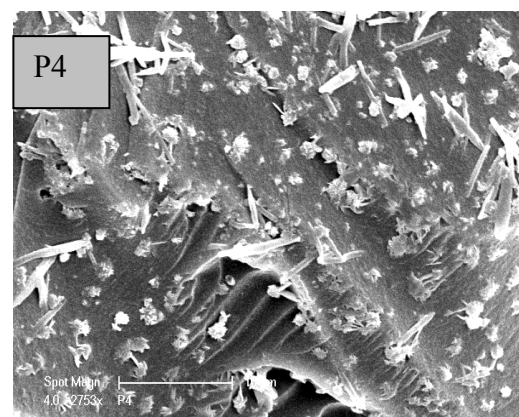
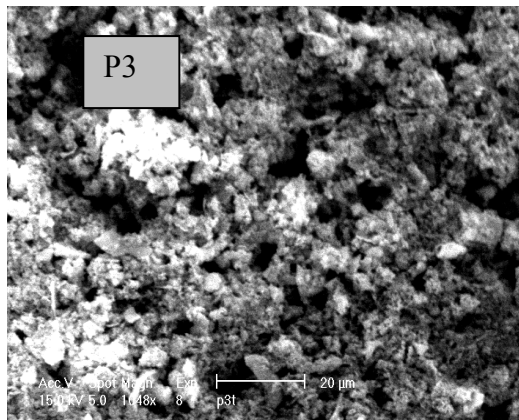


Fig. 2. SEM images of P1-P6 samples.

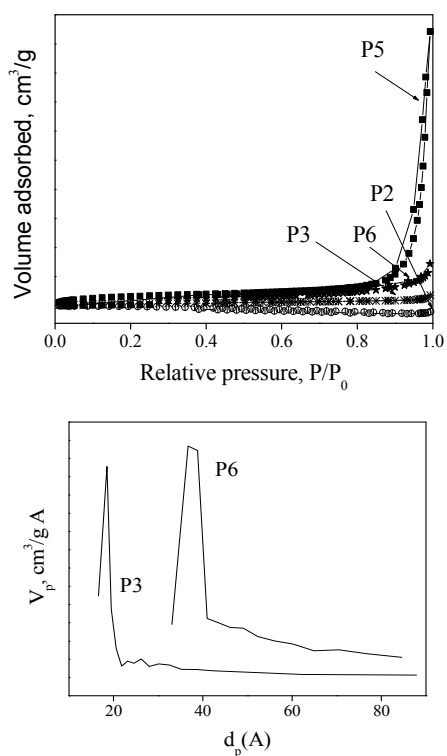


Fig. 3.  $N_2$  sorption isotherms and pore size distributions of hybrid materials.

TEM images of organic-inorganic hybrids (Fig.4.) show the presence of mesopores with little and large diameters.

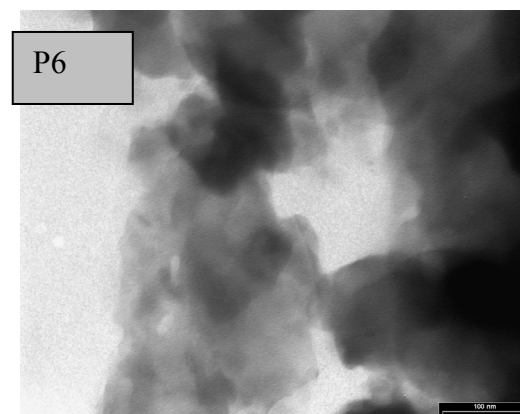
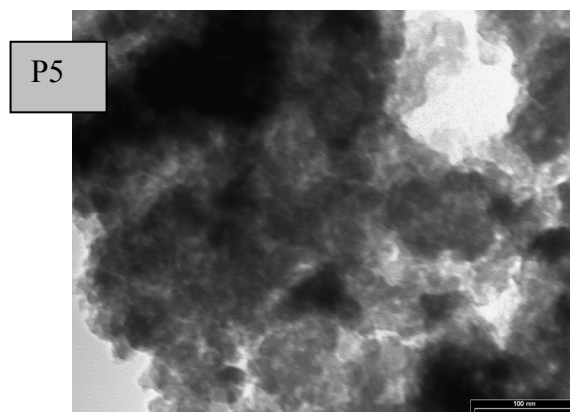
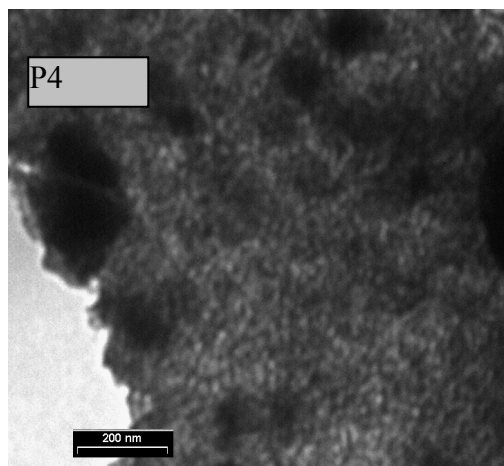
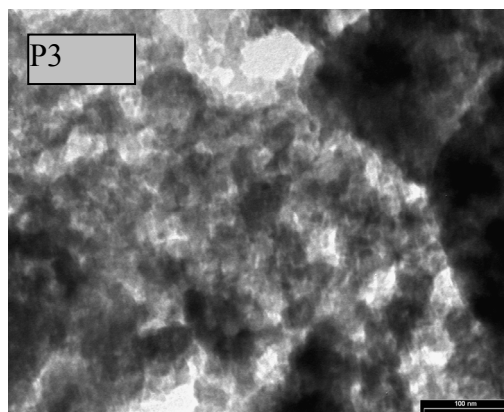
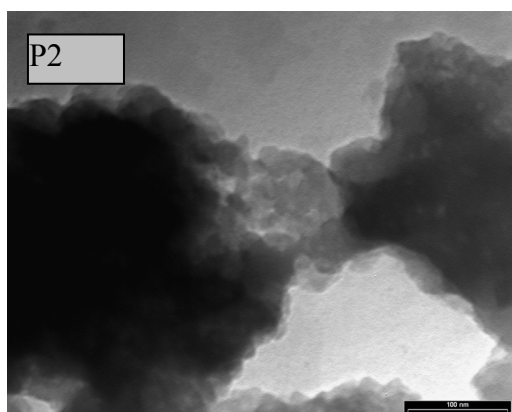
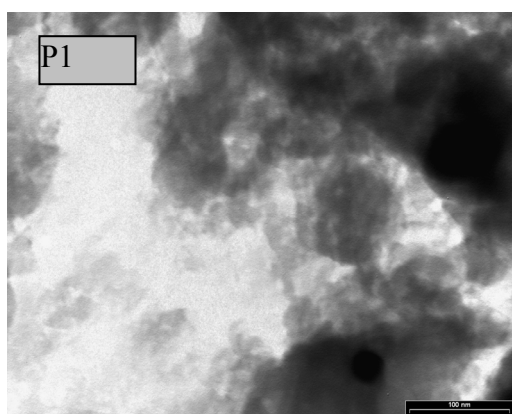


Fig. 4. TEM images of P1 –P6 samples

#### 4. Conclusions

New organic-inorganic hybrids containing double bonds were obtained by sol-gel method. Hybrid were characterized by FTIR, SEM, TEM, and N<sub>2</sub> adsorption-desorption. SEM pictures show a mesoporous structure. Dimension of particles and dimension of the pores are higher from P1 sample to P5.

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