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Phosphonate/Phosphonic acid grafted on St-DVB polymer/SiO$_2$ hybrid

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The synthesis and characterization of new hybrid materials was obtained by a two-stage reaction with producing phosphonate (phosphonic acid) grafted on St-DVB copolymer as core and silica particles' grafting of tetraethylorthosilicate as shell. The obtained hybrids were characterized by FT-IR spectroscopy, Thermal Analysis (TG, DTG, and DTA), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and N_2 adsorption-desorption izotherms. Structure of porous materials is viewed by SEM and TEM. Hybrid materials obtained are characterized by high thermal stability. Phosphonate polymer-silica hybrids show by adsorption-desorption isotherms a silica shell with spherical aggregates of micoporous nanoparticles.

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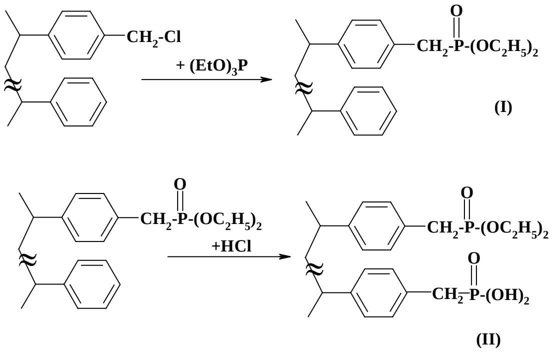
1. Introduction

Two main classes of hybrid materials based on the nature of the interaction between organic and inorganic parts were evidenced by Judeinstein and Sanchez [1]: hybrids with the organic part trapped in the inorganic matrix or bound by weak interactions and hybrids with the organic and the inorganic parts linked by strong chemical bonds. In the past two decades, considerable efforts have been made in both the academic and engineering fields to explore applications of inorganic/polymer hybrid materials, because these new materials have the potential to afford novel and excellent physicochemical properties due to the combination of an organic polymer shell and an inorganic core [2]. The overall properties of a hybrid material are established not only by the individual components but also by the global phase and interfacial properties [3]. These hollow particles such as hollow polymer particles and hollow inorganic particles have attracted more and more attentions because of their potential application in some fields such as controlled release of drugs, catalyst, protection of active species, removal of pollutants, artificial cells and confined reaction vessels [4, 5]. Among these hollow particles, the hollow silica microspheres are of high interest because of their biocompatibility, low density, and high thermal and mechanical stability. The strong chemical interaction between organic and inorganic compounds has obtained by sol-gel processing but also by surface modification of an inorganic or organic support [6]. In this context we herein report on the synthesis of the core–shell hybrid microspheres by a two-stage reaction with producing phosphonate (phosphonic acid) grafted on St-DVB copolymer as core and silica particles' grafting as shell. Our aim was to obtain hybrid supports for metal complexes like phosphonates and organophosphonates with applications in oxidation liquid phase of the organic compounds. The importance of the metal phosphonates and organophosphonates has been established especially in application such as catalysis, adsorption and separation [7]. These materials are expected to play a key role in tailored design of inorganic–organic hybrid open framework materials.

2. Experimental

2.1. Synthesis of the St-DVB copolymers functionalized with phosphonate/phosphonic group

All of the reagents and solvents were analytical grade and used without further purification. A 5-g sample of chlorometylated copolymer (4.72 mmoles Cl/g. copolymer) and triethylphosphite were added into 50 ml dioxan. The molar ratio of chloromethyl groups: phosphite was 1: 1.5. The mixture was maintained under stirring for 24 h at the solvent reflux temperature. The polymer beads separated by filtration, were washed with ethanol, 1,2-dichloromethane and ethyl ether and dried in a vacuum oven at 50 °C for 24 h. The phosphonate ester grafted on macromolecular supports (I) was hydrolyzed with HCl 37 % at reflux for 15 hours.



Scheme 1. Preparation of the polymer-grafted phosphonates-phosphonic acid [8].

2.2. Obtaining the hybrid materials with phosphonate/phosphonic group grafted polymer - silica by sol-gel method

Tetraethylorthosilicate was prehydrolized at room temperature for 40 minutes in a mixture of H_2O and HCl 37% at a molar ratio of [TEOS]: [H_2O]: [HCl] = 1:6:0.02 (volume of TEOS was 3.5 ml) providing a pH = 1 and thus obtain solution A. Solution A was added in drops over phosphonates polymer (2 g) (samples: I and II) suspended in tetrahydrofuran (40 ml) and shaken vigorously for 24 hours at room temperature. Then the product was filtered and washed on the frits with ethanol (3 x 20 ml). The final product was dried in a vacuum oven at 50 °C for 24 hours. Hybrid materials (HPE and AAP) were obtained.

2.3. Characterization

The obtained materials were characterized by Fourier transform infrared spectroscopy with a spectrophotometer Jasco FTIR, scanning electron microscopy (SEM) with a Philips XL-20 microscope, transmission electron microscopy (TEM) with Philips Tecnai microscope. N_2 adsorption-desorption isotherms were obtained from the volumetric adsorption analyzer (Micromeritics). The thermal properties of the precursors and the hybrid materials were characterized through thermogravimetric analysis (TGA) and differential thermal analysis (DTA), which were performed on a TGA/SDTA 851-LF1100 – Mettler apparatus at a heating rate of 10 ^{o}C/min under air atmosphere and temperature range from 25 to 1100 ^{o}C. The phosphorus content was determined according to modified Schoninger method [9-11]. A sample of the polymer-supported phosphonates was burnt out in an oxygen atmosphere and P_2O_5 obtained was adsorbed in water. The solution obtained was titrated with an aqueous solution of cerium (III) 0.005 M in the presence of Eryochrome Black T as indicator.

3. Results and discussion

3.1. Characterization of phosphonate/phosphonic group grafted on St-DVB polymer

The characteristics of diethylphosphonate and phosphonic acid polymeric are shown in the table below:

Table 1. The characteristics of diethylphosphonate (I) and phosphonate/phosphonic acid (II) grafted on macromolecular support S-DVB.

Groups [8]	P (%)	y^a	z^b	y-z	G_F	G_{F1}, mmoles phosphonic acid/g	G_{F2}, mmoles phosphonates/g	Mmi^d	Mmf^e
I $(C_2H_5O)_2P$	6.20	0.35	-	-	2.06^c	-	-	171.00	-
II $P(O)(OH)_2$	3.20	-	0.17	0.15		1.11	0.95	-	155.90

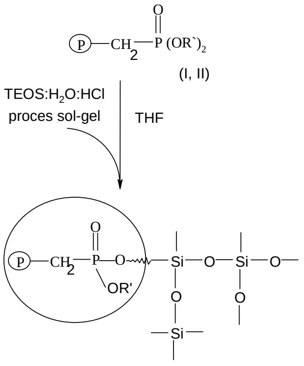
$$^{a}\ y=\frac{\%P\cdot M_{mi}}{100\cdot n_P\cdot A_P-\%P\cdot(M_{SFf}-M_{SFi})}\quad ^{b}\ z=\frac{100\cdot y\cdot A_P-\%P\cdot M_{mi}}{100\cdot A_P+\%P\cdot(M_{SFf}-M_{SFi})},\ ^{c}\ G_F=\frac{y}{M_{mf}},\ G_{F1}=\frac{z}{M_{mf}},\ G_{F2}=\frac{y-z}{M_{mf}},$$

$$^{e}\ M_{mf}=M_{mi}+z\cdot(M_{SFf}-M_{SFi}),$$

$$^{d}\ M_{mi}=r\cdot M_{DVB}+(x-y)\cdot M_{SFCH2Cl}+y\cdot M_{SFi}+(1-r-x)\cdot M_S$$

3.2. Characterization of hybrid materials with phosphonate grafted polymer - silica

The method of obtaining hybrid materials of type phosphonate polymer-silica by sol-gel method is shown in Scheme 2.



where: R' = -C_2H_5 (I); -C_2H_5 and -H (II).
Schema 2. Schematic synthesis of hybrid materials: phosphonate (phosphonic acid) grafted on St-DVB copolymer as core and silica particles' grafting as shell.

The obtaining of phosphonates polymer-silica hybrid materials is done by two stages: 1. the obtaining phosphonates polymer precursor (Scheme 1), 2. the preparation phosphonates polymer-silica hybrid materials by sol-gel method (Scheme 2). Bonding to the inorganic part, M-O-P involves the formation of stable bonds. The stability and the easiness of M-O-P bonds formation is well illustrated by many examples of hybrid materials containing organophosphorus coupling molecules reported in the literature [12-17].

The characteristics of phosphonate polymer-silica hybrids are presented in the table below:

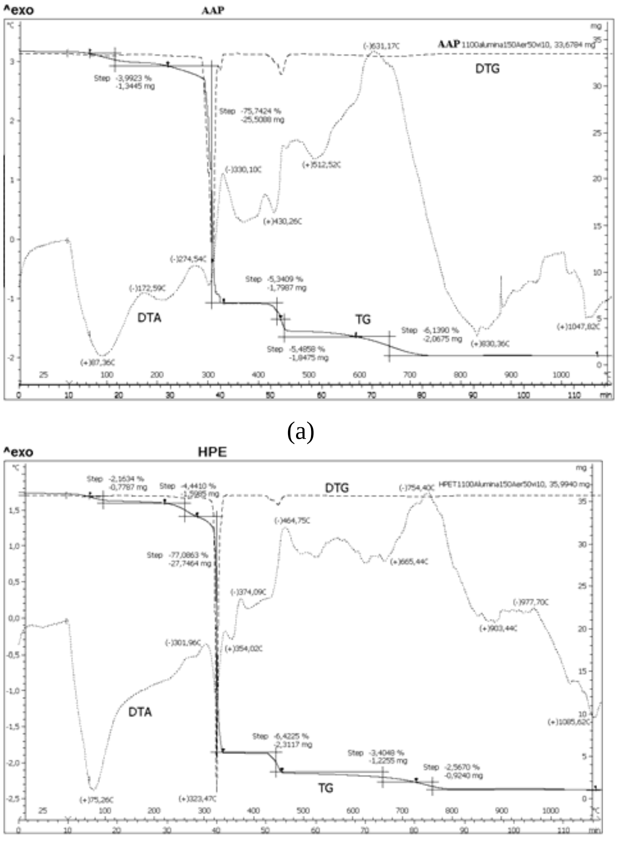
Table 2. Data characteristic of hybrids phosphonates grafted on styrene copolymers - divinylbenzene – silica.

No.	Code[*]	R’ from $OP(OR’)_2$	SiO_2 (%)	P (%)	Td[a]
1	AAP	-H	2.97	3.20	301.05
2	HPE	$-C_2H_5$	2.78	6.20	323.47

[a]Td is the suitable temperature for maximum rate of decomposition (inflection point, °C). * Hybrid material obtained after treatment with TEOS (sol-gel method)

The thermal stability of the phosphonate St-DVB polymer/SiO_2 hybrid was evaluated by thermogravimetric analysis on a METTLER STAR SW9, in air atmosphere, at a heat rate of 10 °C/min from 25ºC to 1100 ºC.

Fig. 1 (a-b) presents DTA-TG curves for samples AAP and HPE. The samples HPE, AAP presents a little endothermic at about 77 °C with a slight loss of mass. A weight loss of about 5% is observed up to temperatures of 200 °C due to evaporation physically adsorbed water on hybrid material. More weight loss is observed in the temperature range from 300 °C and 760 °C, which are attributed to decomposition of phosphonate and that main chain degradation of polymer phase.



(a)

(b)

Fig. 1. Thermal analysis of samples (AAP (a), HPE (b)) was achieved in air with heating rate of 10 °C / min in the range 25 °C to 1100 °C.

Phosphonate polymer-silica hybrid materials are compounds containing links Si-O and Si-C. They are characterized by high thermal stability (above 310 °C) due to Si-O link strength.

IR spectra indicate the formation of Si-O-P bonds, by the presence of a large band in the 850-1300 cm-1 region where are overlapping and the characteristic vibrations of the Si-O and P=O links.

The primary requirement is imposed on the use of styrene-divinylbenzene copolymers is the existence of a suitable porous structure to allow adequate diffusion of reagents to the active centers of polymer structure. This phenomenon depends on the gonflare or solvation of the copolymer in the reaction medium (tetrahydrofuran), which controls the effective size of pores and their volume.

The morphology of the hybrid materials was visualized by SEM electron microscopy (Figs. 2 and 3). SEM images show formation of spherical aggregates of silica particles with high channels to organic core for all the materials. A significantly increasing of the spherical aggregates of silica was evidenced for the shell of the phosphonic acid on St-DVB polymer (sample AAP) in comparation with phosphonate grafted grafted on St-DVB polymer (sample HPE). We explained this as the result of interaction between TEOS and phosphonic, respectively phosphonate groups during sol-gel process and change the rate of hydrolysis and condensation. In case of sample AAP the condensation of silica species begins on the entire surface as result of interaction with OH of the phosphonic groups. The uniformity of the silica layer and aggregates are higher (Fig. 2).

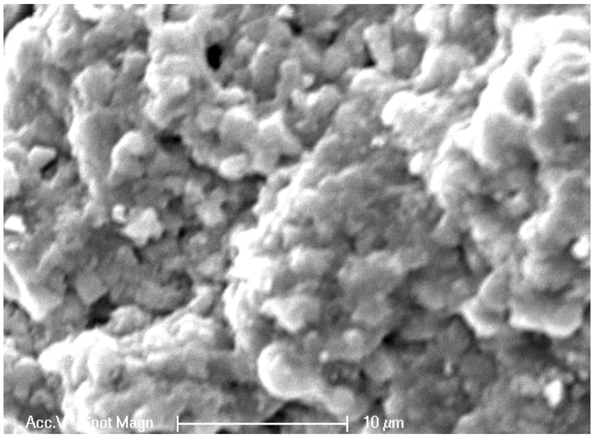


Fig. 2. SEM image of the phosphonate polymer hybrid material - silica (AAP) obtained after treatment with TEOS (sol-gel method).

In case of the hybrid HPE sample the hydrolysis process favorite the interaction between TEOS molecules and no uniform distribution of the silica aggregates on the surface (Fig. 3).

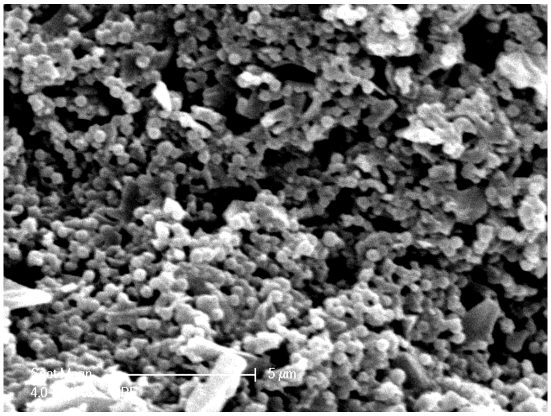


Fig. 3. SEM image of phosphonic acid polymer hybrid material - silica (HPE) obtained after treatment with TEOS (sol-gel method).

The high porosity of the inorganic shell of silica polymer obtained by sol-gel process on the functionalized St-DVB polymer was evidenced by TEM microscopy (Fig. 4).

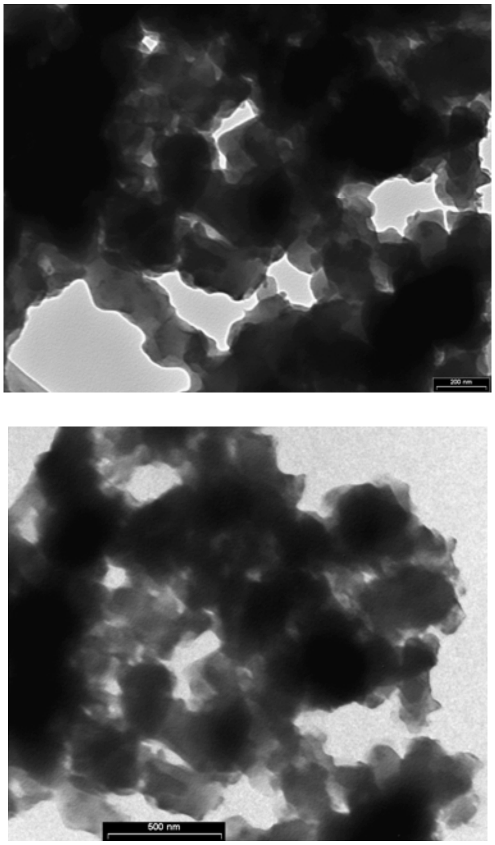


Fig. 4. TEM images of phosphonic acid hybrid polymer - silica (HPE) obtained after treatment with TEOS.

The high percent of the macropores, evidenced by TEM microscopy, was confirmed by N_2 adsorption-desorption (Fig. 5).

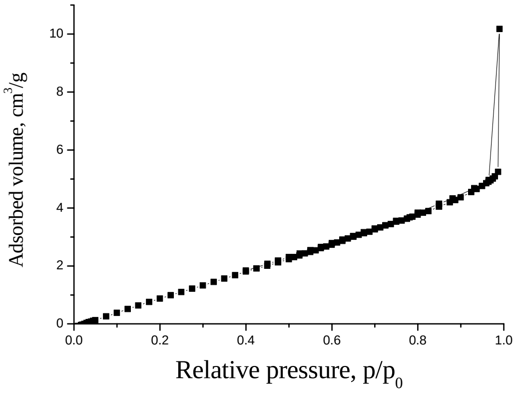


Fig. 5. N_2 adsorption-desorption isotherms for HPE.

The information obtained by electron microscopy and N_2 adsorption-desorption shown a silica shell with spherical aggregates of microporous nanoparticles. The space between spherical aggregates forms the mesoporous.

4. Conclusions

The sol-gel method was used for obtaining hybrid materials. Characteristic absorption band of Si-O-Si groups appear at about 1000 cm^{-1}. Structure of porous materials is viewed by SEM and TEM. Hybrid materials obtained are characterized by high thermal stability (above 310 °C). Phosphonate polymer-silica hybrids by adsorption-desorption isotherms shown a silica shell with spherical aggregates of microporous nanoparticles.

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