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INTERPENETRATED NETWORK OF PHOSPHORUS CONTAINING HYBRIDS MATERIALS OBTAINED BY SIMULTANEOUS RADICAL POLYMERIZATION AND NONHYDROLYTIC SOL-GEL PROCESS UNDER SONICATION CONDITIONS

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The paper the synthesis of hybrid materials containing organophosphorus compounds as coupling molecules, having interpenetrated network obtained by simultaneous radical polymerization and sol-gel process under ultrasound conditions. The hybrid were characterized by infrared spectroscopy and by scanning electron microscopy.

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1. Introduction

The term hybrid material is used for many different systems spanning a wide area of different materials, such as crystalline highly ordered coordination polymers, amorphous sol–gel compounds, materials with and without interactions between the inorganic and organic units.[1] Hybrid materials in which the organic and the inorganic parts are linked by strong chemical bonds are usually called Class II hybrids, according to Judeinstein and Sanchez’s classification.[2] Molecular approaches of molecular and solid state chemistry and nanochemistry have reached a very high level of sophistication. The coupling of organic and inorganic moieties is most often implemented by sol–gel processing.[3] While the hydrolytic sol-gel process has been studied extensively over the last 25 years as a facile route to organic-inorganic hybrids, [4,5] only in the last 15 years the corresponding non-hydrolytic sol-gel process has been recognized as a useful route to inorganic oxides. [6-8] The non-hydrolytic sol-gel route has been evaluated for the synthesis of silica,[9,10] titania,[11,12] and alumina[13,14] and mixed or binary oxides[15-17] such as aluminosilicates and silica-titania systems. Although the hydrolytic sol-gel route is of considerable utility for the synthesis of hybrids, the development of alternative approaches is important in the context of broadening the scope of hybrid science and accessible products and properties.

The non-hydrolytic sol-gel process has recently been extended to the synthesis of novel metal oxide-phosphonate hybrids.[18] The synthesis is a two-step process involving initial non-hydrolytic reaction of a metal alkoxide with a phosphonic acid or ester to form the M-O-P bonds followed by conventional hydrolytic reaction of the residual alkoxide groups to form the M-O-M

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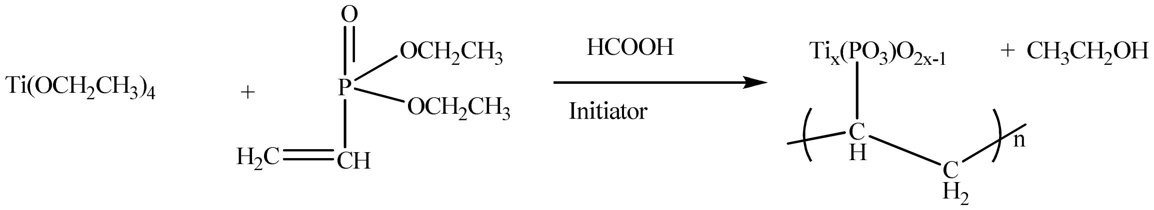
linkages. Layered metal oxide-phosphonate hybrids can also be made by a related route. Titanium, zirconium, and tin phosphonates have all been synthesized by nonhydrolytic reaction of the metal(IV) halide with a dialkyl- or dichlorophenylphosphonate or methylphosphonate.[19]

The study of chemical effects of ultrasound is a rapidly growing research area. [20-22] Some of the most important recent aspects of sonochemistry have been its applications in the synthesis and modification of both organic and inorganic materials.[23,24] High-intensity ultrasound can induce a wide range of chemical and physical consequences. The chemical effects of ultrasound fall into three areas: homogeneous sonochemistry of liquids, heterogeneous sonochemistry of liquid-liquid or liquid-solid systems, and sonocatalysis (which overlaps the first two). Applications of ultrasound to materials chemistry are found in all of these categories. Physical effects of high-intensity ultrasound, which often have chemical consequences, include enhanced mass transport, emulsification, bulk thermal heating, and a variety of effects on solids.[25] Ultrasound for the preparation of both main-group and transition metal oxides has found some significant use. For example, the ultrasonic irradiation of $Si(OC_2H_5)_4$ in water with an acid catalyst produces a silica “sonogel”. [26] In our previous paper [27] we obtained organic inorganic hybrids starting from metal alcoxides and polyvinylphosphonic acid.

In this paper we present the synthesis of hybrid materials containing organophosphorus compounds as coupling molecules, not mentioned in the studied literature, having interpenetrated network obtained by simultaneous radical polymerization and sol-gel process under ultrasound conditions. The organophosphorus compound are condensed with Ti-O-bond and in the same time their vinyl groups are polymerized (Scheme 1).



Scheme 1. Syntesis of interpenetrated network

2. Experimental

$Ti(OEt)_4$ (TEOTi), bis(2-chloroethyl) vinylphosphonate (2ClEtVF), diethylvinylphosphonate (DEVF) were purchased from Sigma Aldrich and used without purification. Formic acid (FA) (Sigma Aldrich), ammonium peroxidisulfate(PDS) and benzoyl peroxide (POB) were purchased by Merck, respectively by Sigma Aldrich and were used as received. The hybrid composites were obtained in one pot synthesis. First, oxidant ammonium peroxodisulfate or benzoyl peroxide (3% mol/vinylphosphonic acid) was added in 25 ml formic acid and vigorously stirred. Then, bis(2-chloroethyl) vinylphosphonate or diethylvinylphosphonate (0.1 mol) was added and the mixture was vigorously stirred at ambient temperature then 0.1 mol $Ti(OEt)_4$, was added. The mixture was kept 30 min under sonication condition, aged two days and hybrids were dried 5 hour at 100^oC

The obtained hybrids were investigated using FTIR, SEM. The IR absorption spectra were recorded with a Jasco 430 spectrometer (spectral range 4000-400 cm^{-1}, 256 scans, and resolution 2 cm^{-1}) using KBr pellets. The SEM images were obtained using Inspect S microscope. It was used an ultrasound apparatus MRC D80H with operating frequency 43 KHz.

3. Results and discussion

The performed syntheses are presented in Table 1.

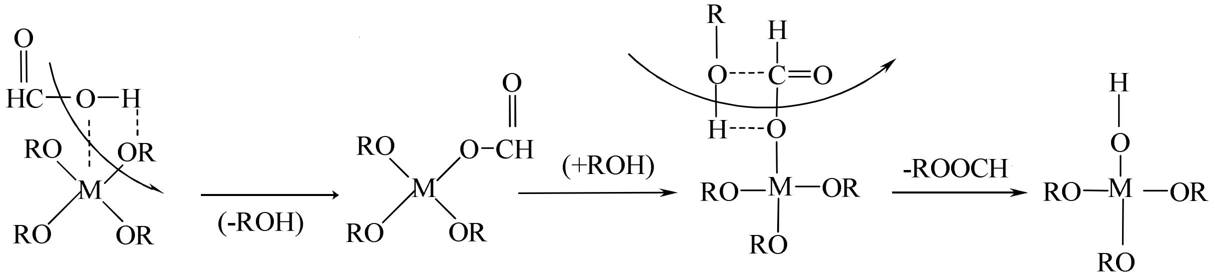
Table1. Performed syntheses.

Code	Etoxid	Phosphonate	Initiator	Solvent
SGex(10)	TEOTi	2ClEtVF	PDS	FA
SGex(10/1)	TEOTi	2ClEtVF	POB	FA
SG2	TEOTi	DEVF	PDS	FA
SG2/1	TEOTi	DEVF	POB	FA

The use of organophosphorus precursors in sol–gel technique is very attractive for the preparation of organic-inorganic hybrid materials.

The formic acid plays two roles: solvent for reagents and catalyst for polymetal oxide-polyphosphonate network. A somewhat different approach to synthesizing hybrids in a nonaqueous system has been described by Sharp. [28-30] It is arguable whether this is truly a “non-hydrolytic” approach since water is generated in situ during the reaction. This route involves the use of a strong carboxylic acid such as formic acid as solvent and catalyst for the sol-gel process, the acid also acting as a good solvent for a number of polymer systems.

During the acidolysis, M-OH (M=Ti) groups are formed and ethanol is released as an intermediate (**Scheme 2**).



Scheme 2. Hydrolysis of metal alcoxides in formic acid

Similarly phosphonic ester precursors hydrolyze as well in formic acid, ethanol is eliminated and phosphonic acid is formed as an intermediate

Heterocondensation between the metal alcoxide and phosphonic coupling molecules leads to the formation of P–O–M (M=Ti) bonds, while homocondensation between two metal alcoxide molecules leads to the formation of M–O–M bonds. 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 (Scheme 3).

$$\text{M-O-R} \quad + \quad \text{P-O-H} \longrightarrow \text{M-O}^{+}\text{(H)-R} \; + \; \text{P-O}^{-} \longrightarrow \text{M-O-P} \quad + \quad \text{R-OH}$$

Scheme 3. The formation of M–O–P bonds

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.

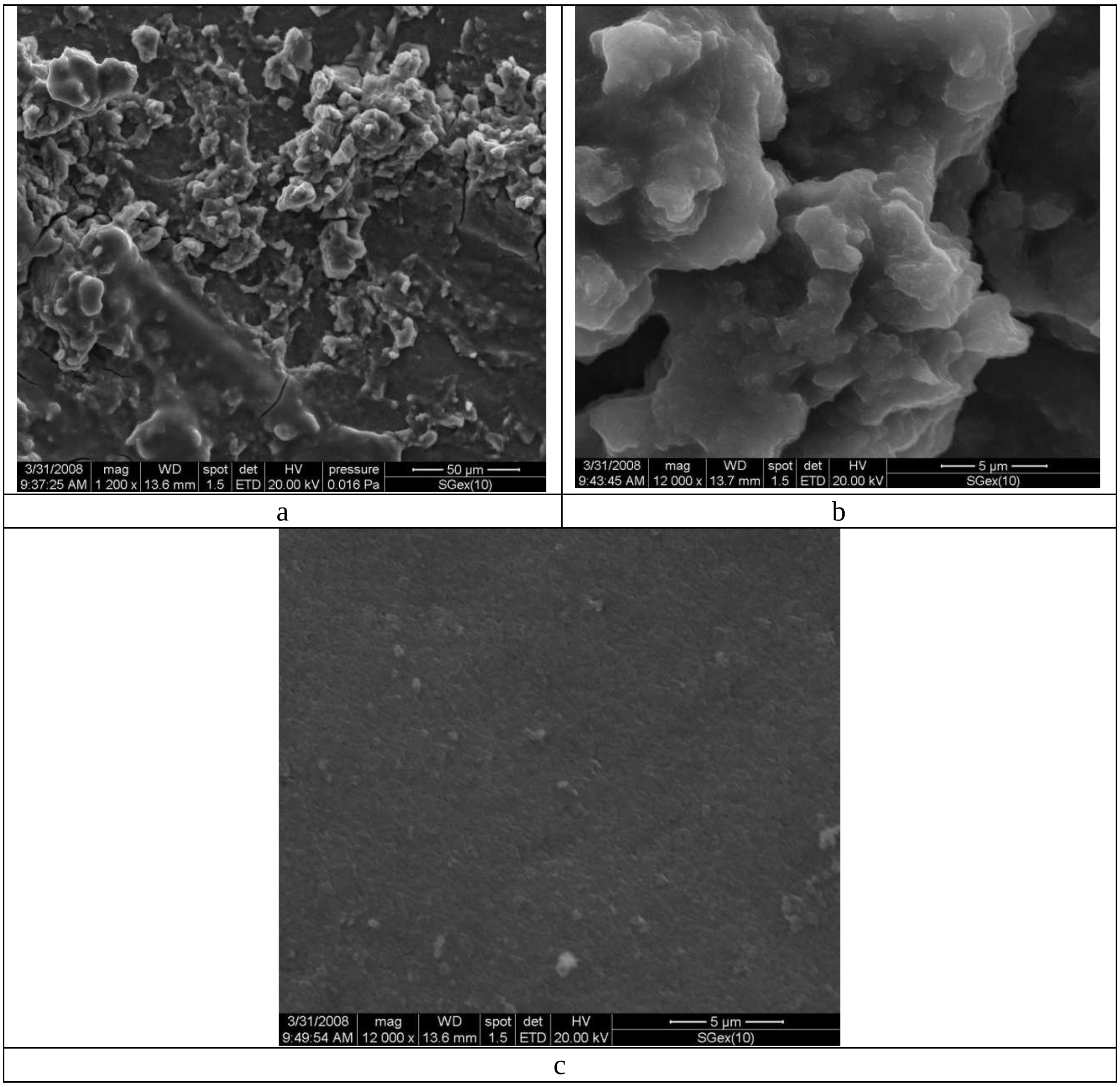
The majority of organic polymers are prepared from monomers containing a reactive double bond which undergo chain growth or addition reactions. These polymerize by a variety of mechanisms and, with various degrees of interest, ultrasound has been applied to examples of each type. The most straightforward preparative method is that initiated by radicals. As already noted, cavitation can produce high concentrations of radicals. Hence, application of ultrasound to vinyl monomers provides an alternative, highly controllable method of initiation. The primary role of ultrasound in this type of reaction is to produce the radicals needed to initiate polymerization. This can take place by two routes. Sonication of monomers produces radicals through decomposition inside the bubble or at its interface; alternatively, the decomposition of added initiators such as peroxides or azo compounds could be accelerated.

Combining the two technique sol-gel and sonication organic-inorganic interpenetrated networks can be obtained.

The strong bands at 1040-910 cm^{-1} and 1150cm^{-1} due to (P-O)H and P = O stretching and the absence of band (-C=C-) around 1700 cm^{-1} in FT-IR spectra are characteristic to the polyvinyphosphonic chain. The decrease or absence of (P-O)H stretching bands at 1040-910 cm^{-1} is a measure of polycondensation. The absence of peaks at 1097 and 1125 cm^{-1} which can be assignable to the Ti-OEt groups and presence of broad peak at 1130 cm^{-1} is assignable to the Ti-O-P group, indicates that sol-gel polycondensation proceeds successfully.

The absence of C-H stretching bands at 2984, 2932, 2905, and 2871 cm^{-1} from the OEt groups confirms the complete cleavage of the M-OEt groups.

SEM images of hybrid materials are shown in Fig. 1, 2.



a

b

c

Figure 1. SEM images of SGex (10)-2008 1a) magnitude 1600, b) magnitude 6000 si c) magnitude12000.

Hybrid SGex (10)-2008 obtained in nonhydrolitic and ultrasound conditions shows an amorfus aspect. At a higher magnitude the material prezents an omogenous aspect.

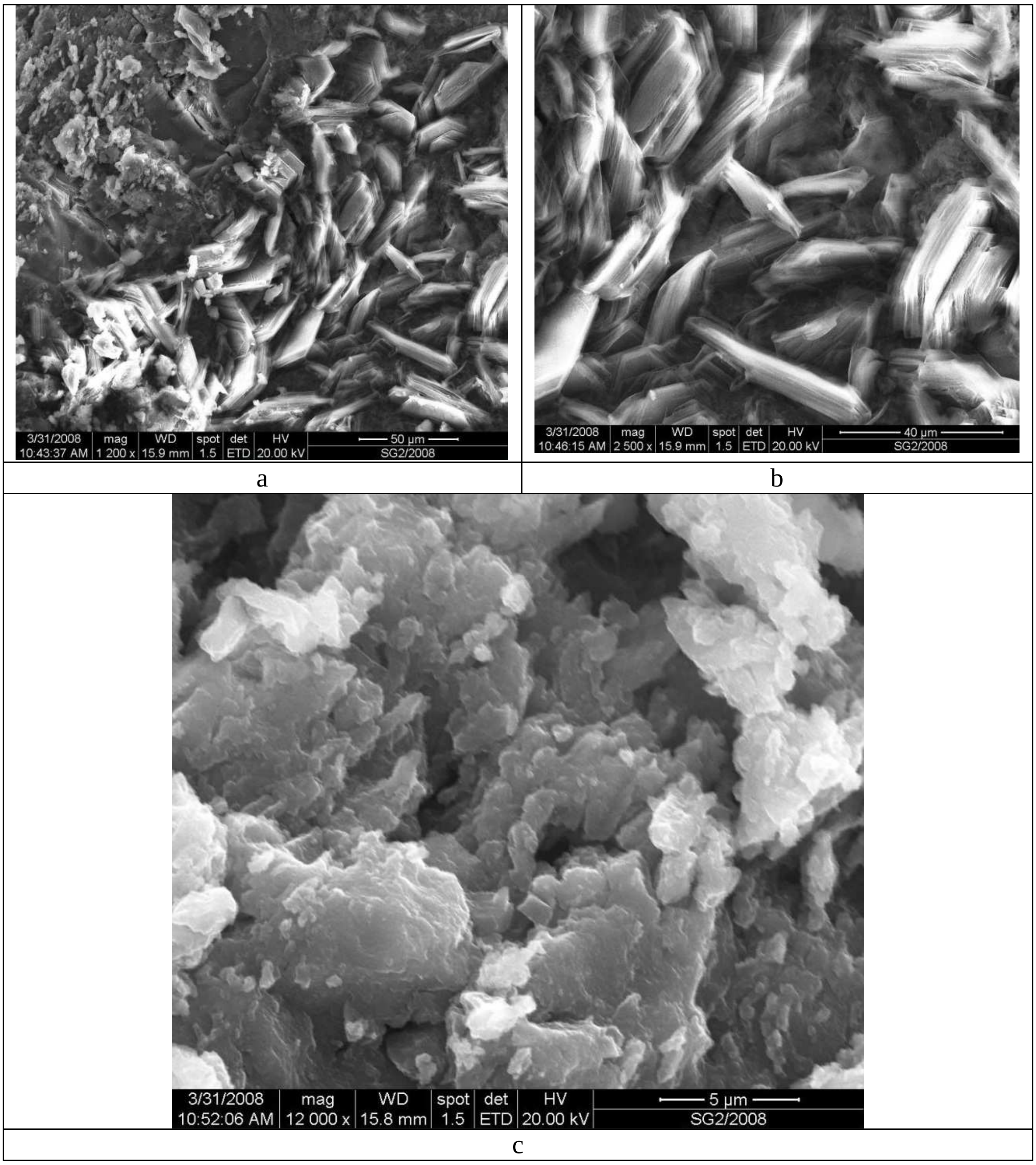


Fig. 2. SEM images of SG2-2008 1a) magnitude 1200, b) magnitude 2500 si c) magnitude 12000.

Hybrid SG2-2008 prezents at a low magnitude a compact structure. To at higher magnitude the material prezents stratified zones having iregular lamelar structure.

4. Conslusions

The use of organophosphorus coupling molecules in sol–gel processing is very attractive for the preparation of highly homogeneous hybrid materials. However, a dissolution–precipitation process, leading to the formation of metal phosphonate or phosphinate phases, can occur depending on the chemical stability of the inorganic substrate and the reaction conditions.

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