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Polystyrene/silica microspheres with core/shell structure as support of tungstophosphoric acid

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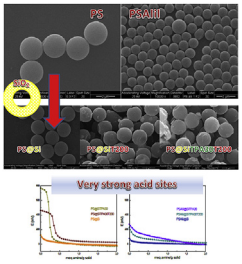
HIGHLIGHTS

- Tungstophosphoric acid on core/shell polystyrene/silica microspheres were prepared.
- Spheres presented a narrow size distribution and SiO_2 nanoparticles uniform layer.
- Mesoporous tungstophosphoric acid impregnated solids were achieved.
- Tungstophosphate anion with undegraded Keggin structure is present in the solids.
- Solids have very strong acid sites being suitable for use in acid catalyzed reactions.

GRAPHICAL ABSTRACT



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ABSTRACT

The immobilization of tungstophosphoric acid (TPA) on polystyrene/silica microspheres with core/shell structure by the incipient wetness impregnation technique was studied. The materials were synthesized employing polystyrene (PS) spheres or polystyrene spheres with the addition of 3-amino-1-propene as core, which were coated with silica by a modified Stöber method, using tetraethylorthosilicate as precursor. Spheres with a narrow size distribution and a uniform layer formed by silica nanoparticles were obtained, as observed by SEM and TEM. After impregnation with TPA, the samples were calcined at 200 °C in order to obtain the final materials. The solids impregnated with TPA presented N_2 adsorption –desorption isotherms characteristic of mesoporous materials. In addition, the characterization by FT-IR and ^{31}P NMR of all the solids impregnated with TPA gave evidence of the presence of the tungstophosphate anion with Keggin structure, and by potentiometric titration it was estimated that the solids present very strong acid sites. So, they are good candidates to be used in reactions catalyzed by acids, specifically for imidazole synthesis.

1. Introduction

Nanosized materials of the core/shell type have become very important due to their high functionality and properties, which can be easily modified by changing either the composition of the materials they contain or their core/shell ratio [1].

The combination of the materials employed in their synthesis

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can vary widely. Polymer microspheres such as polystyrene (PS) and poly(methyl methacrylate) (PMMA) and silica microspheres are often used as core spheres, and metal nanoparticles or oxide nanoparticles as shells [2]. The composites can include both inorganic cores and shells such as SiO_2/TiO_2 or ZnO/TiO_2, as well as an inorganic/organic core/shell such as Zr/PMMA or TiO_2/PS, or organic/inorganic core/shell such as PS/SiO_2 or PS/TiO_2. The choice of the core and the shell solely depends on the application that will be given to each material [3]. A nice and comprehensive review of these types of solids was recently reported by Chaudhuri and Paria [4].

A two-step process is usually used to prepare core/shell particles. Firstly, the core particles are obtained and afterwards, the precursor material of the shell is deposited on the core particles. This procedure is done by different methods, according to the core and the shell materials [4]. Core/shell microspheres with a solid core and a porous silica shell have been increasingly used, e.g., for efficient separations, catalysis, and biomedical applications [2,5–7]. The silica coating is usually deposited on polymer microspheres.

The material behavior is notably influenced by the particle size and the shell thickness [8]. It can be remarked that a small width of the porous shell is an advantage as the diffusion path length is short, so giving faster mass transfer in both packed separation columns [9] and catalytic reactions, because the entry, the transport and the release of different substances are facilitated [10].

Some of these materials are used for the production of hollow solids, through the application of a sacrificial core technique. When an organic core is used, it is removed by dissolution with a suitable solvent or by calcination [11,12]; instead, for the inorganic cores, dissolution by acids or bases is used [13,14].

Previous work has shown that the tungstophosphoric acid (TPA) can be supported on diverse materials, obtaining suitable materials for use as catalyst in reactions heterogeneously catalyzed by acids [15–20].

The heteropolyacids have special properties that make them particularly valuable for catalysis. Among them, their high Brønsted acidity, high solubility in water and oxygenated solvents, as well as an interesting stability when supported on different oxides and polymers can be highlighted. The last property is highly important, as the heteropolyacids present low specific surface area when they are employed in their bulk structure [21,22], while it considerably increases when they are supported.

In the present work the synthesis and characterization of solid acid catalysts, prepared using core/shell spheres of polystyrene/mesoporous silica as support, and impregnated with tungstophosphoric acid (TPA) employing the incipient wetness impregnation technique, are presented. Polystyrene spheres or polystyrene modified by the addition of a comonomer (allylamine) were used as core for the preparation of the support. These cores were covered with silica using a modified Stöber method [23], by means of hydrolysis and condensation of tetraethylorthosilicate (TEOS) in an ethanol–water solution using ammonium hydroxide as catalyst of the sol–gel reaction. Finally, the carriers were impregnated with TPA and then calcined. All the solids were characterized by different physicochemical techniques in order to observe the influence of the different preparation conditions on the characteristics of the synthesized materials, which were prepared to be later used as catalysts in an acid-catalyzed reaction.

2. Materials and methods

2.1. Preparation of polystyrene and allylamine added polystyrene cores

The polystyrene (PS) spheres were obtained employing the best conditions found in previous work [24]. They were prepared from 10 g of styrene utilizing 0.1 g of 4,4′ azobis 4-cyanovaleric acid (ACVA) as polymerization initiator in the presence of 0.3 g of polyvinylpyrrolidone (PVP) as stabilization agent of the dispersion, using ethanol as solvent. The mixture was placed in a 250 cm^3 reactor equipped with a reflux condenser, a temperature controller and a magnetic stirrer. N_2 was bubbled for 15 min in order to remove oxygen from the reactor. The temperature of the system was raised up to 70 °C and then the initiator, dissolved in a small quantity of ethanol, was added. The polymerization was carried out by stirring at 300 rpm for 24 h. After this time, the latex spheres were washed with ethanol to remove any remains of surfactant agent and then, they were stored dispersed in ethanol.

Following the same synthesis operative procedure, PS spheres with the addition of 1 cm^3 of 3-amino-1-propene (allylamine) as comonomer were prepared, thus obtaining the PSAlil material.

2.2. Preparation of silica-coated PS and PSAlil

To obtain the silica coating, PS spheres or PSAlil spheres, in a quantity of 60% w/w with respect to the silica quantity to be prepared, were weighed and placed in 40 cm^3 of ethanol and were then sonicated for 10 min in order to obtain a homogeneous dispersion. A modified version of Stöber method [23] was used for silica synthesis, which proceeds via hydrolysis/condensation of tetraethylorthosilicate (TEOS) in an alcohol/ammonium hydroxide reaction medium. Seven cm^3 of TEOS as silica precursor and 1 cm^3 of ammonium hydroxide (28% w/w) as catalyst of the sol–gel reaction were employed. The condensation reaction was performed at 50 °C with constant stirring for 20 h.

After this time, the coated spheres were separated by centrifugation and repeatedly washed with distilled water to remove the catalyst remains. Finally, they were dried at room temperature and then placed in a stove at 60 °C for 24 h, thus obtaining the solids that will be named PS@Si and PSAlil@Si.

2.3. Preparation of core/shell spheres with tungstophosphoric acid

Employing the incipient wetness impregnation technique and using a 30% (w/w) solution of tungstophosphoric acid ($H_3PW_{12}O_{40}.23H_2O$) (TPA) in ethanol–water (1:1 v/v), the following materials were impregnated: latex spheres with and without allylamine addition coated with silica (PS@Si) and (PSAlil@Si). The quantity of TPA solution was fixed in order to obtain 30% TPA w/w in the final material. The system was kept at room temperature till complete dryness. Afterward, the obtained solids (PS@SiTPA30 and PSAlil@SiTPA30) were weighed. Besides, the quantity of non-impregnated TPA in the washings with ethanol from the vessel where the impregnation was carried out was quantified by atomic absorption spectrometry. These materials were then calcined at 200 °C to obtain the spheres that will be named PS@SiTPA30T200 and PSAlil@SiTPA30T200. The nomenclature of the prepared solids is summarized in Table 1.

Table 1
Solid nomenclature.

Support	Solid impregnated with 30% TPA	Solid calcined at 200 °C
PS@Si	PS@SiTPA30	PS@SiTPA30T200
PSAlil@Si	PSAlil@SiTPA30	PSAlil@SiTPA30T200