

## INCLUSION OF $[H_3PW_{12}O_{40}]$ AND $[H_4SiW_{12}O_{40}]$ INTO A SILICA GEL MATRIX VIA “SOL-GEL” METHODOLOGY

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### ABSTRACT

Here we report the inclusion of two Keggin Polyoxometalates (POMs),  $[H_3PW_{12}O_{40}]$  and  $[H_4SiW_{12}O_{40}]$ , into silica gels by integrating them during the preparation of the  $SiO_2$  matrix via “sol-gel” methods. Aerogels were produced by supercritical drying of the wet gels impregnated with the POMs, and lyogels were obtained by means of a lyophilization process. These materials were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transformed infrared (FT-IR) spectroscopy and thermoanalytical techniques (TGA-DSC). We found that a large fraction of POMs are lost during the aging time, and solvent exchange for lyophilization. However the thermal stability of the bare matrix is modified by the inclusion of POMs. Some aggregates with a high content of POMs were found via SEM-EDX.

**KEYWORDS:** Silica Gel, polyoxometalates, aerogel, lyogel, Keggin,

### 1. INTRODUCTION

Silica aerogels were firstly prepared by Kistler during 1931,<sup>1</sup> however, they start to be widely studied and used only thirty years later, thanks to the development of a convenient synthetic procedure by Nicolaon and Teichner, based on the employment of tetramethylortosilicate (TMOS) as the silicon pool.<sup>2,3</sup> This allows the preparation of materials with several properties such as high porosity, specific surface area, low bulk density, low thermal conductivity and low dielectric constant. These properties make silica aerogels important for industry as thermal insulators,<sup>4,5</sup> catalyst supports,<sup>6,8</sup> adsorbents,<sup>9,10</sup> sound insulation and host materials for drug delivery systems.<sup>11</sup> The “sol-gel” procedure developed by Teichner’s group is one of the most used routes for the preparation of solid porous materials, since their easiness to prepare stable colloidal solutions (“sol”), which are followed by the anisotropic condensation of colloidal particles that give rise to the formation of a “gel” during a gelification stage.<sup>12</sup> The solvent can be eliminated in subsequent steps, and depending of the methodology employed, a “xero”-, “lio”- or “aero-gel” can be obtained. The supercritical drying removes the solvent from the silica without collapsing the internal structure of the gel, obtaining an “aerogel” that retains the porous structure and channels defined in the wet gel. The lyophilization, or freeze-drying, technique removes the solvent by sublimation at low temperature and low pressure. While in most cases the gel crumbles during the lyophilization, resulting in a porous powder, monolithic “lyogels” have been obtained.<sup>13</sup>

We focus our attention on the preparation of mesoporous materials functionalized with Polyoxometalates (POMs). They possess unique properties as resistance toward oxidative conditions, hydrolysis at controlled pH conditions and thermal stability, which convert them in promising candidates for applications in oxidative catalysis.<sup>14,15</sup>

POMs have been recently dispersed into mesoporous materials, however, the methodology employed only considered simple physisorption or electrostatic interactions with positively charged support, acting like counterions, being not strongly bonded to the support.<sup>16-21</sup> On the other hand, vacant POMs have been covalently attached to the walls of hybrid supports,<sup>22,23</sup> or embedded into a silica matrix prepared employing sol-gel methods.<sup>24,25</sup>

The aim of this article is to carry out the inclusion of polyoxometalates into silica gels by integrating them during the “sol” stage of preparation, proceeding later with the drying of them, obtaining aerogels and lyogels, which are characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transformed infrared (FT-IR) spectroscopy, X-ray photoelectron spectroscopy (XPS), and thermoanalytical techniques (TGA-DSC).

### 2. EXPERIMENTAL DETAILS

#### 2.1 Reagents

Tetraethoxysilane (TEOS), methanol (MeOH) with a purity of 99.8%,

ethanol (EtOH) with a purity of 98%, concentrated 37% hydrochloric acid (HCl) and ammonium hydroxide 28-30% solution ( $NH_4OH$ ) were purchased from Sigma-Aldrich and used without further purification. Deionized water ( $H_2O$ ) was prepared by an ion exchange system (18  $\Omega$  and pH 5.70).  $[H_3PW_{12}O_{40}]$  and  $[H_4SiW_{12}O_{40}]$  were prepared as described by Rosenheim and Jaenicke<sup>26</sup> and North<sup>27</sup> respectively.

#### 2.2 Gel Preparation

For the preparation of gel, a modification of the method proposed by Wu *et al.*<sup>28</sup> was used. Equivalent molar quantities were employed according to the reaction, 1 TEOS : 6 MeOH : 4  $H_2O$  :  $4 \times 10^{-3}$  HCl. This batch solution was prepared as follows: 110.8 mL of TEOS, 121.51 mL of MeOH, 36 ml of deionized water and 2 mL of concentrated HCl were placed in a flask and stirred for 1 hour. After 1 hour, the solution was divided into different gelling bottles and different quantities of a solution of  $[H_3PW_{12}O_{40}]$  1.0M and  $[H_4SiW_{12}O_{40}]$  1.0 M were added under vigorous stirring. To induce the gelification process, the catalyst used was 1%  $NH_4OH$  in  $H_2O$ . The gelification time is about 20 minutes. After this time, the wet gels were covered with MeOH and left to aging during 1 week.

#### 2.3 Gel Dry Process

The preparation of the wet gels for the drying process depends of the methodology employed.

Supercritical fluid drying: After 1 week of aging, the wet gels are transferred to a metal basket and wrapped with filter paper to prevent loss of gel, and transferred to the reactor. During the drying, the MeOH is exchanged by  $CO_2$  at 22 °C and ~100 bar within a lapse of 2 h. Then, the temperature is elevated to 45 °C during 2 h in supercritical  $CO_2$  atmosphere at 100 bar. When the process is complete, the system is depressurized slowly until reach ambient conditions.

Lyophilization: The MeOH employed during the aging process must be exchanged by water to carry out the lyophilization. This must be done progressively, by changing the solution day by day, employing a 3:1 MeOH: $H_2O$  mixture, then 1:1 MeOH: $H_2O$  mixture, then 1:3 MeOH: $H_2O$  mixture, and finally renewing pure water during 3 days. Afterwards the samples were frozen with liquid nitrogen and transferred to the lyophilization chamber. The chamber is evacuated until a pressure of 0.05 mbar is reached while the temperature gradually increases to room temperature. The system is left at 0.05 mbar during 16 h to completely remove the solvent by sublimation. When the process is complete, the system is vented until reach ambient conditions.

#### 2.4 Characterization

Infrared spectra of the prepared samples were obtained with a WQF-510A FT-IR spectrometer. For a three-dimensional visualization of the pore structure scanning electron microscopy images (SEM) were acquired with a Quanta FEI 200 FEG-ESEM, and the quantitative analysis to characterize the

gels composition was measured employing energy-dispersive X-ray analysis (EDX). Transmission electron microscopy (TEM) were obtained with a 120 kV JEOL 1210. Thermogravimetric analysis (TGA) and differential scanning calorimetry/differential thermal analysis (heat flow DSC/DTA) were measured in a NETZSCH-STA 449 F1 Jupiter system, under air conditions and up to 800 °C.

### 3. RESULTS AND DISCUSSION

#### 3.1 Gel Preparation

Gels were prepared by employing the “sol-gel” procedure. The advantage is that a homogeneous distribution of the inorganic clusters is obtained when loading the molecular entities during the “sol” stage, as can be appreciated in Figure 1, from the monoliths of the wet gels. Also, it can be noted the high degree of transparency to visible light.

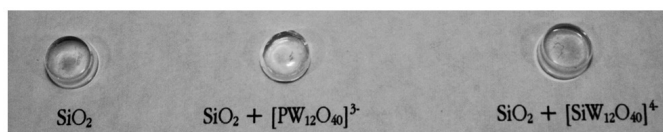


Figure 1: Monoliths of the wet gels

The amount of POMs contained in these gels, relative to the TEOS content is about  $1 \times 10^{-3} = [\text{POM}]/[\text{TEOS}]$ . When higher  $[\text{POM}]/[\text{TEOS}]$  relations are used, the gels exhibit an opaque aspect, and white colour, indicating that the sol state is particulate. The gelification time decrease as the  $[\text{POM}]/[\text{TEOS}]$  ratio increase, in the case of a  $[\text{POM}]/[\text{TEOS}] = 1 \times 10^{-3}$  the gelification time is about 20 min when employing 1%  $\text{NH}_4\text{OH}$  in  $\text{H}_2\text{O}$  as catalyst. Higher concentrations of the catalyst, have a tendency to form white aggregates, which reduce the homogeneity of the wet gels.

These wet gels were dried employing two different methodologies, supercritical fluid drying and lyophilization. In both cases, the structure collapse, however, when supercritical drying is employed, we obtain irregular fragmented aerogels of about 0.5 cm of length, while for lyophilization, fine-light dust lyogels were obtained.

#### 3.2 Gel Microscopic Morphology

The drying methodology has an important effect on the morphology of the gels as can be seen from the SEM images, see Figure 2. Aerogels exhibit a smooth surface while the liogels exhibit a fractured and cracked structure, despite of the POM employed  $[\text{H}_3\text{PW}_{12}\text{O}_{40}]$  or  $[\text{H}_4\text{SiW}_{12}\text{O}_{40}]$ . When considering a magnification of 60000X at SEM, both aerogels and lyogels present a sponge like structure of similar characteristics, in a tridimensional nanoporous network, which contains aggregated silica granules.

Disordered pore arrays can be seen in both type of gels, with variable diameters, between ~15 and 40 nm determined from TEM images.

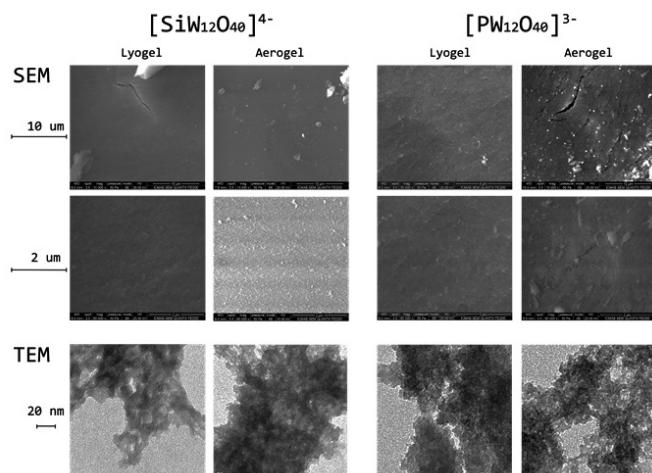


Figure 2: SEM and TEM micrographs of aerogels and lyogels containing  $[\text{SiW}_{12}\text{O}_{40}]^{4-}$  and  $[\text{PW}_{12}\text{O}_{40}]^{3-}$ .

Since the inclusion of POMs is not evident from FT-IR spectroscopy, we measure the tungsten content from SEM-EDX, finding a content of 1.45 and 3.97% of tungsten content for the  $\text{SiO}_2 + [\text{H}_4\text{SiW}_{12}\text{O}_{40}]$  and  $\text{SiO}_2 + [\text{H}_3\text{PW}_{12}\text{O}_{40}]$  aerogels respectively. On the other hand, lyogels present a 0.39 and 3.50% of tungsten for  $\text{SiO}_2 + [\text{H}_4\text{SiW}_{12}\text{O}_{40}]$  and  $\text{SiO}_2 + [\text{H}_3\text{PW}_{12}\text{O}_{40}]$  lyogels respectively. This can be attributed to a desorption process occurring during the aging time in MeOH, and subsequent solvent exchange to proceed with the lyophilization drying. This can explain the lower content of tungsten in liogels compared with aerogels. However, an exhaustive analysis show that POMs are aggregated into  $\text{SiO}_2 + \text{POM}$  islands, as can be observed in Figure 3.

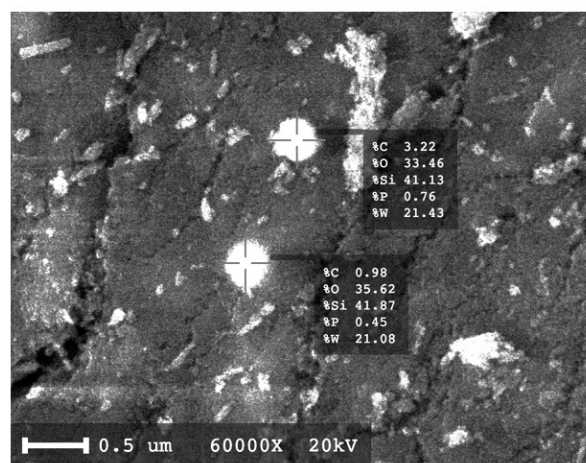


Figure 3: SEM-EDX micrographs showing  $[\text{PW}_{12}\text{O}_{40}]^{3-}$  aggregates

#### 3.3 Thermal Stability

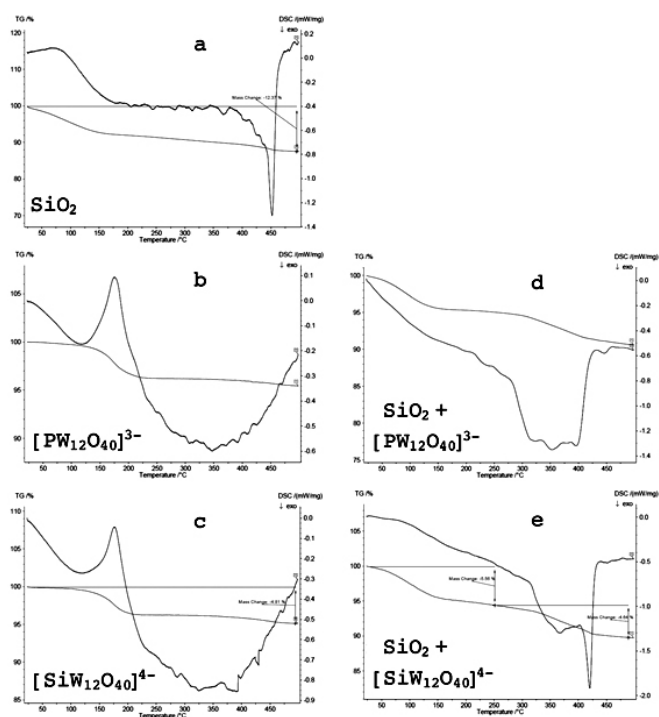
TG/DSC curves of bare silica lyogel as example are presented in Figure 4a, they exhibit a progressive weight loss of 12.37% starting around 50 °C until around 450 °C. DSC show an endothermic process at 74 °C and an exothermic process at 448 °C. Figure 4b and 4c represent the TGA/DSC profiles for  $[\text{H}_3\text{PW}_{12}\text{O}_{40}]$  and  $[\text{H}_4\text{SiW}_{12}\text{O}_{40}]$  respectively. Both present a common exothermic process at 117 °C, and a weight loss of about 3.7% starting around 120 °C. Both POMs are thermally stable, showing an extra weight loss of ~1% until 500 °C. The thermal behaviour of the  $\text{SiO}_2 + \text{POM}$  presented in Figure 4d and 4e shows a weight loss of 5.56% in the case of  $\text{SiO}_2 + [\text{H}_4\text{SiW}_{12}\text{O}_{40}]$  and 4.6% for  $[\text{H}_3\text{PW}_{12}\text{O}_{40}]$  below 150 °C. This is attributed to the desorption of physisorbed water onto the porous material.<sup>29</sup> The exothermic processes occurring at higher temperatures with an extra weight loss of 4.8 and 9.5% for  $\text{SiO}_2 + [\text{H}_4\text{SiW}_{12}\text{O}_{40}]$  and  $\text{SiO}_2 + [\text{H}_3\text{PW}_{12}\text{O}_{40}]$  can be attributed to the elimination of crystalline water and loss of the primary structure of the POMs.<sup>30</sup>

### 4. CONCLUSIONS

Porous  $\text{SiO}_2$ -POM hybrid materials have been prepared via sol-gel methodologies, followed by a lyophilization or supercritical drying.  $[\text{H}_3\text{PW}_{12}\text{O}_{40}]$  and  $[\text{H}_4\text{SiW}_{12}\text{O}_{40}]$  POMs were introduced into the  $\text{SiO}_2$  matrix during the sol stage of preparation, allowing us to obtain a homogeneous material with a high rate of transparency to visible light. The material presents a nanometric disordered pore array. These materials present a POM content varying from 0.4 to ~4 %, mainly due to the lost of a large fraction of POMs during the aging and solvent exchange processes. The thermal stability of the bare matrix is modified by the inclusion of POMs, exhibiting features attributable to POMs. Some aggregates with a high content of POMs were found via SEM-EDX.

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**Figure 4:** TG/DSC curves of a) Bare silica lyogel, b)  $[H_3PW_{12}O_{40}]^{3-}$ , c)  $[H_4SiW_{12}O_{40}]^{4-}$ , d) Silica lyogel containing  $[H_3PW_{12}O_{40}]^{3-}$  and e) Silica lyogel containing  $[H_4SiW_{12}O_{40}]^{4-}$ .

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