Physico-Chemical Characterization of a New Silica-Polyoxometalate Thermally Modified Unit

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A new silica-polioxometalate thermally modified unit has been obtained. The system is characterised by high potential to be used as stationary phase within solid phase extraction process (SPE) for separation and concentration of lanthanide and actinide heteroatoms from natural waters. Physico-chemical characterization of the newly obtained unit is foreseen through the data obtained by Fourier Transformed Infrared Spectroscopy (FTIR), scanning electronic microscopy (SEM) with electron diffraction X-ray (EDX) detection, and X-ray diffraction.

Keywords: silica-polioxometalate, polytungstosilicate, Keggin structure, solid phase extraction, stationary phase

Polyoxometalates (POMs) have been known for almost two centuries ago since the first member of this class has been discovered by Berzelius in 1826 [1]. Nowadays, POM chemistry constitutes a well established subclass in inorganic chemistry [2]. Considering that formation of POMs occurs via self-assembly, the search for novel species with different compositional and structural identity remains a great challenge for synthetic chemists [3].

The intrinsic properties of polyoxometalates are of interest in themselves not only from a fundamental point of view but also to make of them materials of interest in various applications. Beyond their traditional interest as catalysts, polyoxometalates constitute base materials for electrochromics, energy storage (batteries and supercapacitors [4]) conversion devices (fuel cells [5]), sensors and biomedical applications [6].

On the other hand, many of the applications of polyoxometalate clusters as materials require their use in the form of membranes or electrodes, that is, in the form of solid, insoluble materials or coatings. There is therefore a main strategic line of work that has been centred on the inclusion or integration of polyoxometalates in all sorts of substrates, polymeric, inorganic or mineral, and their combination with surfactants or organic carriers.

Among above presented applications of POMs, recently has been investigated their potential use for sequestration and storage of reactive waste, with emphasis on lanthanide and actinide heteroatoms [7-9]. All studies indicate that POMs material have a huge retaining properties for such heteroatoms. Analysis of uranium from different environment sample has recently become of interest [10-14]. Uranium represents one of the most studied actinide heteroatoms which is leached out of rocks and is present in water in the concentration range of 0.1 – 10 $\mu g\ L^{-1}$ [15]. Uranium content of land waters in excess of 1 ppb (1$\mu g\ L^{-1}$) is regarded as an anomaly. This extreme dilution in the presence of relatively high concentration of other ions makes it difficult to be directly measured. Refined analytical methods must be employed to detect such small concentrations.

There are various techniques reported for the determination of total uranium from very high to very low concentrations. Voltammetry, polarography, fluorimetry, X-ray fluorescence spectroscopy (XRF), α-spectrometry, spectrophotometry and ICP spectroscopy are included among these techniques [16].

Recently, solid phase extraction (SPE) has been recognized as an attractive and powerful technique for the enrichment of trace constituents. SPE has been applied to separation of trace amounts of uranium from impurities [17-19].

Various solid phase extraction methods were developed using different types of solid supports such as activated carbon, naphthalene, benzophenone, octadecyl bonded silica membrane disks and polymeric resins, etc. for separation, preconcentration, and recovery of uranium [20-27]. Solid phases with sorbent properties were prepared by chemical modification of an initial support. Such a process involved tedious chemical reactions. Some of these methods had preconcentration factors less than 150 which in fact are very poor. A simple route for preparation of a solid phase based upon impregnation of reagent on the solid support was also proposed [26, 27].

The major drawback to the practical applications of POM synthetic materials as solid support in SPE technique is their high solubility in water and in highly polar organic media [28-31]. This problem could be easily solved when POMs units are fixed on silica or alumina support materials. Thus, immobilization of POMs onto solid support to create heterogeneous materials is necessary for their recovery and possibly their recycling. Some POMs have been integrated into porous inorganic solids e.g. silica or zeolite, and subsequently they have been used as effective and recyclable photocatalysts for photo-degradation and mineralization of aqueous organic pollutants [32-34]. Most of the newly POMs derivatives have been synthesised via sol-gel technique.

Considering our laboratory interest on chemistry and properties of POMs materials [35, 36], the objective of the present work has been focused on the synthesis and physico-chemical characterization of a new silica-polioxometalate thermally modified unit that can be used as stationary phase in solid phase extraction (SPE) technique. Characterisation of the newly synthesised unit has been obtained by Fourier Transformed Infrared Spectroscopy (FTIR), scanning electronic microscopy (SEM) with electron diffraction X-ray (EDX) detection, and X-ray diffraction.

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Experimental part

Chemicals and instrumentation

All chemicals were reagent grade and used as purchased from Aldrich-Sigma and Merck without any further purification. The newly synthesized material was characterized by the mean of several analytical techniques. A Bruker Alpha spectrophotometer has been used for the FT-IR spectra which were recorded in a KBr thin disk. All the FT-IR spectra were recorded with a spectral resolution better than 2 cm^{-1}, with wavenumber accuracy of 0.1 cm^{-1}. A RockSolid interferometer was permanently aligned with a DTGS detector. Scanning electronic microscopy was performed by means of a SEM VEGA II LSH, TESCAN, coupled with an EDX QUANTAX QX2 detector, which does not require liquid nitrogen as cooling media and is about 10 times faster than the traditional Si(Li) detectors.

A Shimadzu X-ray Diffractometer LabX XRD-6000 with CuK alfa anode of 2.0 KW has been used to identify and determine crystalline phases, orientation, structural properties and atomic arrangement in the newly obtained unit.

Syntheses

$K_8[SiW_{11}O_{39}]$ mono-lacunary structure (POM) was synthesized and characterized according to literature methods [37, 38]. Other details for the synthesis are elsewhere presented [35]. Silica gel material has been used as purchased from Merck without any further purification.

Solid mixture of POM:SiO_2 in a 1:1 mass ratio was thermally combined. The mixture was kept for 5 h under normal atmospheric condition at 600 °C. Prior analyses the newly obtained material was washed up with demineralised water and dried for about 4 h under vacuum at 150 °C.

Results and discussions

SEM-EDX analysis

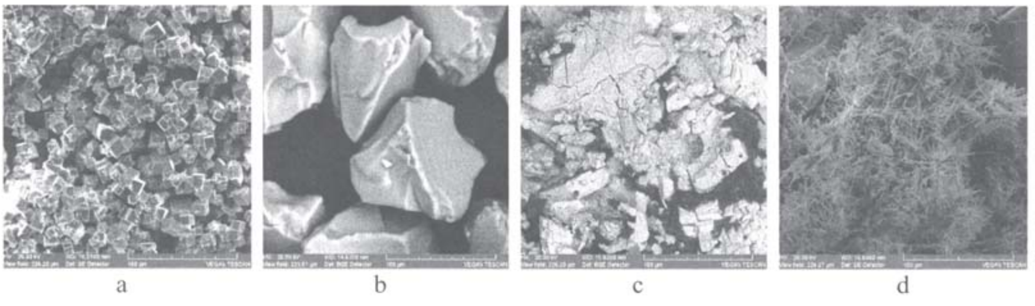
The newly obtained material was firstly investigated in order to check either or not it had different morphological structure when compared with the starting materials. SiO_2-POM solubility was also controlled and all performed tests indicated that the obtained material is water insoluble.

Typical examples of SEM images are presented in figure 1 which suggests existence of clear differences in the morphology of the initial precursors before and after calcinations. As Figure 1d shows thermal treatment applied to SiO_2 : $K_8[SiW_{11}O_{39}]$ in a 1 : 1 mass ratio leads to drastically changes in the morphology of the obtained system if compared with its initial precursors. Moreover, data from SEM-EDX (fig. 2) indicate clearly that the new material, thermally obtained, contains all the components from both starting materials. Figure 2d proves that there is an increase in the SiO_2 amount, coming from silica used as starting material.

The new obtained material is water insoluble when compared with water solubility of $K_8[SiW_{11}O_{39}]$ used as initial precursor. Under these circumstances it can be suggested the SiO_2-POM material has a different crystal structure that can be correlated with the temperature at which crystallisation is carried out and the geometry induced by the formation of new covalent bonds (differences leading to conformational polymorphism). Temperature of 600°C was selected as an appropriate condition for thermal modification of the initial precursor's mixture. Previous thermogravimetric and thermo-differential analyses carried out on $K_8[SiW_{11}O_{39}]$ [35] revealed that at about 500°C large exothermic effects occurred and these were mainly attributed to modifications in the polymorphic structure of the synthesised POM. Details in figure 1c may sustain as well the above presented observation. It can be suggested that $[SiW_{11}O_{39}]^{8-}$, in the presence of mesoporous silica, can favour formation of possible new covalent bonds between SiO_2 and POM precursor leading to a new material with completely new structure. Figure 1d suggests that the newly synthesised material may present a linear geometry when compared with the octahedral one characteristic for $K_8[SiW_{11}O_{39}]$.

FTIR analysis

From FTIR spectra in the 400 - 4000 cm^{-1} range were extracted more information about the material obtained upon thermal combination of SiO_2 and $[SiW_{11}O_{39}]^{8-}$ anion that is characterized by high coordination capacity. Figure 3 presents FTIR spectra of silica, $K_8[SiW_{11}O_{39}]$ and of the new SiO_2-POM unit in the main region (1500 - 400 cm^{-1}) with the figure in extension presenting the spectra over the entire range of investigation (4000 - 400 cm^{-1}). From figure 3 is evident that the newly synthesised material presents different spectral features when compared with those characteristic for SiO_2. Similarities with $K_8[SiW_{11}O_{39}]$ spectral features are evident mainly in the 1000 - 1200 cm^{-1} region. In the 400 - 1500 cm^{-1} range, IR bands characteristic for precursor POM ($K_8[SiW_{11}O_{39}]$) [3,4] were observed also in the SiO_2-POM spectra. The observed bands present similarities although in the SiO_2-POM unit bands with maxima at about 500, 900 and 1100 cm^{-1} are more intense. Based on these observations we can suggest that the Keggin structure of $K_8[SiW_{11}O_{39}]$ keeps its properties in the newly obtained material after SiO_2 addition and thermal treatment. Moreover we can claim that the new obtained material retain almost the same unit structure, especially



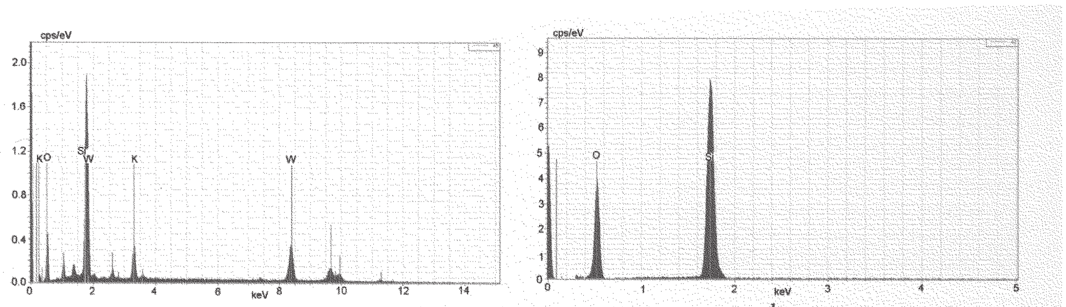
$K_8[SiW_{11}O_{39}]$

SiO_2/thermally treated at 600 °C

$K_8[SiW_{11}O_{39}]$/ thermally treated at 600 °C

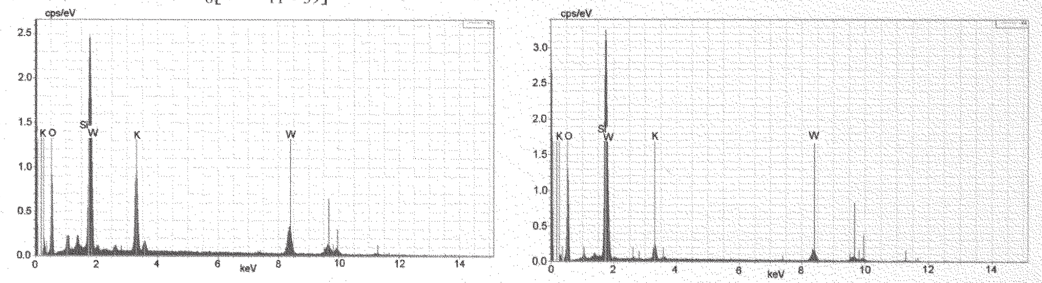
SiO_2- $K_8[SiW_{11}O_{39}]$ after thermo treatment

Fig. 1. SEM images for $K_8[SiW_{11}O_{39}]$ (a), SiO_2/thermally treated at 600 °C (b), $K_8[SiW_{11}O_{39}]$/ thermally treated at 600 °C (c) and SiO_2- $K_8[SiW_{11}O_{39}]$ after similar thermo treatment (d)



a
$K_8[SiW_{11}O_{39}]$

b
SiO_2/thermally treated at 600 °C



c
$K_8[SiW_{11}O_{39}]$/thermally treated at 600 °C

d
SiO_2- $K_8[SiW_{11}O_{39}]$ after thermo treatment

Fig. 2. SEM-EDX chemical composition spectra of the $K_8[SiW_{11}O_{39}]$ - (a), SiO_2/ calcined - (b), $K_8[SiW_{11}O_{39}]$ / calcined - (c), SiO_2- $K_8[SiW_{11}O_{39}]$ after thermic treatment – (d).

the one containing coordination bonds as M=O, M-O-M and M-O [3,4]. Maxima of characteristic bands observed for $K_8[SiW_{11}O_{39}]$ and its new derivative SiO_2-POM thermally obtained are presented in table 1. Four major absorption bands (fig. 3) have been observed in the 400 - 1500 cm^{-1} region, which are the characteristic absorption peaks of heteropoly anions structure. The 924 and 922 cm^{-1} bands were assigned to ν_{as} (W-O$_a$). The absorption bands at 752 and 750 cm^{-1} are assigned to ν_{as} (W-O$_b$-W) while those at 616 and 619 cm^{-1} to ν_{as} (W-O$_c$-W). The adsorption band at 471 and 468 cm^{-1} is assigned to ν_{as} (W-O).

Table 1

MAXIMA OF FTIR VIBRATION BANDS (in cm^{-1}) OF THE NEWLY SYNTHESISED MATERIAL AND ITS PRECURSORS

Assignment	SiO_2-POM	$K_8[SiW_{11}O_{39}]$
ν_{as}(W-O$_a$)	922	924
ν_{as} (W-O$_b$- W)	752	750
ν_{as} (W-O$_c$- W)	616	619
ν_{as}(W-O)	471	468

XRD analysis

Additional analyses of newly synthesised material have been performed by using X-ray technique in order to identify whether or not this material has different crystalline and orientation structure. By comparison of XRD spectra it has been observed that the new material retain part of the $K_8[SiW_{11}O_{39}]$ structure. Figure 4 presents by comparison typically X-ray diffraction spectra recoded for both starting materials next with the new SiO_2-POM compound. As shown by figure 4 in the SiO_2 spectra a broad peak appears at 2θ of about 20° which corresponds to the semicrystalline

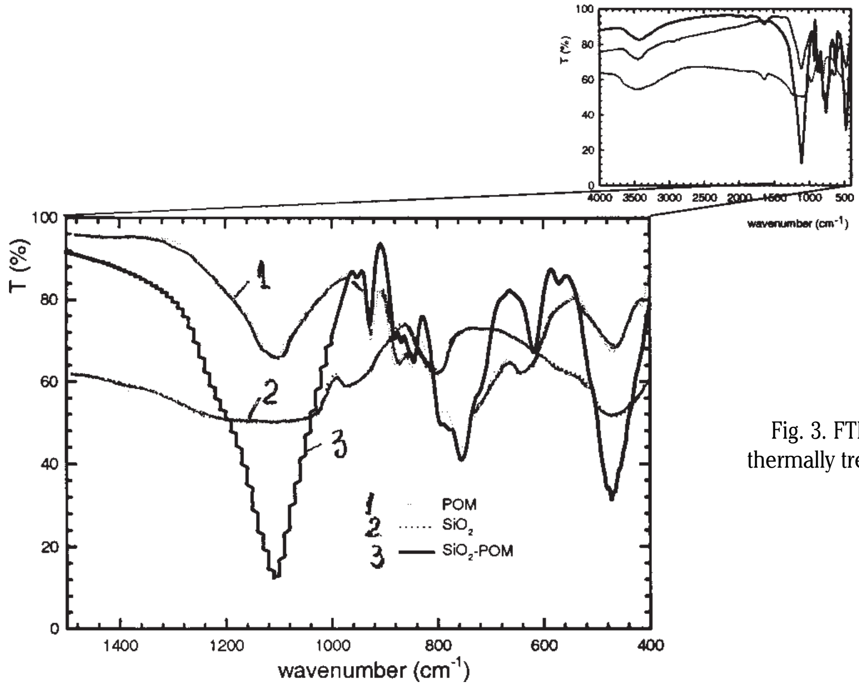


Fig. 3. FTIR spectra of the $K_8[SiW_{11}O_{39}]$ (POM), SiO_2/ thermally treated at 600 °C (SiO_2), SiO_2- $K_8[SiW_{11}O_{39}]$ after thermo treatment (SiO_2-POM)

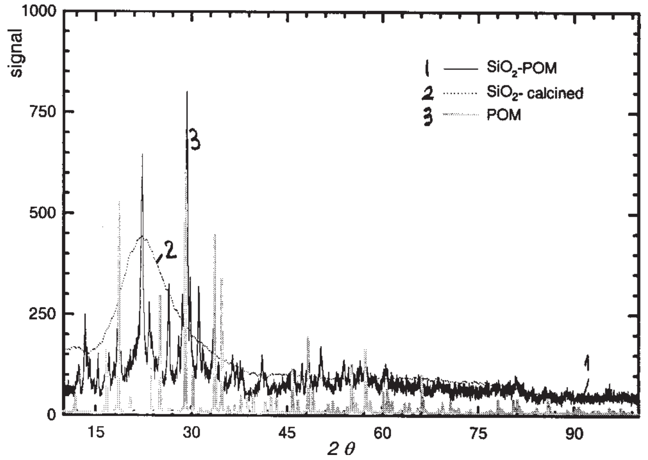


Fig. 4. XRD spectra of the $K_8[SiW_{11}O_{39}]$ (POM), SiO_2/thermally treated at 600°C (SiO_2) and SiO_2- $K_8[SiW_{11}O_{39}]$ after thermo treatment (SiO_2-POM)

phase of SiO_2 materials. For the pure $K_8[SiW_{11}O_{39}]$ there were four peak groups in the 2θ ranges 10-13°, 17-22°, 25-30° and 31-37°, all corresponding to the characteristic peaks of the Keggin structure [39]. The XRD spectra recorded for the newly obtained material (fig.4) shows that SiO_2-POM still keeps the Keggin structure. Moreover, the newly obtained material (SiO_2-POM) exhibits a new peak at 2θ < 15° indicating that the molecules in the new material are ordered at short distances [40].

Conclusions

A new SiO_2-POM material, water insoluble, was successfully obtained via thermal treatment of $K_8[SiW_{11}O_{39}]$ and SiO_2 mixture. The newly obtained material presents totally different morphology when compared with its precursor materials. Spectroscopic techniques (FT-IR, SEM-EDX, XRD) can be employed for the physico-chemical characterisation of the new material. Keggin structure of $K_8[SiW_{11}O_{39}]$ is kept also in the SiO_2-POM material. Efficiency in the synthesis procedure and the Keggin structure make of this material a good candidate for possible practical application such as stationary phase for solid phase extraction (SPE) for the sequestration and binding of heavy-metals, uranyl, thorium and other actinyl cations.

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