

Synthesis and characterization of proton-conducting materials containing dodecatungstophosphoric and dodecatungstosilic acid supported on silica

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Abstract

Solid electrolytes formed by different amounts of phosphotungstic acid (PWA) and silicotungstic acid (SiWA) in silica gel have been prepared and characterized. XRD, IR and DTA analyses performed on the samples in powder form revealed the existence of an interaction between the heteropoly acids and the support. This interaction was stronger in the case of SiWA than in the case of PWA. Nevertheless, the samples with 15 and 30 wt.% of SiWA, which presented higher interaction with the support, and for this had engaged more protons to this end, showed higher proton conductivities with respect to the samples at the same loading of PWA. This fact was justified by the higher number of protons possessed by the SiWA molecules. An increase of proton conductivity was also observed when increasing the relative humidity (r.h.) of atmosphere over the samples and the heteropoly acid loading. This was because at higher r.h., the number of water molecules in the material increased, thus allowing an easier movement of protons and, at higher heteropoly acid loading, because the concentration of mobile protons increased. © 1999 Elsevier Science S.A. All rights reserved.

MAT: $\text{PW}_{12}\text{O}_{40}-\text{SiO}_2$; $\text{SiW}_{12}\text{O}_{40}-\text{SiO}_2$

Keywords: Proton conductor; Solid electrolyte; Proton conductivity; Heteropoly acids

1. Introduction

Heteropoly acids (HPAs) have suitable characteristics to be used as solid electrolytes or as aqueous solutions in fuel cells [1–3]. They are known to show very strong Bronsted acidity as solid electrolytes [4], exceeding that of such conventional solid acids as $\text{SiO}_2-\text{Al}_2\text{O}_3$, $\text{H}_3\text{PO}_4/\text{SiO}_2$, and HX and HY zeolites. The acid strength of concentrated heteropoly acid aqueous solutions in terms of Hammett acidity function is higher than that of constituent oxo-acids and ordinary inorganic acids [4–6]. In fact, the three protons of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and four protons of $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ are completely dissociated in dilute aqueous solutions. It has been recently confirmed by calorimetric titration that anhydrous $\text{H}_3\text{PW}_{12}\text{O}_{40}$ in acetonitrile is a superacid [7]. The strong acidity is caused by two main factors: (1) dispersion of the negative charge over many atoms of the polyanion and (2) the fact that the negative charge is less distributed over the outer surface of the polyanion owing

to the double-bond character of the $\text{M}=\text{O}_t$ bond, which polarises the negative charge of O_t to M [8]. In the course of this manuscript, the term ‘polyanion’, which referred to phosphotungstic and silicotungstic acid, will be also expressed with the term ‘Keggin unit’. Keggin was the first scientist to determine the structure of $[\text{PW}_{12}\text{O}_{40}]^{3-}$ using X-ray analysis [9]. The acidity of the solutions of heteropoly acids is reflected on their proton conductivity which is of the same order of magnitude as that of ordinary mineral acids. Heteropoly acids also show high proton conductivity when they are in crystalline forms with determined numbers of water molecules in their structure [10–12]. Proton conductivities of 0.17 and 0.18 S cm^{-1} were measured by Nakamura et al. [10], respectively, for the phosphomolibdic and phosphotungstic acid containing in their structures 29 water molecules of crystallisation. The proton conductivities of the heteropoly acids in this solid form are higher than those of others known solid conductors. These reasons and others as, for example, the high cost of the membranes used in the actual polymer electrolyte fuel cells (PEFC), led our research activity to investigate some compounds of the heteropoly

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acid family as new solid electrolytes in low-temperature fuel cells [1–3].

In spite of the very promising initial activity results in fuel cells, obtained by preliminary experiments using solid heteropoly acid, the electrolyte dissolved in the water formed by the electrochemical process of current generation [2]. Consequently, the cell leaked some dissolved acid and performance decayed. To overcome the problem of electrolyte dissolution and the consequent short lifetime of the fuel cell, it was believed interesting to investigate the possibility of blocking the heteropoly acid in a host material in such a way that it would maintain high proton conductivity of the original electrolyte [13,14].

The process of immobilisation of a soluble compound in organic or inorganic material can be classified in one of these three categories: physisorption, chemical attachment and entrapment. The physisorption process, consisting normally in the impregnation of the soluble agent in a pre-formed material, does not generally result in stable final materials. In fact, the immobilised agent often leaches or desorbs from the surface [2]. The process of immobilisation by chemical attachment or entrapment are more convenient because very stable materials can be prepared [13].

Phosphotungstic and silicotungstic acids were chosen as conductive materials, and silica-gel as supporting material, in our investigation. Three different compositions, for each heteropoly acid, consisting in 15, 30 and 45 wt.% of proton conductor on silica gel, were prepared following the method of entrapment. The solid is precipitated in gel form from a homogeneous solution containing the precursor of the supporting material and the proton conductor. Analyses are carried out on the final materials to verify if some chemical bond is formed between the conductor and the support, and subsequent characterisations are made to determine their proton conductivity, crystalline structure and stability. Proton conductivities of the samples were measured at room temperature and at relative humidity ranging between 40 and 90%. X ray diffraction (XRD) analyses were performed on different samples and the spectra were compared with those obtained on pure acids and silica gel. Thermal stability has been investigated by differential thermal analysis (DTA) performed on samples containing 30 wt.% of dodecatungstophosphoric acid and dodecatungstosilic acid supported on silica, on pure acids and on silica. IR spectra of pure acids and of samples with supported acids were recorded in order to reveal possible structural changes of supported heteropoly acids.

2. Experimental

2.1. Preparation of proton-conducting materials

The materials have been prepared by using commercial phosphotungstic and silicotungstic acid and tetraethyl orthosilicate (TEOS). The solid acids, as received, contained

10% of crystallisation water in their structure. These and TEOS (purity 99.999%) were purchased from Aldrich.

The samples of HPAs supported on silica gel were prepared by the sol-gel process using the acid-catalysed condensation [15–17]. Thus, an aqueous solution, containing 8 wt.% of HNO_3 , was added to the mixture of one part of tetraethyl orthosilicate (TEOS) and five parts of ethanol. The mixture was stirred for 3 h and then, under continuous stirring, the HPA was added. The obtained suspension was mixed for another 3 h. The suspension was then dried at room temperature. The obtained solid material was crushed in a mortar to obtain a very fine powder and then further dried at 50°C for 2 h. Three samples having different loadings of acid have been prepared for each heteropoly acid. The samples containing 15, 30 and 45 wt.% of phosphotungstic acid on silica will be indicated in the text as PWA15, PWA30 and PWA45 and those containing 15, 30 and 45 wt.% of silicotungstic acid on silica as SWA15, SWA30 and SWA45.

2.2. Characterisation of proton-conducting materials

Proton conductivities of compacted powders were measured at 25°C by locating the samples in a cell with a geometry designed for this purpose. This consisted in a cylinder made of insulating material fixed at a base plane made of graphite and a small piston also made of graphite. The scheme of the cell is shown in Fig. 1. The conductive material, in form of disk, was placed into the cylinder on the base plane. Two disks of expanded graphite were located on the two sides of the sample to lower the resistance contact between the conductive material and the graphite. The graphite piston and the base plane were connected through copper wires with universal bridge operating at 1 kHz of frequency. Before the resistance was measured, the samples were kept for 2 h in atmosphere at controlled humidity. The measurements were carried out at

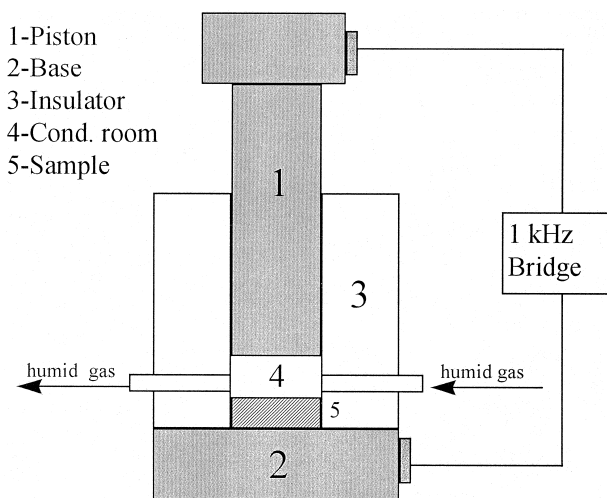


Fig. 1. Scheme of the apparatus used for the conductivity measurements.

Table 1

Proton conductivity values of samples containing different amounts of heteropoly acid in the silica-gel matrix

Sample	Proton conductivity measured at 25°C and different relative humidities					
	40%	50%	60%	70%	80%	90%
PWA15	7.7×10^{-5}	1.0×10^{-4}	1.1×10^{-4}	1.3×10^{-4}	1.5×10^{-4}	2.1×10^{-4}
PWA30	1.8×10^{-4}	2.6×10^{-4}	2.8×10^{-4}	3.4×10^{-4}	3.3×10^{-4}	4.5×10^{-4}
PWA45	9.2×10^{-4}	1.5×10^{-3}	1.4×10^{-3}	1.25×10^{-4}	2.1×10^{-3}	3.2×10^{-3}
SWA15	9.7×10^{-5}	1.3×10^{-4}	1.5×10^{-4}	1.8×10^{-4}	2.1×10^{-4}	2.5×10^{-4}
SWA30	2.0×10^{-4}	3.1×10^{-4}	4.0×10^{-4}	4.3×10^{-4}	5.0×10^{-4}	5.9×10^{-4}
SWA45	4.4×10^{-4}	7.1×10^{-4}	8.0×10^{-4}	1.1×10^{-3}	1.5×10^{-3}	2.0×10^{-3}

relative humidities ranging from 40 to 90%. During the measurements, a pressure of 10 MPa was imposed on the samples using a hydraulic press. The values of resistance registered at the bridge were corrected for the resistance of the connecting wires. Thickness of samples was measured at the end of conductive measurements subtracting from the sandwich containing the solid electrolyte the thickness of the two terminal graphite disks; thickness and geometric area were used to calculate the specific conductivity of the materials. The thicknesses of different samples were in the range 0.09–0.12 cm. Experimental data of conductivity have been reported in form of specific conductivity. No redox reactions occurred at the interface electrolyte/graphite electrode during the conductive measurements.

X-ray powder diffractograms were scanned on samples of silica gel, silica gel containing different amounts of phosphotungstic and silicotungstic acids and on pure heteropoly acids. Analyses were carried out with a Phillips X-Pert diffractometer using a Cu-K α radiation and operating at 40 kV and 30 mA. The diffractometer consisted of a PW1830HT—generator and a PW 3710 control unit which was controlled by a PC computer equipped with Phillips PC-APD software. Continuous scans were collected by using a Bragg–Brentano para-focusing optical system. The X-ray diffraction patterns were collected with a scan rate of 0.5°/min.

Differential thermal analyses were performed on the samples in the range of temperature from 40 to 550°C to take information on the thermal stability and water desorption. Measurements were performed using a Netzsch STA

409 instrument in combination with temperature programmer Netzsch 410 and data acquisition system 414 used with personal computer HP 9000 series 300. The samples were flushed with air at a flow rate of 50 ml/min and analysed at scanning rate of 10°C/min.

IR spectra of powdered samples pressed with dried KBr into discs were recorded in the range of wave numbers 1300 to 400 cm⁻¹ with resolution of 4 cm⁻¹ using FT-IR Perkin Elmer 2000 System to reveal the presence of X-ray amorphous species of supported heteropoly acids and their structural changes.

3. Results and discussion

The results of proton conductivity measurements obtained for the two series of phosphotungstic and silicotungstic acid supported on silica gel samples, conditioned for 2 h in atmospheres of controlled relative humidity, are reported in Table 1 and presented in Figs. 2 and 3. An increase of proton conductivity is observed, for both series of samples, when both the relative humidity and the acid loading in the samples are increased. Relative humidity influences the amount of water which occupies the reticular positions in the crystal structure of the heteropoly acid and also the amount of water adsorbed on the silica gel. Both of these enhance the transport of protons through the material. In fact, both the amount of water molecules that are placed in the reticular structure of heteropoly acid and of those adsorbed in the pores of silica gel generate hydrogen-bonded water (guest) substructure in which the

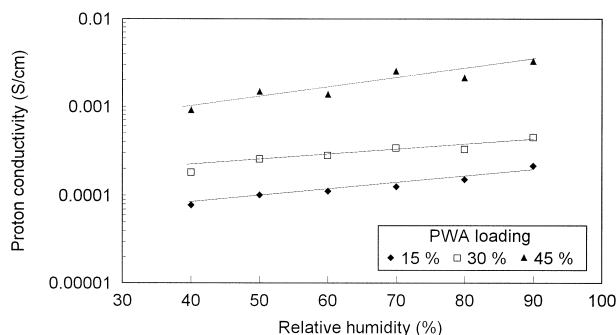


Fig. 2. Proton conductivities of samples at different content of PWA, measured at 25°C and relative humidity ranging from 40 to 90%.

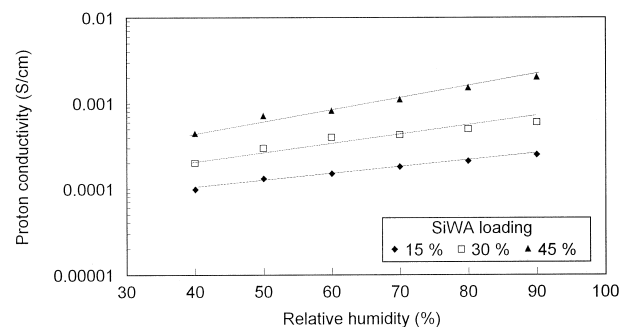


Fig. 3. Proton conductivities of samples at different content of SiWA, measured at 25°C and relative humidity ranging from 40 to 90%.

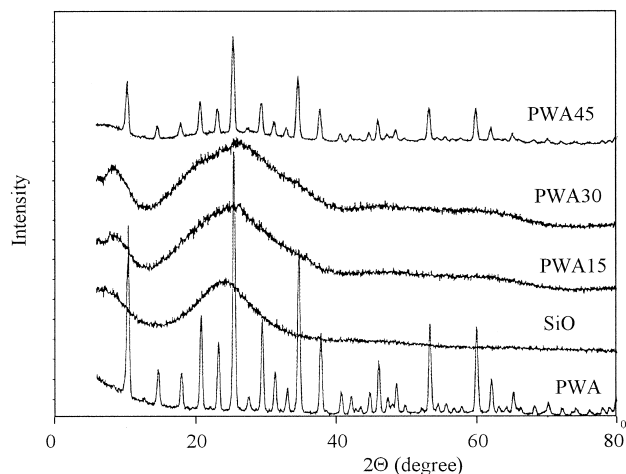


Fig. 4. X-ray diffraction patterns of samples of SiO_2 , PWA and silica with different content of PWA.

protons move (propagate). The increase of proton conductivity as a function of the relative humidity is observed for all the samples. At the same relative humidity, the samples that contain higher loading of HPA exhibit higher proton conductivity. This obviously depended on increasing proton concentration in the materials. For the same reason, the samples SWA15 and SWA30 containing the acid SiWA, which has four protons in its molecule, had higher conductivities with respect to the equivalent samples containing the acid PWA, which has three protons in its molecule. On the contrary, it was observed that, on increasing the loading of acid in silica structure from 30% to 45%, the conductivity was higher in the sample PWA45 than in the sample SWA45. This is due to the fact that in the former sample, part of the phosphotungstic acid is not bonded to the silica structure, with a consequent higher degree of mobility is available for the proton transport, as evidenced by the XRD analyses.

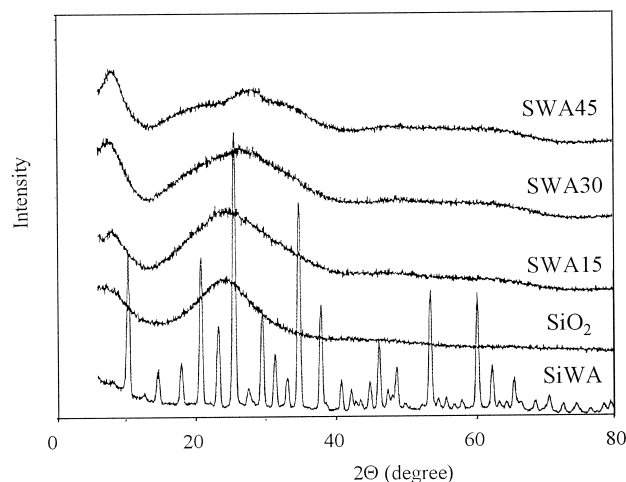


Fig. 5. X-ray diffraction patterns of samples of SiO_2 , SiWA and silica with different contents of SiWA.

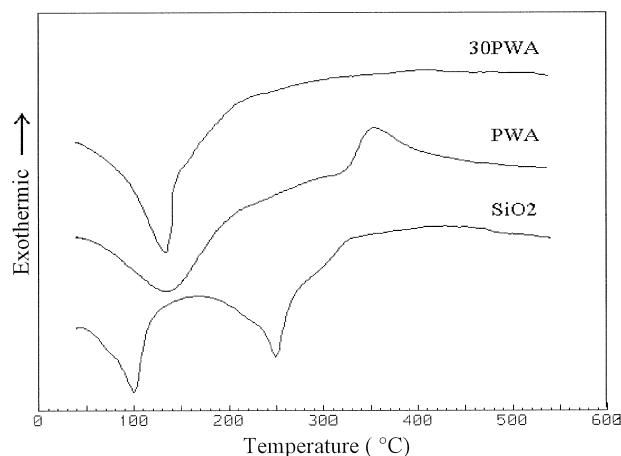


Fig. 6. Differential thermal analyses of silica, PWA and PWA30 samples.

The XRD patterns of SiO_2 bulk, PWA bulk and SiO_2 containing 15, 30 and 45 wt.% of PWA are reported in Fig. 4. Corresponding XRD patterns for SiWA are reported on Fig. 5. No diffraction peaks characteristic for PWA appear in the spectra of materials containing 15 and 30% of the heteropoly acid. This is a consequence of finely dispersed HPAs in the porous structure of silica and the composite behaves as X-ray amorphous. The XRD pattern for material with 45% of PWA shows all the characteristic peaks of the heteropoly acid, thus indicating that part of the acid is in excess, and forms big enough crystallites in the larger pores of silica and on its outer surface to give a diffraction pattern. The X-ray powder diffractograms of the samples containing 15, 30 and 45% of silicotungstic acid on silica gel reveal no characteristic peaks of silicotungstic acid. The silicotungstic acid in these samples is also X-ray amorphous. This demonstrates that the interaction between α -Keggin units of $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ and silica surface within the pores is stronger than interactions between such units of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and silica surface.

The differential thermal analyses have been carried out on silica bulk, pure acids and on the samples PWA30 and

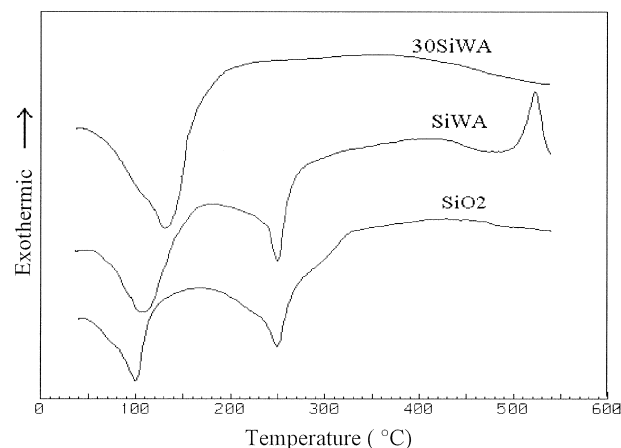


Fig. 7. Differential thermal analyses of silica, SiWA and SWA30 samples.

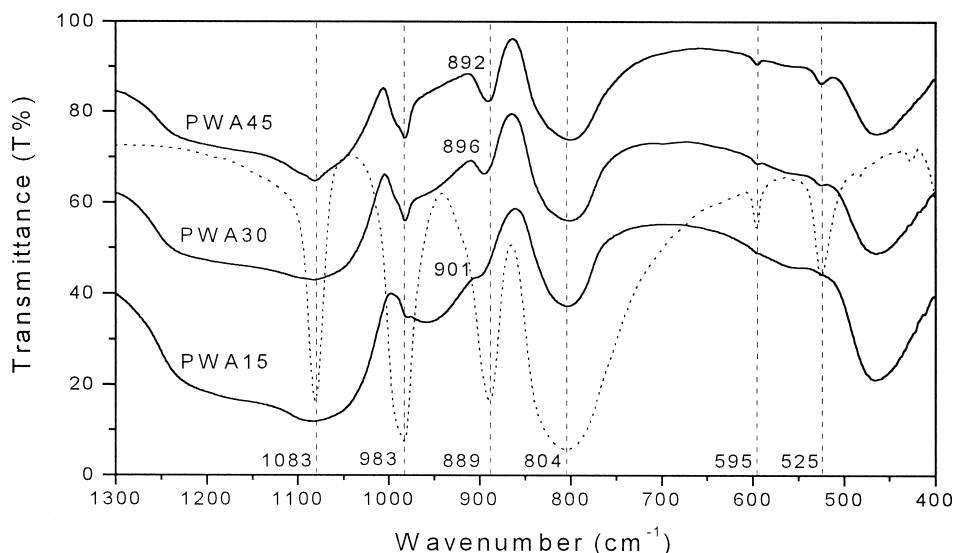


Fig. 8. IR spectra of pure PWA (dotted line) and of PWA supported on silica. Spectra of samples PWA15, PWA30 and PWA45 are shifted by +10, +40 and +50 units of T , respectively.

SWA30. The results of these analyses are reported in Figs. 6 and 7, respectively. All samples exhibit loss of loosely bound water. The peak of this process corresponds to 140°C for the silica bulk, 110°C for the silicotungstic acid, 90°C for phosphotungstic acid, 130°C for SWA30 sample and 120°C for PWA30 sample, respectively. Further loss of crystal water is evident at 240°C for phosphotungstic acid and at 250°C for silicotungstic acid. The observed loss of water at higher temperature of heteropoly acids supported on silica with respect to the only heteropoly acids will have probably a beneficial effect on proton conductiv-

ity above 100°C. This topic will be treated in a future work. The exothermic transformation at 520°C on DTA curve of silicotungstic acid is due to its crystal structure collapse. No such peak is visible on the DTA curve of phosphotungstic acid. No endothermic peaks due to desorption of crystal water from PWA30 and SWA30 samples and no exothermic peaks due to the acid decomposition in these samples have been recorded in the temperature range from 200°C to 550°C. This means that the secondary structure of water between α -Keggin units in the clathrates of HPAs, characteristic for pure acids, has been destroyed

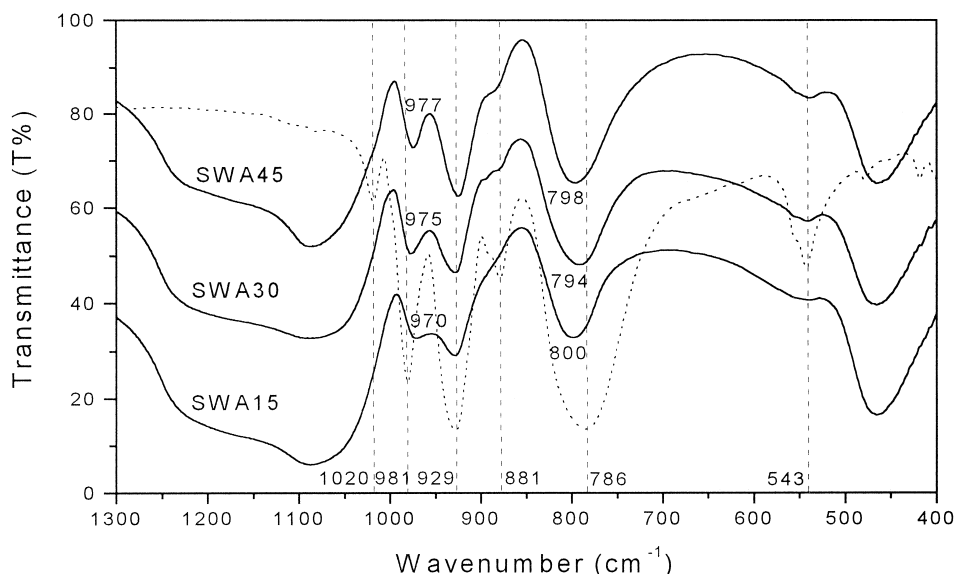


Fig. 9. IR spectra of pure SiWA (dotted line) and of SiWA supported on silica. Spectra of samples SWA30 and SWA45 are shifted by +30 and +40 units of T , respectively.

and replaced with interactions of individual α -Keggin units with silica. The thermal stability of α -Keggin units is thus substantially increased.

The IR spectra of pure PWA and SiWA and of their different amounts supported on silica are presented in Figs. 8 and 9, respectively. They demonstrate that all the bands representing fingerprints of the α -Keggin units structure of both acids are preserved also in the spectra of supported acids. This corroborates the picture that individual α -Keggin units interact with silica surface. Detailed inspection of the bands in the range 1100–500 cm^{-1} characteristic for the structure of both pure acids and acids supported on silica reveals that acids interact with silica in a different manner. The band positions (cm^{-1}) in the spectrum of pure PWA are characteristic for $\alpha\text{-H}_3\text{PW}_{12}\text{O}_{40} \cdot 6\text{H}_2\text{O}$ [18–20]: 1079(s), 984(s), 889(s), 806(vs), 597(w), 525(m). The positions in the spectrum of pure SiWA are characteristic for $\alpha\text{-H}_4\text{SiW}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$ [18]: 1019(w), 981(s), 927(vs), 880(m), 785(vs), 555(sh), 542(m), 476(w). In spectra of the samples with different amounts of PWA supported on silica, one can observe a small, but progressive shift of ν_{as} ($\text{W-O}_b\text{-W}$) band from 889 cm^{-1} in pure PWA to 901 cm^{-1} in the sample with 15 wt.% PWA supported on silica. The frequency shift of about 12 cm^{-1} reveals that the α -Keggin unit of PWA interacts with the surface of silica mostly through corner-shared oxygens (O_b). The picture is different in the spectra of the samples with different amounts of SiWA supported on silica. Here the band of ν_{as} ($\text{W-O}_b\text{-W}$) at 880 cm^{-1} observed in the spectrum of pure SiWA nearly disappears in the spectra of supported samples. Also, the band of ν_{as} ($\text{W-O}_c\text{-W}$) shifts from 786 cm^{-1} in pure SiWA to 800 cm^{-1} in 15 wt.% SiWA supported on silica, and the band of ν_{as} (W-O_d) from 981 in pure SiWA to 970 cm^{-1} in 15 wt.% SiWA supported on silica. Shifts in the spectra of supported SiWA samples led to conclusion that SiWA interacts with silica stronger than PWA. This is the consequence of different stability effects in HPAs when the central cation is substituted [21].

4. Conclusions

The samples of $\alpha\text{-H}_3\text{PW}_{12}\text{O}_{40}$ (PWA) and $\alpha\text{-H}_4\text{SiW}_{12}\text{O}_{40}$ (SiWA) supported on silica prepared by sol–gel procedure have demonstrated that up to 30 wt.% of PWA and up to 45 wt.% of SiWA can be entrapped within the silica structure and that their thermal stability is substantially enhanced.

Powder XRD, IR and DTA analyses of supported HPAs reveal that the usual clathrate structure formed by α -Keggin units interconnected through hydrogen-bonded water molecules in pure acids is replaced by interaction of individual α -Keggin units with silica surface within pores.

This interaction is stronger in the case of SiWA than in the case of PWA. Proton conductivities of samples containing 15 and 30 wt.% of SiWA were higher with respect to the corresponding samples containing PWA, because the former acid has more protons in the molecule than the latter one. However, the sample containing 45 wt.% of SiWA has a lower conductivity with respect to the sample containing 45 wt.% of PWA. This occurs because in the latter sample, some parts of the acid have no interaction with the silica-gel, and thus, a higher number of mobile protons can move in the material.

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