



Synthesis, characterization and catalytic evaluation of $H_3PW_{12}O_{40}$ included in acrylic acid/acrylamide polymer for the selective oxidation of sulfides



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ABSTRACT

A series of hybrid materials (SAPTPA) based on tungstophosphoric acid $H_3PW_{12}O_{40}$ (TPA) included in acrylic acid/acrylamide polymer (SAP) were synthesized. The samples were characterized by FT-IR, XRD, ^{31}P MAS-NMR, DTA-TGA, and the acidic properties were determined by means of potentiometric titration with *n*-butylamine. Materials with 10, 20, 30 and 40% (w/w) TPA content in the solid (SAPTPA10, SAPTPA20, SAPTPA30 and SAPTPA40, respectively) were prepared by impregnating the polymer with tungstophosphoric acid water solutions. According to FT-IR and ^{31}P MAS-NMR studies, the main species present in the samples is the $[PW_{12}O_{40}]^{3-}$ anion, which was partially transformed into $[P_2W_{21}O_{71}]^{6-}$ and $[PW_{11}O_{39}]^{7-}$ anions during the synthesis and drying steps.

Taking into account XRD results, these species are highly dispersed in the polymer matrix or appear as noncrystalline phases. The DTA-TGA results show that SAPTPA materials did not undergo any remarkable chemical changes up to 200 °C. Additionally, the SAPTPA materials showed strong acid sites whose number increased as the TPA content in them was higher.

The materials obtained by impregnation of TPA onto the polymer matrix present suitable physico-chemical properties to be used as catalysts in the selective oxidation of sulfides to the corresponding sulfoxide/sulfone using acetonitrile as solvent and H_2O_2 35% w/v as a clean oxidant.

The SAPTPA40 catalyst was appropriate for the selective sulfide oxidation in heterogeneous conditions and can be reused without significant loss of its catalytic activity. A convenient and selective procedure for oxidizing sulfides to sulfoxides or sulfones by varying the H_2O_2 /substrate ratio and the temperature was found.

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1. Introduction

Green chemistry is becoming a wide field in chemistry in general and in organic synthesis in particular. Among the 12 principles of green chemistry, one of the main subjects is the use of a green, recoverable and reusable heterogeneous catalyst [1]. The need for greener techniques leads to using different environmentally friendly reaction conditions; among them, the replacement of pollutant inorganic acid catalysts, such as sulfuric or hydrochloric acids by reusable solid acids and the use of room temperature avoiding media heating, are still very necessary. The application of solid acids

in organic transformation has an important role because they have many advantages, such as ease of handling, decreased plant corrosion, and more environmentally safe waste disposal procedures [2].

Catalysis using heteropolyacids and related compounds (HPC) is a field of increasing importance worldwide. Numerous developments are being carried out in industrial processes and basic research. In view of their remarkable catalytic properties, HPC are applied both in bulk or supported form, and homogeneous or heterogeneous catalysis is possible. The HPC with Keggin structure are polynuclear complexes mainly composed of molybdenum, tungsten, or vanadium as polyatoms (M), and phosphorus, silicon, or germanium as central atom or heteroatom (X). The Keggin structure is formed by a central tetrahedron XO_4 , surrounded by 12 octahedra MO_6 . They could be either multielectron oxidants or strong acids, with an acid strength higher than that of the classical acids

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[3–5]. Recently, our research group reported green catalytic acid and oxidation procedures using Keggin HPC [6–10].

Polymeric materials are a new kind of interesting supports that can be used when the catalysts are employed in reactions carried out at relatively low temperatures, due to the relatively low thermal stability of some of them [11,12]. The superporous polymers are hydrogels that have a high capacity of absorption and water retention. These materials are composed of cross-linked polymers in the form of three-dimensional network [13]. The capacity of absorption is related to the flexibility of the network, the presence of hydrophilic groups ($-\text{COOH}$, $-\text{CONH}_2$, $-\text{OH}$, $-\text{SO}_3\text{H}$), the degree of cross-linking and the porosity of the polymer [12]. There is a large variety of hydrogels, so they can be used in many applications, such as surgery, biotechnology, medicine, agriculture, and in pharmacy for controlled drug release [14,15].

In the present work a polymer (SAP), composed of acrylic acid (AA) and acrylamide (AM) as monomers, *N,N*-methylenebisacrylamide (MBA) as a cross-linking agent and ammonium persulfate (APS) as a polymerization initiator [13], was synthesized and used as support. The hybrid materials were obtained by SAP impregnation with tungstophosphoric acid water solutions and were characterized by different physicochemical techniques.

On the other hand, sulfoxides and sulfones are important intermediates in organic chemistry due to their application in fundamental research and other extended usage, especially because chiral sulfoxides are versatile intermediates for the preparation of biologically and medically important products [16]. Omeprazole and the pesticide Fipronil are two typical examples of the extensive application of these intermediates in pharmaceutical and fine chemical industries [16]. The most widely used method for the preparation of sulfoxides and sulfones is the oxidation of the corresponding sulfide. For this reason, sulfide oxidation to sulfoxides and sulfones has been the subject of many studies, and several methods for this transformation have been reported in the literature [17–22]. Some traditional oxidizing reagents used for this purpose include nitric acid, trifluoroperacetic acid, hydrogen peroxide, nitromethane solution in dilute $\text{NO}_3\text{H}/\text{H}_2\text{SO}_4$, iodic acid, other hypervalent iodine reagents, and CAN (cerium ammonium nitrate), among others [23–26].

This paper reports on the preparation and characterization of TPA included in superporous polymers (SAPTPA) to be used as catalysts in the heterogeneous oxidation of dibenzylsulfide to the corresponding sulfoxide and/or sulfone, with aqueous hydrogen peroxide. The selective oxidation reaction of dibenzylsulfide in homogeneous conditions using TPA was also studied for comparative purposes. For other sulfides with different molecular structure, the oxidation with SAPTPA was also investigated in order to establish a correlation between the structure of the sulfide and its oxidation easiness.

2. Experimental

2.1. Synthesis of the superporous polymer (SAP)

The superporous polymer was synthesized according to the method reported by Dorkoosha et al. [13]. For a typical synthesis of SAP, the following substances were added subsequently into a test tube at ambient temperature: 300 μL acrylamide 50%, 200 μL acrylic acid 50%, 70 μL *N,N*-methylenebisacrylamide 2.5%, 25 μL ammonium persulfate 20%, 0.25 μL *N,N,N',N'*-tetramethylethylenediamine 20% and 100 mg of sodium bicarbonate. After the addition of each solution, the reaction mixture was vigorously shaken. The polymerization occurs approximately 10 min after the addition of all the components.

2.2. Supported catalyst preparation based on tungstophosphoric acid (TPA)

The hybrid materials were synthesized by impregnation of dehydrated superporous polymer (SAP) previously obtained with aqueous solutions of tungstophosphoric acid.

The impregnation was conducted by contacting 1 g of dehydrated SAP with 10 mL of a solution of $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 23\text{H}_2\text{O}$ (Fluka p.a.) (TPA), until complete absorption of the SAP spheres. The concentration of TPA solution was varied to obtain concentrations of 10, 20, 30 and 40% of TPA weight by weight in the resultant material. Finally, the materials were dried at ambient temperature until constant weight. The samples will be denominated SAPTPA10, SAPTPA20, SAPTPA30, SAPTPA40, respectively.

The TPA content in the SAPTPA samples was estimated as the difference between the W amount contained in the tungstophosphoric acid water solution originally used for the impregnation and the amount of W that remained in the beaker after removing the dried samples. The amount of W in the water solutions was determined by atomic absorption spectrometry using a Varian AA Model 240 spectrophotometer. The calibration curve method was used with standards prepared in the laboratory. The analyses were carried out at a wavelength of 254.9 nm, bandwidth 0.3 nm, lamp current 15 mA, phototube amplification 800 V, burner height 4 mm, and acetylene–nitrous oxide flame (11:14). The results obtained reveal that the TPA contents in the samples were 9.8, 19.6, 29.5, and 39.4% (w/w) for SAPTPA10, SAPTPA20, SAPTPA30, SAPTPA40, respectively.

2.3. Catalyst characterization

2.3.1. FT-IR analysis

FT-IR spectra of supports and catalysts were obtained in the wavenumber range 400–4000 cm^{-1} using a Bruker IFS 66 FTIR spectrometer.

2.3.2. XRD analysis

Powder XRD patterns of the studied samples that had been analyzed by FT-IR were recorded. The equipment used is a Philips PW-1732 with built-in recorder, using $\text{Cu K}\alpha$ radiation, nickel filter, 20 mA and 40 kV in the high voltage source, and scanning angle between 5 and 608 of 2θ at a scanning rate of 18 per min.

2.3.3. ^{31}P nuclear magnetic resonance (^{31}P -NMR)

The ^{31}P magic angle spinning–nuclear magnetic resonance (^{31}P MAS-NMR) spectra of the samples were recorded with Bruker Avance II equipment, using the CP/MAS ^1H – ^{31}P technique. A sample holder of 4 mm diameter and 10 mm in height was employed, using 5 ms pulses, a repetition time of 4 s, and working at a frequency of 121.496 MHz for ^{31}P at room temperature. The spin rate was 8 kHz, and several hundred pulse responses were collected. Phosphoric acid 85% was employed as external reference.

2.3.4. TGA–DTA

The TGA–DTA measurements of the solids were carried out using a Shimadzu DT 50 thermal analyzer. The thermogravimetric and differential thermal analyses were performed under argon or nitrogen respectively, using 25–50 mg samples and a heating rate of 10 $^\circ\text{C}/\text{min}$. The studied temperature range was 20–600 $^\circ\text{C}$.

2.3.5. Acidity measurements

The acidity of the solid samples was measured by means of potentiometric titration. The solid (0.05 g) was suspended in acetonitrile (Merck), and stirred for 3 h. The suspension was then titrated with 0.05 N *n*-butylamine (Carlo Erba) in acetonitrile using

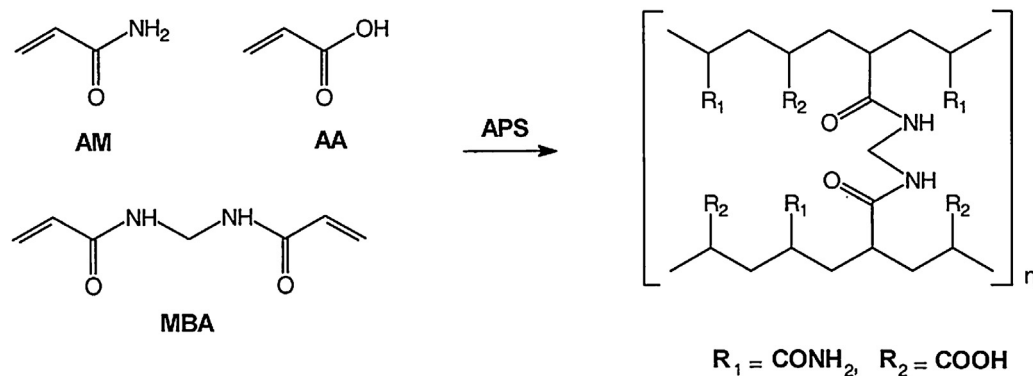


Fig. 1. Synthesis of SAP using acrylic acid (AA) and acrylamide (AM) as starting monomers, *N,N'*-methylenebisacrylamide (MBA) as a cross-linking agent and ammonium persulfate as polymerization initiator.

Metrohm 794 Basic Titrino apparatus with a double junction electrode.

2.4. Catalytic test

2.4.1. General remarks

All reagents were purchased from Merck and Aldrich and used without further purification. The product distribution was quantified by GC, and reactions were also monitored by thin layer chromatography analysis. The products were characterized by the determination of the mass spectra. All yields refer to pure products

2.4.2. General test for the oxidation

Sulfide oxidation studies were performed with dibenzylsulfide as the model reagent and with 35% w/v aq. H_2O_2 as oxidant in the selected solvent, in a batch reactor under magnetic stirring at different temperatures, using the bulk and synthesized catalyst in homogeneous or heterogeneous conditions, respectively. The oxidation of dibenzylsulfide was typically carried out by heating a solution of 1 mmol (214 mg) of the substrate and 1 mmol% of bulk or supported catalyst in 5 mL of solvent, at the experiment temperatures (see tables). A variable amount of aqueous H_2O_2 35% w/v was used. The sample was collected from the mixture at time intervals. About 20 μL of the reaction mixture was taken for each sample, which was then diluted in a mixture of $\text{H}_2\text{O}-\text{CH}_2\text{Cl}_2$ (2 mL). The CH_2Cl_2 layer was shaken with anhydrous Na_2SO_4 . The reaction products were analyzed by gas chromatography using a Shimadzu 2010. The percentages of each compound in the reaction mixture were directly estimated from the corresponding chromatographic peak areas. The products were all known compounds and were identified by GC–MS using PerkinElmer equipment.

2.4.3. Catalyst reuse

Stability tests of the SAPTPA40 catalyst were carried out running three consecutive experiments, under the same reaction conditions. After each test, the catalyst was separated from the reaction mixture by filtration, washed with acetonitrile (2×2 mL), dried under vacuum, and then reused.

2.4.4. Electron densities of sulfur atom determination

The densities of the sulfur atoms in the sulfide were determined after optimization of their conformation. The conformations of the compounds were drawn by means of the “model build” module available in HyperChem 5.0. Each molecular structure was firstly pre-optimized with the Molecular Mechanics Force Field (MM^*) procedure, and the resulting geometry was further refined by means of the semiempirical method PM3 (Parametric Method-3). A gradient norm limit of 0.01 kcal \AA^{-1} was chosen.

2.4.5. Electron impact mass spectra of the representative compound

2.4.5.1. Dibenzylsulfoxide. Colorless solid. m.p.: 129–130 °C. EM, m/z (relative intensity): 230 (M^+) (5%), 181 (2%), 180 (3%), 91 (100%), 65 (9%), 39 (3%).

2.4.5.2. Benzyl phenyl sulfoxide. Colorless solid. m.p.: 121–123 °C. EM, m/z (relative intensity): 216 (M^+) (10%), 182 (16%), 165 (2%), 125 (5%), 91 (100%), 77 (11%), 65 (18%).

2.4.5.3. Diphenylsulfoxide. Colorless solid. m.p.: 69–71 °C. EM, m/z (relative intensity): 202 (M^+) (83%), 185 (18%), 154 (73%), 109 (90%), 97 (48%), 77 (78%), 65 (59%), 51 (100%), 39 (32%).

2.4.5.4. Benzyl phenyl sulfone. Colorless solid. m.p.: 148–149 °C. EM, m/z (relative intensity): 232 (M^+ , 4%), 167 (2%), 165 (2%), 152 (15%), 91 (100%), 77 (11%), 65 (17%), 51 (13%).

2.4.5.5. Dibenzyl sulfone. Colorless solid. m.p.: 127–129 °C. EM, m/z (relative intensity): 218 (M^+ , 36%), 153 (7%), 125 (100%), 97 (12%), 77 (37%), 51 (23%).

3. Results and discussion

3.1. Catalysis characterization

Fig. 1 shows the chemical structure of the synthesized superabsorbent polymer. The groups $-\text{CONH}_2$ and $=\text{NH}$ present in the SAP can be protonated in the presence of a strong acid such as TPA, the existence of electrostatic interaction of these groups and the anions $[\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}]^{x-}$ (where $1 < x \leq 3$) being possible. It has been reported that proton transfer from TPA to the amine group, resulting in an electrostatic bond between $-\text{NH}_3^+$ and $[\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}]^{x-}$, is responsible for the efficient immobilization of the heteropolyanion [27,28].

The FT-IR spectrum of TPA (**Fig. 2**) shows bands at 1081, 982, 888, 793, 595, and 524 cm^{-1} , which are in agreement with those reported in the literature for the $\text{H}_3\text{PW}_{12}\text{O}_{40}$ acid [29]. The first five bands are assigned to the stretching vibrations $\text{P}-\text{O}_a$, $\text{W}-\text{O}_d$, $\text{W}-\text{O}_c-\text{W}$, $\text{W}-\text{O}_c-\text{W}$, and to the bending vibration $\text{O}_a-\text{P}-\text{O}_a$, respectively. The subscripts indicate oxygen bridging W and the P heteroatom (a), corner sharing (b) and edge sharing (c) oxygen belonging to WO_6 octahedra, and terminal oxygen (d).

The bands assigned to the stretching vibrations $\text{W}-\text{O}_c-\text{W}$, $\text{W}-\text{O}_b-\text{W}$ and $\text{P}-\text{O}_a$ are clearly observed in the spectrum of the sample SAPTPA40 (bands at 802, 891 and 1078 cm^{-1} , respectively), superimposed on the characteristic bands of SAP (**Fig. 2**), while the one corresponding to vibration $\text{W}-\text{O}_d$ appears as a shoulder. In addition,

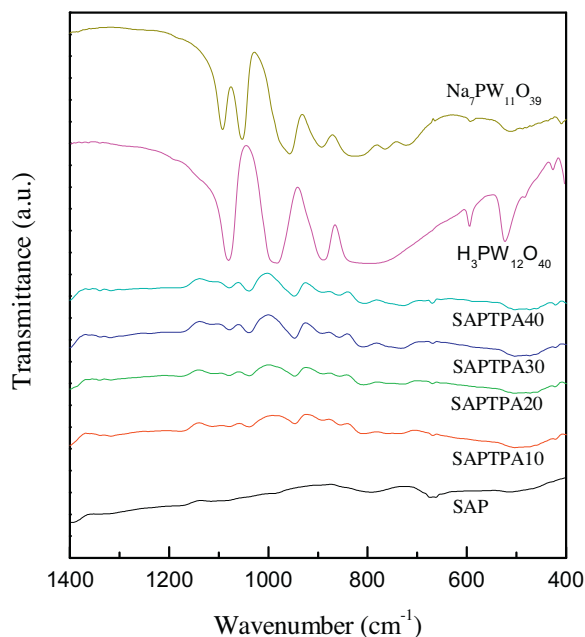


Fig. 2. FT-IR spectra of the samples SAP, SAPTPA10, SAPTPA20, SAPTPA30, SAPTPA40, TPA and $\text{Na}_7[\text{TPA}_{11}\text{O}_{39}]$.

the presence of bands at 856, 949 and 1037 cm^{-1} can be assigned to the formation of the $[\text{PW}_{11}\text{O}_{39}]^{7-}$ lacunary anion, which presents bands at 1100, 1046, 958, 904, 812, and 742 cm^{-1} (Fig. 2), in agreement with the literature [29].

The main FT-IR bands of the dimer $[\text{P}_2\text{W}_{21}\text{O}_{71}]^{6-}$ assigned to the stretching vibrations P-O, W-O, W-O-W appear at wavenumber values similar to those characteristic of the $[\text{PW}_{12}\text{O}_{40}]^{3-}$ anion [30], so their presence cannot be confirmed based on FT-IR results only.

The aforementioned set of bands is also present in the FT-IR spectra of SAPTPA30, SAPTPA20 and SAPTPA10 samples, although their intensity is lower due to a lower TPA content.

The ^{31}P MAS-NMR spectra of SAPTPA10, SAPTPA20, SAPTPA30, and SAPTPA40 samples (Fig. 3) display a wide band with a maximum at around -13.6 ppm , together with a shoulder at -13 ppm . They were attributed to the $[\text{PW}_{12}\text{O}_{40}]^{3-}$ anion and to the $[\text{P}_2\text{W}_{21}\text{O}_{71}]^{6-}$ dimeric species, respectively [31,32]. This technique has not been able to corroborate the presence of lacunary phase. The downfield shift and the increase of the line width observed, compared to the TPA (-15.3 ppm), can be ascribed to the interaction among the anion and the $-\text{CONH}_2$ and $=\text{NH}$ groups present in the SAP. The interaction can be assumed to be of the electrostatic type due to the transfer of protons to $-\text{CONH}_2$ and $=\text{NH}$, similarly to which has been proposed for the interaction with silica and zirconia [33,34].

Taking into account the FT-IR and ^{31}P MAS-NMR results, it can be established that the $[\text{PW}_{12}\text{O}_{40}]^{3-}$ anion is the main species in the samples. However, it was partially transformed

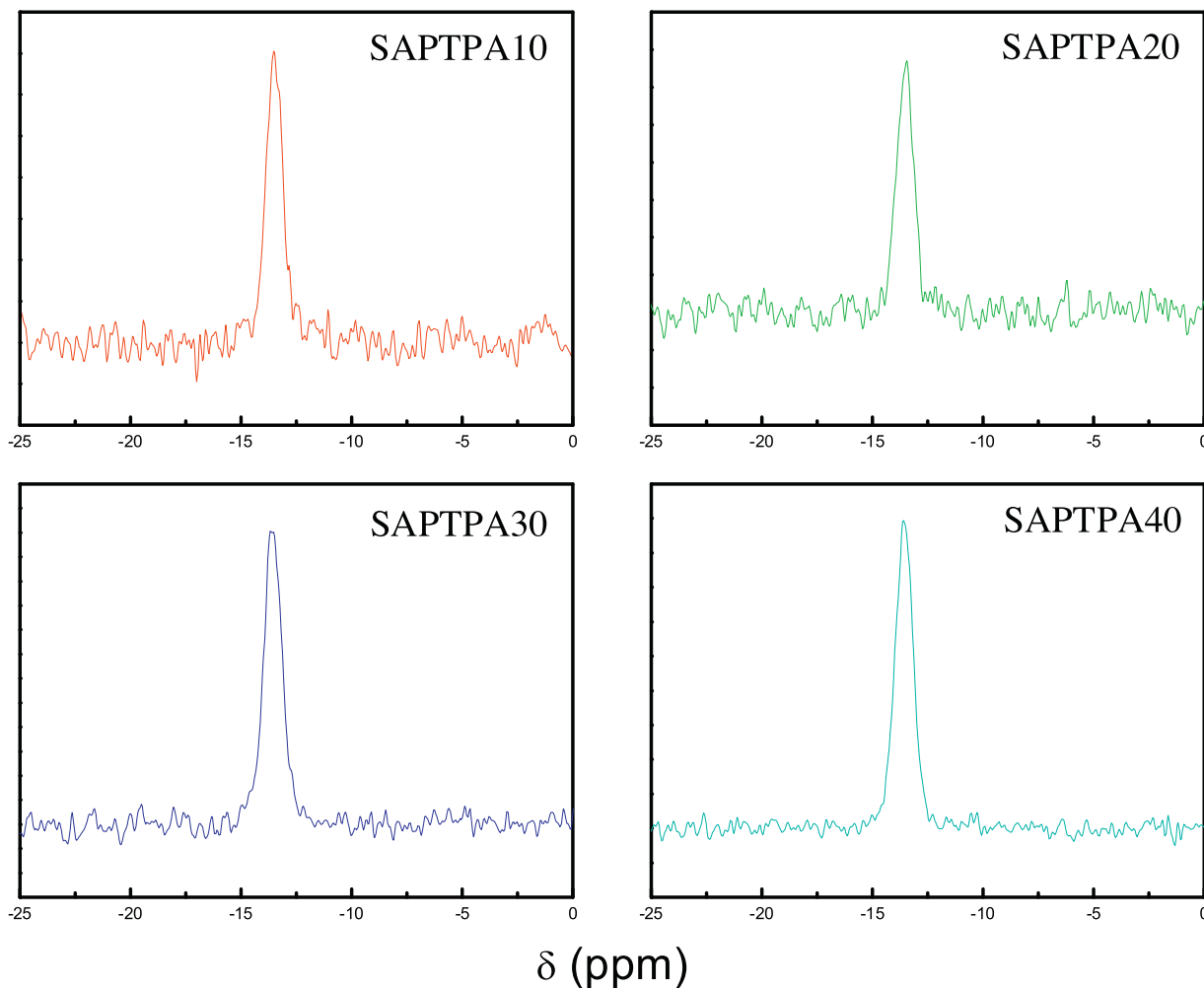


Fig. 3. ^{31}P -NMR of the samples SAP-TPA10, SAP-TPA20, SAP-TPA30 and SAP-TPA40.

into $[P_2W_{21}O_{71}]^{6-}$ and $[PW_{11}O_{39}]^{7-}$ anions during the synthesis and drying steps. The transformation is due to the limited stability range of the $[PW_{12}O_{40}]^{3-}$ anion in solution [35]. Pope suggested that the following transformation scheme: $[PW_{12}O_{40}]^{3-} \rightleftharpoons [P_2W_{21}O_{71}]^{6-} \rightleftharpoons [PW_{11}O_{39}]^{7-}$ occurred when the hydroxyl concentration was increased and it can be considered as a valid path followed by the TPA species during the synthesis of the samples.

The DTA diagram of SAP (Fig. 4) exhibits two endothermic peaks at 68 °C and 138 °C, which are assigned to the elimination of moisture and absorbed water respectively, which may be accompanied by the elimination of monomer residues used in the synthesis [36]. The water release can also originate from the formation of anhydride groups [37]. From the TGA diagram, we estimated the weight loss associated with these eliminations as 0.59% of the initial mass. At temperatures higher than 200 °C, irreversible chemical changes in the SAP take place. The endothermic peak at 238 °C was assigned to the formation of imides (intra- and intermolecular) and nitrile groups from the amide groups of acrylamide, accompanied by the release of water and ammonia, respectively. In the 200–300 °C temperature range the release of carbon dioxide from the decomposition of the anhydride groups has also been reported [38].

Above 300 °C in the DTA diagram appear three endothermic peaks at 322, 387, and 475 °C, which can be assigned to imide decomposition (with liberation of carbon dioxide and water), the polymeric chain rupture (with liberation of acrylic acid) and the formation of long hydrocarbon chains [36,38]. According to TGA

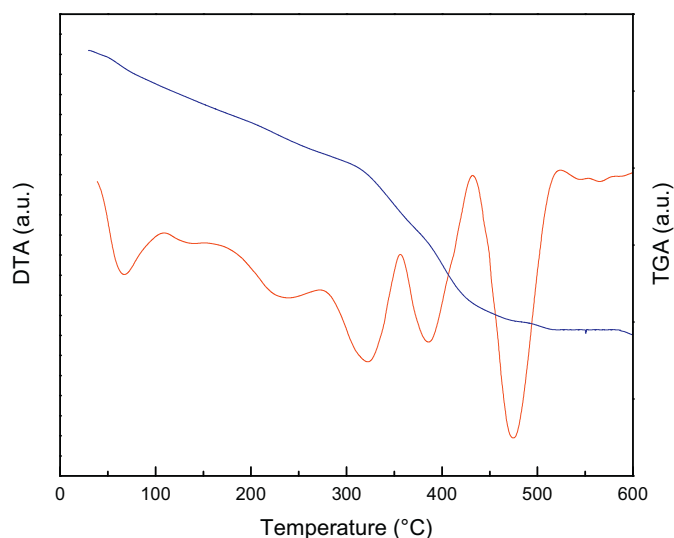


Fig. 4. DTA and TGA diagrams of SAP.

results, the amount of carbonaceous residue obtained at 600 °C corresponds to 22% of the initial weight of SAP.

The TGA diagrams of SAPTPA10, SAPTPA20, SAPTPA30, and SAPTPA40 samples (Fig. 5) show features similar to those of the SAP diagram up to 450 °C. Above this temperature value, an additional weight loss occurs, which shifts to lower temperatures in parallel

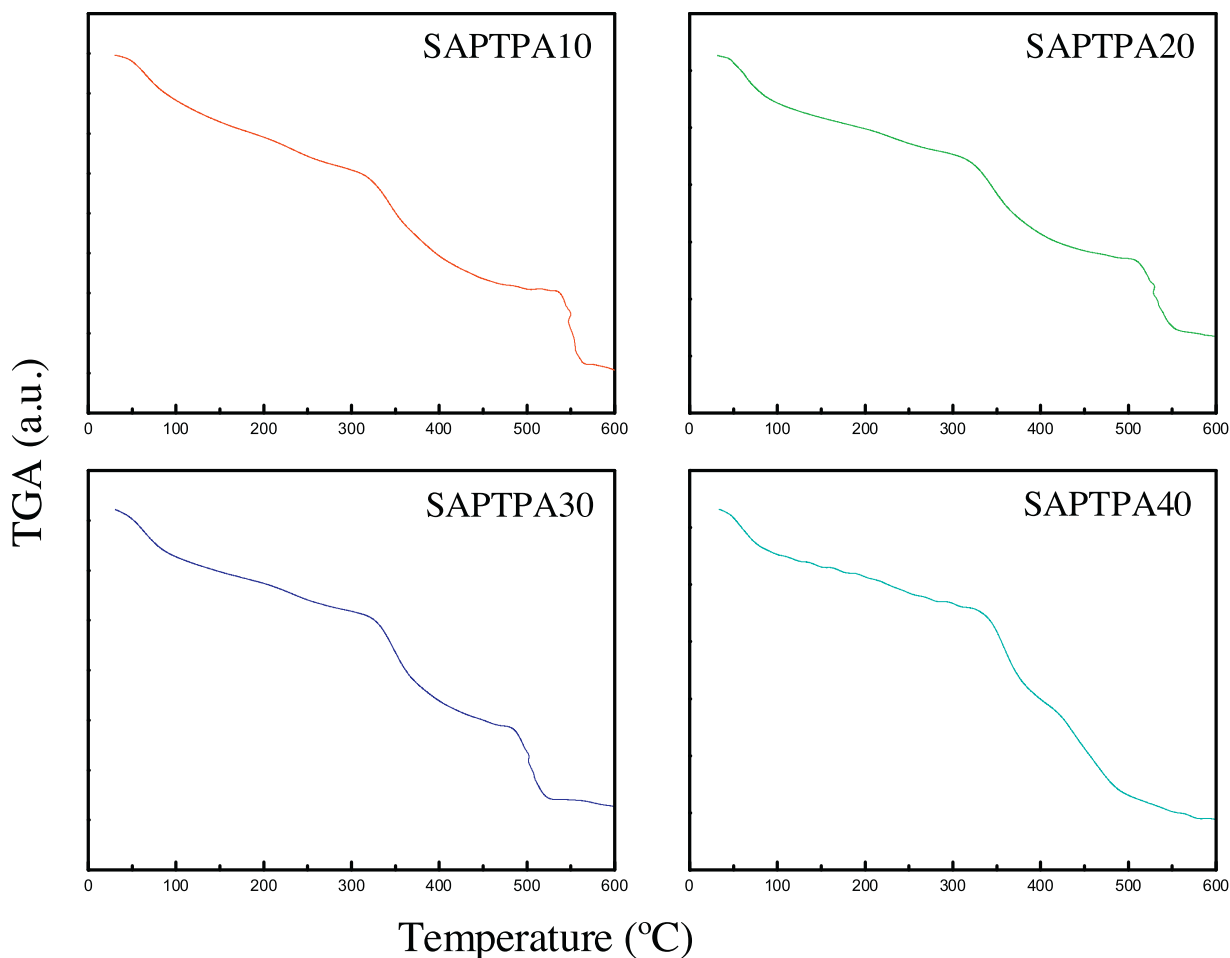


Fig. 5. TGA diagrams of the samples SAP-TPA10, SAP-TPA20, SAP-TPA30 and SAP-TPA40.

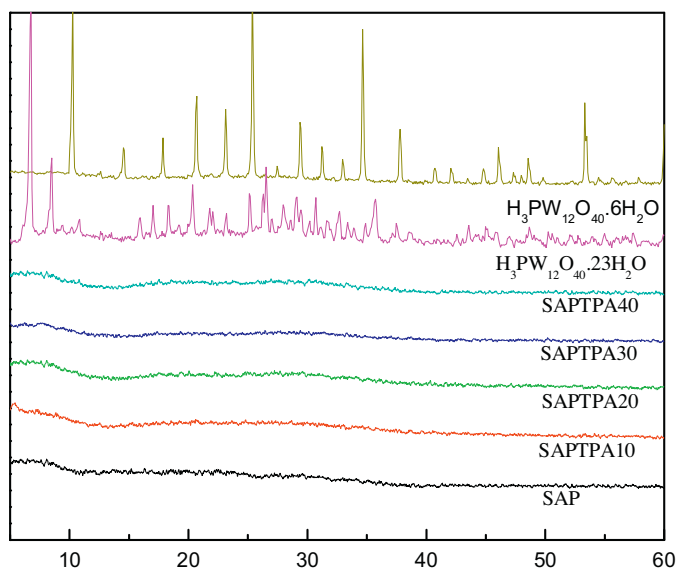


Fig. 6. XRD diagrams of the samples SAP, SAPTPA10, SAPTPA20, SAPTPA30, SAPTPA40 and TPA hydrates.

with the increment of the TPA content. TPA incorporation affects the depolymerization and degradation processes of SAP, as a result of which a reduction of the carbonaceous residue takes place.

DTA diagrams of the SAP samples impregnated with TPA present similar features to those of the polymer. However, the endothermic peaks above 200 °C, assigned to the chemical transformations and subsequent degradation of SAP, appear at lower temperatures. Additionally, a new exothermic peak (in the range 560–580 °C), assignable to the decomposition of TPA [39], appears in all samples.

The XRD patterns of the SAPTPA10, SAPTPA20, SAPTPA40, and SAPTPA30 samples are similar to that obtained for the SAP (Fig. 6). They do not exhibit any characteristic diffraction lines of tungstophosphoric acid $H_3PW_{12}O_{40}$, its more common hydrates ($H_3PW_{12}O_{40} \cdot 6H_2O$ and $H_3PW_{12}O_{40} \cdot 23H_2O$) or other crystal phases resulting from its transformation [40]. This is attributable to the fact that TPA has been highly dispersed in the polymer matrix or to its presence as noncrystalline phases.

The acidity measurements of the catalysts by means of potentiometric titration with *n*-butylamine let us estimate the number of acid sites and their acid strength. It was suggested that the initial electrode potential (E_i) indicates the maximum acid strength of the sites and the value of meq amine/g solid where the plateau is reached or the area under the curve indicates the total number of acid sites (N_s). The acid strength of these sites may be classified according to the following scale: $E_i > 100$ mV (very strong sites), $0 < E_i < 100$ mV (strong sites), $-100 < E_i < 0$ (weak sites), and $E_i < -100$ mV (very weak sites) [40,41].

According to the potentiometric titration curves (Fig. 7), the acid strength of the SAPTPA10 ($E_i = 55$ mV), SAPTPA20 ($E_i = 65$ mV), SAPTPA30 ($E_i = 89$ mV), and SAPTPA40 ($E_i = 124$ mV) samples is higher than that of the SAP ($E_i = -4$ mV), but lower than that of bulk TPA ($E_i = 620$ mV) [42]. The lower acid strength of the SAPTPA samples compared to bulk TPA could be assigned to the fact that the protons in the $H_3PW_{12}O_{40} \cdot 6H_2O$ are present as H^+ (H_2O)₂ species, whereas in the SAPTPA samples they are interacting with the nitrogen of $-CONH_2$ and $=NH$ groups.

The number of sites (N_s) determined by this technique slightly increases with the increasing amount of TPA incorporated by impregnation.

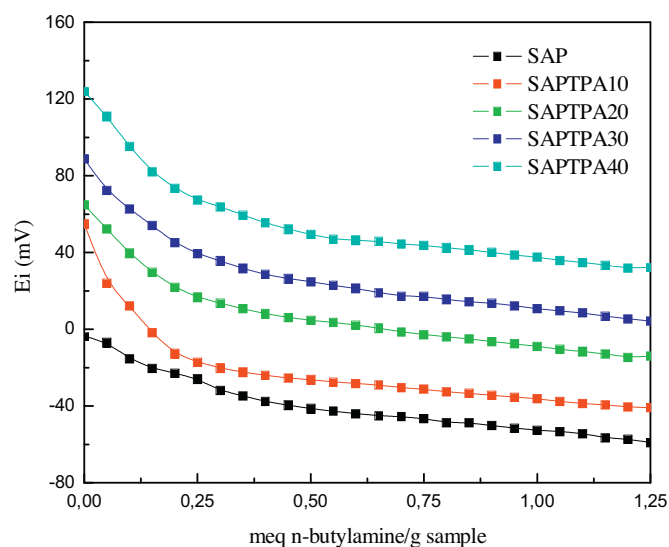


Fig. 7. Potentiometric titration of SAP samples impregnated with TPA.

Table 1

Oxidation of DBS by H_2O_2 in the presence of catalyst $H_3TPA_{12}O_{40}$. Influence of different solvent.

Entry	Solvent	Conversion % ^a	Selectivity ^b (%)
1	H_2O/CH_3CN	80	69
2	CH_3CN	98	94
3	MeOH	99	76
4	EtOH	97	81
5	Acetone	93	78
6	1,4-Dioxane	88	82
7	$CHCl_3$	68	76

Reaction conditions: 5 mL of solvent; 1 mmol of DBS; 1 mmol of H_2O_2 (35% w/v); 0.01 mmol% of $H_3TPA_{12}O_{40}$; RT (20 °C); 2 h; with stirring.

^a Determined by GC on the crude reaction mixture.

^b Selectivity = sulfoxide/(sulfoxide + sulfone).

3.2. Catalytic tests

3.2.1. Oxidation of dibenzylsulfide under homogeneous conditions using bulk TPA

The oxidation of DBS using H_2O_2 , which did not proceed in the absence of TPA under mild conditions, was used as a model reaction. In order to find the optimum reaction conditions, the influence of different factors, such as reaction solvent, time, H_2O_2 and catalyst amount, and temperature, on the conversion and selectivity of the oxidation reaction, was studied.

We first studied the DBS oxidation reaction, using hydrogen peroxide 35% w/v (1 mmol) as an oxidant, employing 5 mL of DBS solution (1 mmol) and TPA (1 mmol%), using different solvents to carry out the reaction at room temperature. The results listed in Table 1 show that the reaction is slightly sensible to the solvent nature, except in the case of $CHCl_3$. The oxidation carried out in acetonitrile gives the best result. A conversion of 98% was obtained with a sulfoxide selectivity of 94% (Table 1, entry 2). Similar conversion results were obtained using polar solvents such as methanol or ethanol (Table 1, entries 3 and 4) but the sulfoxide selectivity was lower (76% and 81%, respectively). Generally, sulfoxides are insoluble in water, but when a water–acetonitrile 1:1 (v/v) mixture is used for performing the oxidation, an 80% conversion was obtained with a sulfoxide selectivity of 69% (Table 1, entry 1). Poor conversion and selectivity were obtained in a less polar solvent such as chloroform, where the conversion and selectivity were 68% and 76%, respectively (Table 1, entry 7). As acetonitrile was the best solvent, it was used to perform the next experiments.

Table 2
Oxidation of DBS by H₂O₂ in the presence of catalyst H₃TPA₁₂O₄₀. Influence of the reaction time.

Entry	Time (h)	Conversion % ^a	Selectivity ^b (%)
1	0.5	30	100
2	1	68	98
3	2	98	94
4	5	98	85

Reaction conditions: 5 mL of acetonitrile; 1 mmol of DBS; 1 mmol of H₂O₂ (35% w/v); 0.01 mmol% of H₃TPA₁₂O₄₀; RT (20 °C) with stirring.

^a Determined by GC on the crude reaction mixture.

^b Selectivity = sulfoxide/(sulfoxide + sulfone).

Table 3
Oxidation of DPS by H₂O₂ in the presence of catalyst H₃TPA₁₂O₄₀. Influence hydrogen peroxide (35% w/v) amount.

Entry	Time (h)	H ₂ O ₂	Conversion % ^a	Selectivity ^b (%)
1	1	1	68	98
2	1	3	78	94
3	1	5	83	92
4	1	10	96	91

Reaction conditions: 5 mL of acetonitrile; 1 mmol of DBS; 0.01 mmol% of H₃TPA₁₂O₄₀; RT (20 °C) with stirring.

^a Determined by GC on the crude reaction mixture.

^b Selectivity = sulfoxide/(sulfoxide + sulfone).

Table 4
Oxidation of DBS by H₂O₂ in the presence of catalyst H₃TPA₁₂O₄₀. Effect of catalysis amount.

Entry	Catalyst amount %	Conversion % ^a	Selectivity ^b (%)
1	0.5	73	98
2	1	98	94
3	2	99	92
4	5	99	90

Reaction conditions: 5 mL of acetonitrile; 1 mmol of DBS; 1 mmol of H₂O₂ (35% w/v); catalyst: H₃TPA₁₂O₄₀; RT (20 °C), 2 h, with stirring.

^a Determined by GC on the crude reaction mixture.

^b Selectivity = sulfoxide/(sulfoxide + sulfone).

Table 2 shows the result for the DBS oxidation as a function of reaction time using TPA as catalyst. The experimental reaction conditions were: 5 mL of acetonitrile; 1 mmol of DPS, 1 mmol of H₂O₂ (35% w/v) and 20 °C. It can be observed that the conversion of DBS increased with the reaction time up to 2 h (Table 2, entry 3), and then it remained practically constant. In all cases the sulfoxide selectivity was excellent (higher than 85%).

The H₂O₂ concentration effect on the conversion of DBS and selectivity of reaction was studied, and four different H₂O₂ amounts were used: 0.1, 0.3, 0.5 and 1 mL, respectively (Table 3). The conversion increases slowly with the increment of the H₂O₂ amount, and the selectivity (higher than 91%) remains practically constant.

Table 4 displays the effect of the amount of catalyst on the conversion and selectivity in the oxidation of DBS. It can be seen that the conversion increased from 73% to 98% when the amount of TPA increased from 0.5% to 1% after 2 h. No relevant changes of reaction conversion and selectivity were observed with further increase in the amount of H₃PW₁₂O₄₀ (5 mmol%). Thus, 1% of TPA is a suitable amount for DBS oxidation under the reactions conditions tested.

The effect of temperature on the conversion rate and selectivity was also studied keeping the H₂O₂/substrate ratio constant. We found that at 20 °C the reaction is highly selective (91%) to sulfoxide with 100% conversion of the substrate at a reaction time of 2 h. On increasing the reaction temperature, the conversion rate increases and a complete transformation of the substrate to sulfone was achieved at 40 °C. Similar results were obtained at 55 and 70 °C.

In summary, we found the optimal reaction conditions for the selective oxidation of DBS in order to obtain dibenzylsulfoxide or dibenzylsulfone, under homogeneous conditions using bulk TPA as catalyst.

3.2.2. Under heterogeneous conditions using TPA included in the polymeric matrix

Based on the results obtained using bulk TPA as catalyst in homogeneous conditions, we subsequently studied the catalysts synthesized in this work (SAPTPA10, SAPTPA20, SAPTPA30, and SAPTPA40). The objective was to verify whether these new catalysts can carry out the selective oxidation of sulfides in heterogeneous conditions and whether the catalysts can be reused without appreciable loss of their catalytic activity.

Keeping in mind the reaction conditions evaluated for DBS oxidation under homogeneous conditions using bulk TPA as catalyst, we initially studied the optimal conditions for the selective oxidation of sulfides to sulfoxides (under heterogeneous conditions) using: 1 mmol of substrate (DBS), the weight of SAPTPAXX containing 0.01 mmol of TPA, 5 mL of acetonitrile, a substrate/hydrogen peroxide ratio (35% w/v) 1:1 and a temperature of 20 °C. The blank experiment (without catalyst) shows that the conversion of sulfide for a reaction time of 20 h was only 15% (Table 5, entry 1) and the selectivity to sulfoxide was 100% (no formation of sulfone was detected by GC analysis). When SAPTPA40 (72 mg to obtain a TPA:DBS ratio equal to 0.01) is used under the same reaction conditions, the conversion increases to 55% (Table 5, entry 10). In this case the dibenzylsulfoxide selectivity achieved is 95%. The conversion of DBS using SAPTPA30 is only of 20% with 100% sulfoxide selectivity (Table 5, entry 9). The conversion and selectivity results obtained using SAPTPA20 and SAPTPA10 (Table 5, entries 7 and 8) were similar to those achieved without catalyst (blank experiment). So, under these conditions, SAPTPA40 was able to selectively oxidize DBS to dibenzylsulfoxide (with selectivity similar to those obtained using TPA under homogeneous conditions). Although the conversion was lower, Shaabani and Rezayan [43] showed that the selective oxidation of sulfides to sulfoxides or sulfones in the presence of aqueous H₂O₂ was promoted by Brønsted acidity. Furthermore, Ishii et al. [44] reported the influence of the acidity rate on the formation of peroxo complexes. According to the acidity measurements of the SAPTPA samples by means of potentiometric titration with *n*-butylamine, the acidity decreases as follows: SAPTPA40 > SAPTPA30 > SAPTPA20 > SAPTPA10. Taking into account our results and previous reports [43,44], we can suggest that the acidity strongly affects the catalytic activity of the SAPTPA samples.

Then, we studied the optimal conditions established for the selective oxidation of sulfides to sulfones: 1 mmol of substrate (DBS), the weight of SAPTPA containing 0.01 mmol of TPA, 5 mL of acetonitrile, a substrate/hydrogen peroxide ratio of 35% w/v 10:1 and a temperature of 70 °C.

The blank experiment (without catalyst) shows that the conversion of sulfide for 13 h was 100% (Table 5, entry 2). Under these conditions, dibenzylsulfoxide selectivity was 90%. Then we performed four experiments using the catalyst synthesized in the present work, for the selective oxidation of DBS to the corresponding sulfone, under the same conditions (Table 6, entries 3–6). In all experiments sulfide was selectively transformed into the corresponding sulfone without secondary product formation. We found that the time required for total conversion of DBS to sulfone decreases in parallel with the increment of the amount of TPA in the catalyst, as result of an increase in the sample acidity.

The reusability of the catalysts was investigated in the sequential reaction of DBS oxidation. At the end of each run the catalyst was removed, washed with acetonitrile, dried in vacuum at 40 °C and reused. The results of the first and second reuses are shown in

Table 5
Oxidation of DBS using SAPTPA catalysis.

Entry	Catalyst	Relation H ₂ O ₂ /substrate	Temperature (°C)	Time (h)	Conversion (%) ^a	Sulfoxide selectivity ^b (%)	Sulfone selectivity ^c (%)
1	None	1:1	20	20	15	100	–
2	None	10:1	70	13	100	90	10
3	SAPTPA10	10:1	70	13	100	–	100
4	SAPTPA20	10:1	70	13	100	–	100
5	SAPTPA30	10:1	70	11	100	–	100
6	SAPTPA40	10:1	70	7	100	–	100
7	SAPTPA10	1:1	20	20	17	100	–
8	SAPTPA20	1:1	20	20	17	100	–
9	SAPTPA30	1:1	20	20	20	100	–
10	SAPTPA40	1:1	20	20	55	95	5
11	SAPTPA40	1:1	20	20	55	96	4
12	SAPTPA40	1:1	20	20	54	93	7

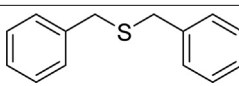
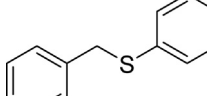
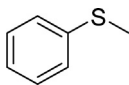
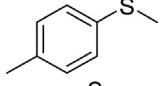
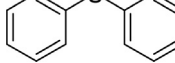
Reaction conditions: 5 mL of acetonitrile; 1 mmol of DBS; 1 or 10 mmol of H₂O₂ (35% w/v); 0.01 mmol% of catalyst; 20 °C or 70 °C; with stirring.

^a Determined by GC on the crude reaction mixture.

^b Sulfoxide selectivity = sulfoxide/(sulfoxide + sulfone).

^c Sulfone selectivity = sulfone/(sulfoxide + sulfone).

Table 6
Comparison of the time required for the complete oxidation of various substrates to sulfone.

Entry	Substrate	Substrate/atomic charge on S atom (q)	SAP TPA10	SAP TPA20	SAP TPA30	SAP TPA40
1		–0.031	13	13	11	7
2		0.076	15	15	12	8
3		0.085	18	18	14	10
4		0.085	18	18	14	10
5		0.165	24	24	22	20

Reaction conditions: 5 mL of acetonitrile; 1 mmol of DBS; 10 mmol of H₂O₂ (35% w/v); 0.01 mmol% of catalyst; 70 °C; with stirring.

Table 5, entries 11 and 12, and they showed that the catalyst can be reused without any significant loss of its catalytic activity. Similar results were obtained in subsequent reuses.

In order to evaluate the possible TPA solubilization, an additional test was performed. The SAPTPA40 sample was refluxed in acetonitrile for 6 h, filtered and dried in vacuum till constant weight. The refluxed acetonitrile was used as solvent for attempting the reaction without adding the catalyst. After 20 h under reaction, DBS conversion was 17%, almost the same value obtained for the blank experiment without catalyst (Table 5, entry 1).

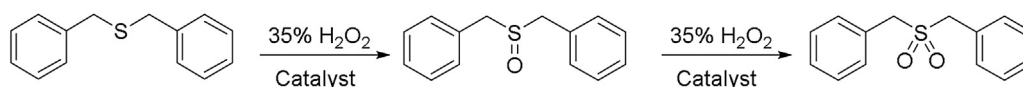
3.2.3. Reactivity study and plausible mechanism

The easiness of DBS oxidation in comparison to other sulfides was studied, and the results for the SAPTPA10, SAPTPA20, SAPTPA30, and SAPTPA40 catalysts are presented in Table 6. It can be seen that the time required to obtain the complete conversion of DBS into the corresponding sulfone was the shortest. The reactivity of five different sulfides was investigated using computational methods. The relationship between the electron densities on the sulfur atoms, which were estimated by Hyperchem 5, and the oxidative facility of the sulfur-containing compounds were analyzed. The electron densities on the sulfur atom of the five sulfides varied between –0.031 and 0.165. Table 6 shows that the time required for the complete oxidation of the substrates to the corresponding sulfone increases in parallel with

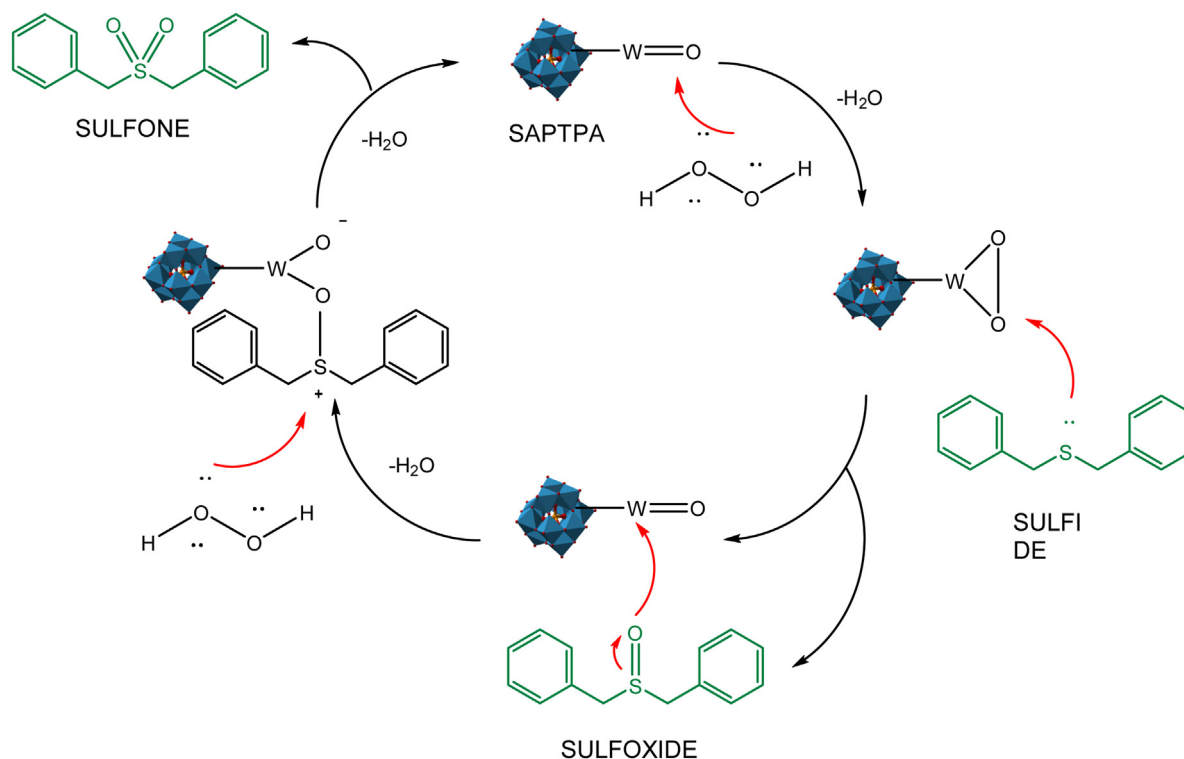
the increment of the electron densities on the sulfur atom. From the results obtained, the following reactivity order can be established: diphenylsulfide < methyl phenyl sulfide = methyl 4-methylphenyl < benzyl phenyl sulfide < dibenzyl sulfide. This different reactivity is associated with the electron density on the sulfur, since a higher electron density on this atom facilitates the attack on the electrophilic form of the peroxy oxygen–catalyst system (Scheme 1).

The mechanism of sulfide oxidation to sulfoxide or sulfone was well studied using different catalytic systems with nucleophilic or electrophilic properties [45–50]. Particularly Ahmad et al. [51] reported a comprehensive kinetic study about the use of polyperoxotungstates as catalyst in this transformation. This reaction involves the formation of peroxy-tungstate species and the subsequent nucleophilic attack of the sulfur atom in the sulfide on those species. Additionally, it is known that sulfides are oxidized to sulfoxides by electrophilic oxidants. The electrophilicity of the peroxide oxygen in H₂O₂ is increased by an oxometal group (W=O_d) in the heteropolyacids (Scheme 2). The interaction of hydrogen peroxide with TPA generates an electrophilic intermediate (peroxy oxygen/metal), which produces an electrophilic attack on the sulfur atom in the sulfide, generating the corresponding sulfoxide.

The mechanism for the oxidation of sulfoxide to the corresponding sulfone requires the presence of an oxidant with nucleophilic character. First, it involves the formation of a TPA-sulfoxide inter-



Scheme 1. Oxidation of dibenzyl sulfide (DBS).



Scheme 2. Plausible mechanism of sulfide oxidation to sulfone.

mediate through the nucleophilic attack on the tungsten atom in the TPA by the oxygen in the sulfoxide, and then the nucleophilic attack of the sulfur atom in TPA-sulfoxide by H_2O_2 via a $\text{S}_\text{N}2$ mechanism [47–50].

4. Conclusion

A series of materials based on a polymer composed of acrylic acid, acrylamide and *N,N'*-methylenebisacrylamide impregnated with tungstophosphoric acid water solutions were successfully synthesized.

According to FT-IR and ^{31}P MAS-NMR results the main species present in the samples is the $[\text{PW}_{12}\text{O}_{40}]^{3-}$ anion, which was partially transformed into $[\text{P}_2\text{W}_{21}\text{O}_{71}]^{6-}$ and $[\text{PW}_{11}\text{O}_{39}]^{7-}$ anions during the synthesis and drying steps. Taking into account XRD results, these species are highly dispersed in the polymer matrix or appear as noncrystalline phases.

The DTA-TGA results show that SAPTPA materials do not undergo any remarkable chemical changes up to 200 °C. So, they can be used to catalyze reactions at higher temperatures than those used in the present work.

Moreover, the SAPTPA samples showed strong acid sites whose number increases as the TPA content in them is higher.

We found a convenient and selective procedure for oxidizing sulfides to sulfoxides or sulfones, using H_2O_2 35% (w/v) aqueous hydrogen peroxide, a catalytic amount of SAPTPA, varying the H_2O_2 /substrate ratio and the temperature.

According to the results presented in this work, the materials obtained by impregnation of TPA onto the polymer matrix present suitable physicochemical properties to be used as cata-

lysts in the selective oxidation of sulfides to the corresponding sulfoxide/sulfone using environmentally benign oxidants. Mild reaction conditions, high activity and selectivity, easy preparation and reusability of the catalyst make the present protocol a greener alternative for the synthesis of sulfoxides and sulfones.

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