



Novel catalyst based on mono- and di-vanadium substituted Keggin polyoxometalate incorporated in poly(acrylic acid-co-acrylamide) polymer for the oxidation of sulfides



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ABSTRACT

Composite materials based on $[PV_xW_{12-x}O_{40}]^{(3+x)-}$ with $x = 1$ or 2 (PVW and PV2W respectively), included in poly(acrylic acid-co-acrylamide) gel (PAACA), were synthesized. The samples were characterized by different techniques such as FT-IR, ^{31}P MAS-NMR, ^{51}V -NMR, XRD, DTA-TGA, UV-vis DRS, and the acidic properties were estimated by means of potentiometric titration with n-butylamine. Samples containing 10, 20 and 30% (w/w) of polyoxotungstovanadate (POTV) were prepared by inclusion of the POTV in the polymer during its synthesis. According to Fourier transform infra-red and magic angle spinning-nuclear magnetic resonance studies, the predominant anion present in the samples is $[PV_xW_{12-x}O_{40}]^{(3+x)-}$, and there is no evidence of its decomposition during the synthesis of hybrid materials and the drying step. According to XRD results, these anions are greatly dispersed in the PAACA or present as amorphous phases.

UV-vis DRS data reveal that the samples synthesized using POTV with two vanadium atoms (PAACA-PV2W) exhibit lower values of absorption edge energy than those prepared using PVW (PAACA-PVW), which correlates with a higher oxidizing capacity.

The potentiometric titration shows strong acid sites of the hybrid materials, and their number increases with the number of vanadium atoms and with the amount of POTV incorporated in the PAACA grid.

The hybrid materials prepared by inclusion of POTV during the polymer synthesis exhibit appropriate physicochemical features to catalyze the oxidation of diphenyl sulfide (DPS) to its sulfone employing acetonitrile as solvent H_2O_2 as a green oxidant. The samples with 30% w/w of POTV, which show higher catalytic performance, are suitable for the DPS oxidation and can be reused without remarkable drop of their catalytic activity. Furthermore, they show high activity as a catalyst in the oxidation reaction of 4,4'-diamino diphenyl sulfide to the corresponding sulfone (dapsone) used for malaria treatment.

1. Introduction

Catalysis by polyoxometalates (POMs) is a field of growing value worldwide. The extensive chemistry of these compounds is related to the composition of the heteropolyanion [1–3], and the application of POMs in different fields such as photodegradation, medicine, catalysis and material science has been reported [4–16]. Their versatility is because they can act as reversible multielectron oxidants and very strong acids [17–21]. Taking into account their outstanding catalytic properties, POMs are used in homogeneous or heterogeneous catalysis and in bulk or supported form [22–27]. The use of solid acids in organic transformations has many advantages compared with conventional acids, including simplified product isolation, mild reaction conditions,

easy recovery and catalyst reuse, decreased plant corrosion, and more environmentally safe waste disposal procedures [28–32].

The development of new catalytic systems for selective organic synthesis is one of the principal goals in Organic Chemistry. The processes are essential for the conservation of the ecosystems. In the last years, procedures involving catalysis and green oxidants such as hydrogen peroxide, molecular oxygen and organic peroxides have been developed [33–36]. These are useful systems to oxidize organic substrates and present high efficiency due to their low cost, safety in storage and operation, and mild reaction conditions.

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

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of some of them [37]. These materials are composed of cross-linked polymeric chains in the form of a three-dimensional network [38]. They can absorb and retain large amounts of water, which depends on the type of monomer, the porosity, the cross-linking degree and the presence of hydrophilic groups in the polymer ($-\text{COOH}$, $-\text{CONH}_2$, $-\text{OH}$, $-\text{SO}_3\text{H}$).

On the other hand, sulfones are important intermediates in organic chemistry due to their application in fundamental research and other extended uses. The most widely used method for the preparation of sulfones is the oxidation of the corresponding sulfide; some traditional oxidizing reagents used for this purpose include HNO_3 , H_2CrO_4 , KMnO_4 [39–41], SeO_2 , MnO_2 , O_3 , NaBO_3 [42], among others [43–45]. For this reason, sulfide oxidation has been the subject of many studies, and several methods for this transformation have been reported in the literature [46,47]. Dapsone is very important in the pharmaceutical field due to its use as a drug for malaria and leprosy treatment, and also in dermatology for the treatment of different skin diseases [48–52].

In the present work, a polymer (PAACA) 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 [38] was synthesized and used as support.

The hybrid materials were obtained by inclusion of POTV in the PAACA during its synthesis, and the materials were characterized by different physicochemical techniques.

The aim of this paper is the preparation and characterization of $[\text{N}(\text{Prop})_4]_{(3+x)}[\text{PV}_x\text{W}_{12-x}\text{O}_{40}]$ included in superporous polymers to be used as catalysts in the heterogeneous oxidation of diphenyl sulfide to the corresponding sulfone, with aqueous hydrogen peroxide. The oxidation reaction of diphenyl sulfide (DPS) in homogeneous conditions using the bulk POMs was also studied for comparative purposes. Furthermore, the best conditions found in the oxidation test were used in the oxidation reaction of 4,4'-diamino diphenyl sulfide to obtain dapsone, a known drug for malaria treatment (Scheme 1).

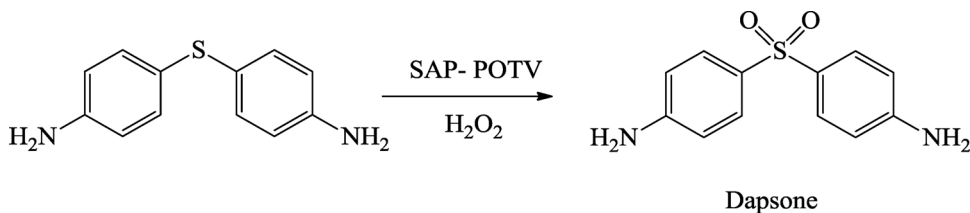
2. Experimental

2.1. Synthesis of $[\text{N}(\text{Prop})_4]_{(3+x)}[\text{PV}_x\text{W}_{12-x}\text{O}_{40}]$ with $x = 1$ or 2

The POTVs were synthesized according to the literature data [53]. $\text{NaHPO}_4 \cdot 12\text{H}_2\text{O}$ (0.025 mol) was added to an aqueous solution of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (0.019 mol) under continuous stirring, and the pH was adjusted with HCl (36% v/v) to 2.8. After stirring, 3.75 ml (PVW) or 5.00 ml (PV2W) of vanadium stock solution was added dropwise. The orange color solution was acidified with concentrated HCl to adjust the pH up to 3.4. The organic salts of POTVs were obtained by the addition of 0.012 mol of tetrapropylammonium bromide. The yellow (PVW) or orange (PV2W) solid formed was filtered and dried under vacuum until constant weight. Vanadium (V) stock solution was prepared by mixing NH_4VO_3 (0.25 mol) with NaOH (0.50 mol) in 500 ml of distilled water.

2.2. Synthesis of POTV included in a poly (acrylic-co-acrylamide) gel (PAACA)

The poly (acrylic-co-acrylamide) gel was prepared following the method described by Dorkoosh [38] (for a typical synthesis of PAACA see supplementary information).



Scheme 1. Oxidation reaction of 4,4'-diamino diphenyl sulfide to dapsone.

2.3. Materials characterization

2.3.1. FT-IR analysis

Fourier transform infra-red spectra of POTV, PAACA, PAACA-PVWX and PAACA-PV2WX materials were obtained in the wavenumber range $400\text{--}4000\text{ cm}^{-1}$ using a Bruker IFS 66 Fourier transform infra-red spectrometer.

2.3.2. XRD analysis

XRD diagrams of the materials were recorded employing Philips PW-1732 equipment, using Cu K α radiation, nickel filter, 20 mA and 40 kV in the high voltage source, and scanning angle between 5 and 60° of 2 θ at a scanning rate of 2°/min.

2.3.3. ^{31}P and ^{51}V nuclear magnetic resonance (P-NMR and ^{51}V -NMR respectively)

The ^{31}P and ^{51}V magic angle spinning-nuclear magnetic resonance spectra of the materials were registered with Bruker Avance II-300 equipment (see supplementary information).

2.3.4. Diffuse reflectance spectroscopy

UV-vis DRS spectra of the samples were registered using a Perkin Elmer Lambda 35 spectrophotometer, to which a diffuse reflectance chamber (Labsphere RSA-PE-20) is attached, in the 200–800 nm wavelength range. The absorption edge energy (Eg) was determined from diffuse reflectance spectra using the Kubelka–Munk remission function $[\text{F}(\text{R} \infty)]$ and $[\text{F}(\text{R} \infty)\text{h}\nu]^{1/2}$ curve [54,55].

2.3.5. TG-DTA

The TG-DTA analyses of the samples were accomplished by a Shimadzu DT 50 equipment. They were made under Ar atmosphere, in the temperature range 20–650 °C using 25–50 mg of the solid and a heating speed of 10 °C/min.

2.3.6. Acidity measurements

The acid strength and the number of acid sites were estimated from the *n*-butylamine potentiometric titration results (for more details about the technique see supplementary information)

2.4. Catalytic test

2.4.1. General observations

All reagents were acquired from Merck and Aldrich and used without additional purification. The amount of product was analyzed by GC, and the reactions were controlled by thin layer chromatography (TLC). The products were identified by mass spectra or ^1H -NMR spectra. The yields were estimated after product purification. Aqueous H_2O_2 (35% w/v) was purchased from Merck, and the exact strength at the time of utilization was determined by iodometric titration.

2.4.2. General test for the oxidation

Diphenyl sulfide was used as the model reagent for sulfide oxidation studies. They were performed with H_2O_2 (aq. solution) as the oxidant, acetonitrile as the solvent, in a batch reactor at 25 °C, using POTV (PVW and PV2W) and synthesized hybrid materials (PAACA-PVWX and PAACA-PV2WX) as homogeneous or heterogeneous catalysts

respectively. We made experiments using excess of H_2O_2 (10 mmol of H_2O_2 per 1 mmol of sulfide). We also tested the oxidation reaction using lower amount of oxidant (0.3 and 0.5 ml of 35% w/v H_2O_2) but very long reaction times were required to obtain suitable conversion values. So we decided to use 1 ml of 35% w/v H_2O_2 for the catalytic test. More details about the experimental conditions and the identification of the products were added in the supplementary information.

2.4.3. Catalyst reuse

Stability tests of the PAACA-PV2W30 catalyst were studied performing three consecutive reactions, under the same conditions. After each test, the catalyst was isolated from the reaction mixture, washed with acetonitrile (2×2 mL), dried under vacuum, and then reused.

2.4.4. Product identification

2.4.4.1. Diphenyl 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%).

2.4.4.2. 4,4'-diamino diphenyl sulfone (dapsone). Colorless solid. M.p.: 174–176 °C. $^1\text{H-NMR}$: 5.98–6.25 (s, 4H, NH_2), 6.5–8 (m, 8H, ArH), CDCl_3 .

3. Results and discussion

3.1. Materials characterization

The infrared spectra of $\text{H}_3\text{PW}_{12}\text{O}_{40}$, $[\text{N}(\text{prop})_4]_4[\text{PVW}_{11}\text{O}_{40}]$ and $[\text{N}(\text{prop})_4]_5[\text{PV}_2\text{W}_{10}\text{O}_{40}]$ (Fig. 1) show absorption bands characteristic of the Keggin structure in the range 700–1100 cm^{-1} , in concordance with the literature [53,56]. The spectrum of $[\text{PW}_{12}\text{O}_{40}]^{3-}$ anion displays bands at 1080, 982, 890, 793, 595 and 524 cm^{-1} , assigned to the stretching vibrations P–Oa, W–Od, W–Ob–W, W–Oc–W, and to the bending vibration Oa–P–Oa, respectively [57]. 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 spectra of PVW and PV2W show that the band at 1080 cm^{-1} assigned to the ν_3 vibration of the central PO_4 tetrahedron splits into two (1096 and 1070 cm^{-1}) and three (1095, 1078 and 1062 cm^{-1}) components, respectively, due to the symmetry decrease of the PO_4 tetrahedron. Furthermore, the increment of the V atoms in the heteropolyanion shifts IR bands to lower frequencies, in particular, the one assigned to the W–Od band (Table 1). These results, which are in

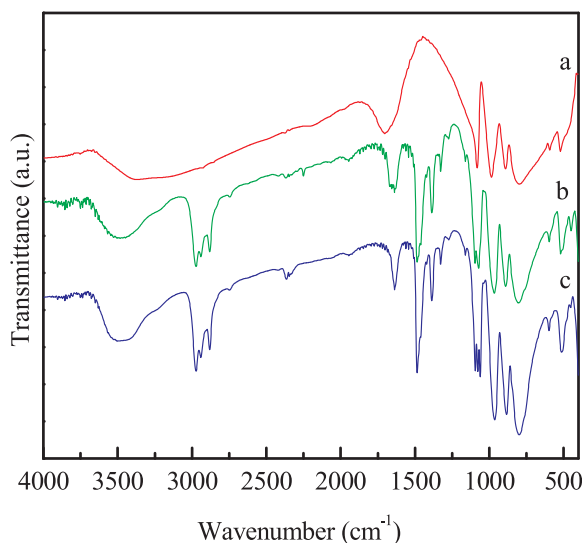


Fig. 1. FT-IR spectra of PW (a), PVW (b) and PV2W (c).

Table 1

Vibration frequencies (cm^{-1}) of PW, PVW and PV2W.

Compounds	ν W–Od	ν W–Ob–W	ν W–Oc–W	ν X–Oa
PW	982	890	793	1080
PVW	963	889	810	1096, 1070
PV2W	960	889	807	1095, 1078, 1062

agreement with those previously reported, confirm that the V(V) was incorporated into the primary structure of the Keggin anion.

Additionally, the FT-IR spectra of PVW and PV2W exhibit the characteristic bands of organic cation alkyl chains at 1380, 1412, 2880 and 2975 cm^{-1} assigned to the vibration of the C–H bonds.

The ^{31}P MAS-NMR spectra corresponding to PVW and PV2W materials (Fig. 2) show a single line with a maximum at –14.2 and –13.5 ppm respectively, which are in agreement with the values reported in the bibliography [58,59]. The downfield shift observed, compared to the PW (–15.3 ppm), is assigned to the decrease of the ^{31}P nucleus screening as a result of the replacement of one or two W by V [60].

On the other hand, the ^{51}V -NMR spectra of PVW and PV2W samples display two lines (with maximum at –546 and –550 ppm) and one line (with maximum at –552 ppm) respectively, in concordance with the values previously reported for the $[\text{PVW}_{11}\text{O}_{40}]^{4-}$ and $[\text{PV}_2\text{W}_{10}\text{O}_{40}]^{5-}$ anions [59,61].

The previously mentioned FT-IR characteristic bands of $[\text{PVW}_{11}\text{O}_{40}]^{4-}$ and $[\text{PV}_2\text{W}_{10}\text{O}_{40}]^{5-}$ anions are present in the FT-IR spectra of the hybrid materials PAACA-PVWX (Fig. 3) and PAACA-PV2WX (Fig. 4) overlapping those belonging to the PAACA. Additionally, their intensity diminishes due to the decrease of polyoxotungstovanadate content.

The ^{31}P MAS-NMR spectra of PAACA-PVW10, PAACA-PVW20, and PAACA-PVW30 samples display a line with a maximum at around –14.0 ppm, attributed to the $[\text{PVW}_{11}\text{O}_{40}]^{4-}$ anion [59]. The slight downfield shift observed, compared to the PVW (–14.2 ppm), can be ascribed to the interaction between the anion and the –CONH₂ and =NH groups present in the PAACA. The interaction can be assumed to be of the electrostatic type due to the transfer of protons to –CONH₂ and =NH, as has been proposed for the interaction with silica and zirconia [62,63]. Similar results were obtained for the PAACA-PV2W hybrid materials. Their ^{31}P MAS-NMR spectra reveal the presence of a line at around –13.1 ppm assignable to the $[\text{PV}_2\text{W}_{10}\text{O}_{40}]^{5-}$ anion interacting with the –CONH₂ and =NH groups.

According to FT-IR and ^{31}P MAS-NMR results we can establish that the Keggin structure of both $[\text{PVW}_{11}\text{O}_{40}]^{4-}$ and $[\text{PV}_2\text{W}_{10}\text{O}_{40}]^{5-}$ anions remains unaltered after their inclusion in the polymer matrix.

The TGA diagrams of PVW and PV2W materials show a weight loss in the range 200–250 °C corresponding to the organic cation decomposition through a Hoffman's elimination reaction [64,65]. According to the DTA diagrams, the thermal decomposition of the Keggin anions $[\text{PVW}_{11}\text{O}_{40}]^{4-}$ and $[\text{PV}_2\text{W}_{10}\text{O}_{40}]^{5-}$ takes place at 450 and 430 °C respectively [66,67].

We previously reported [68] that the DTA diagram of PAACA exhibits two endothermic peaks at 68 °C and 138 °C, which were assigned to the elimination of moisture and absorbed water respectively, and may be accompanied by the elimination of residues of the monomer used in the synthesis [69]. At temperatures higher than 200 °C, three endothermic peaks due to irreversible chemical changes in the PAACA (such as the formation of imides, nitrile groups from the amide groups of acrylamide and hydrocarbon chain rupture) are present [70,71].

The DTA diagrams of PAACA-PVWX and PAACA-PV2WX hybrid materials present similar features to those of the PAACA. However, a new exothermic peak, in the range 400–450 °C, appears in all samples due to the decomposition of PVW and PV2W anions respectively [66,67]. According to the DTA-TGA results, the hybrid materials are

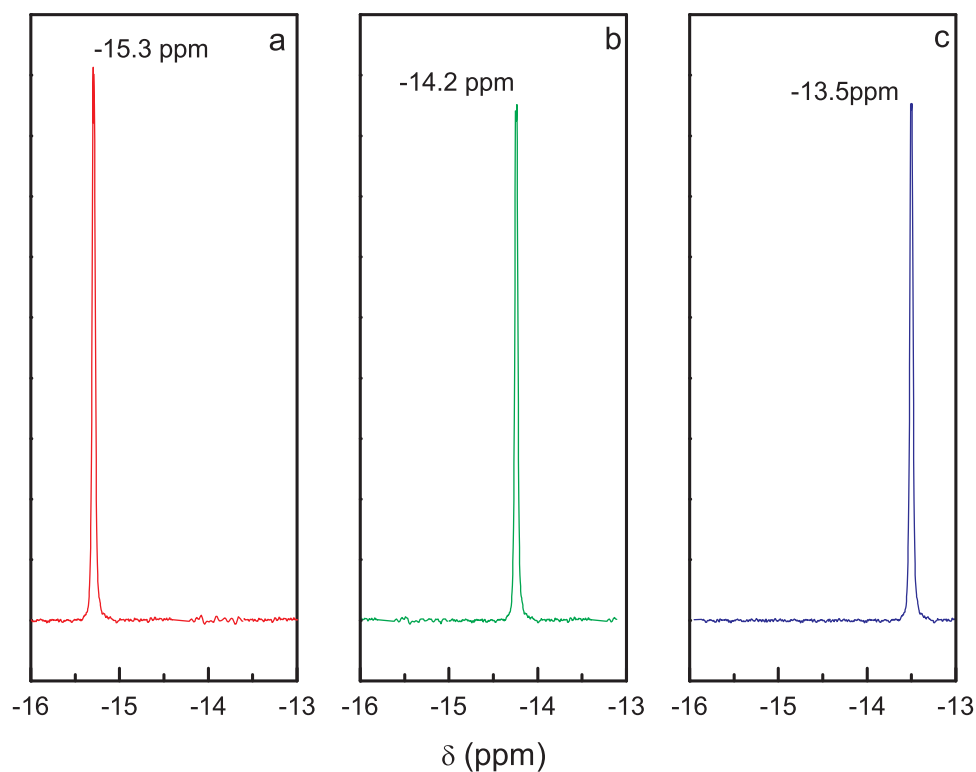


Fig. 2. ^{31}P -NMR of: PW (a), PVW (b) and PV2W (c).

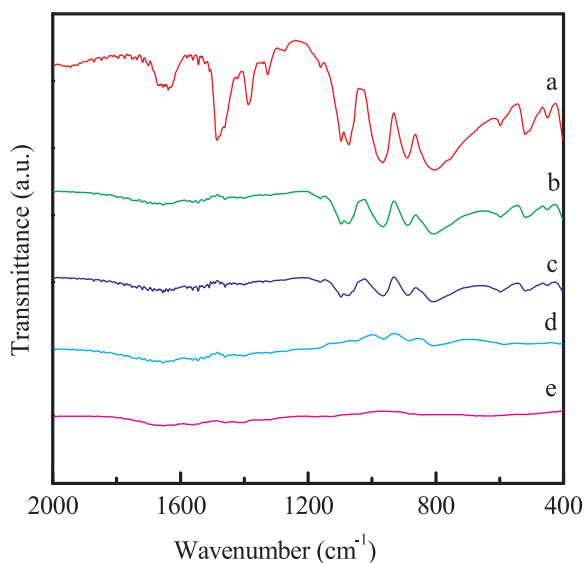


Fig. 3. FT-IR spectrum of: PVW (a), SAP-PVW30 (b), SAP-PVW20 (c), SAP-PVW10 (d) and SAP (e).

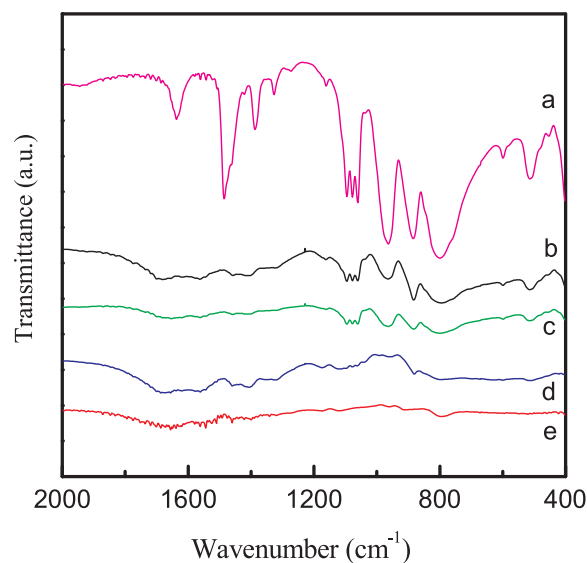


Fig. 4. FT-IR spectrum of: PV2W (a), SAP-PV2W30 (b), SAP (c), SAP-PV2W20 (d) and SAP-PV2W10 (e).

thermally stables till 200 °C. So, they could be used as heterogeneous catalysts at temperatures higher than 25 °C. However, the H_2O_2 decomposition increased significantly when the temperature was raised. So we decided to make the oxidation experiments at 25 °C.

The XRD patterns of the PAACA-PVWX and PV2WX (X = 10, 20 and 30% w/w) samples are similar to that obtained for the PAACA (Fig. 5). They do not exhibit any characteristic diffraction lines of PVW or PV2W [72,73]. This is attributable to the fact that both POTVs are highly dispersed in the polymer matrix or present 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. The initial electrode potential (Ei)

indicates the maximum acid strength of the sites. The area under the curve accounts for the total number of acid sites that the titrated solid presents. 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) [62,63].

According to the potentiometric titration curves (Fig. 6), the acid strength of the PAACA-PVW10 ($E_i = 50$ mV), PAACA-PVW20 ($E_i = 90$ mV) and PAACA-PVW30 ($E_i = 138$ mV) samples is higher than that of the PAACA ($E_i = -4$ mV), but lower than that of bulk PVW ($E_i = 172$ mV). The same behavior is observed for PAACA-PV2W10 ($E_i = 56$ mV), PAACA-PV2W20 ($E_i = 156$ mV) and PAACA-PV2W30 ($E_i = 178$

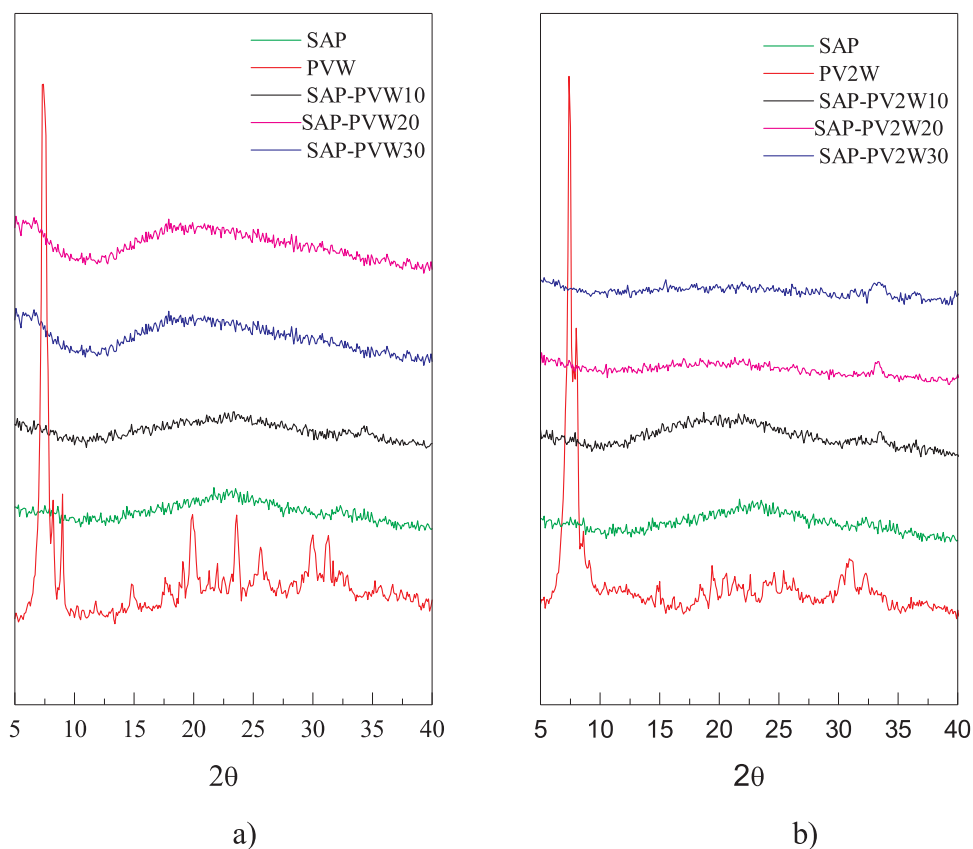


Fig. 5. XRD diagrams of: a) SAP, PVW and SAP-PVWX, X = 10, 20 and 30%w/w, b) SAP, PV2W and SAP-PV2WX, X = 10, 20 and 30%w/w.

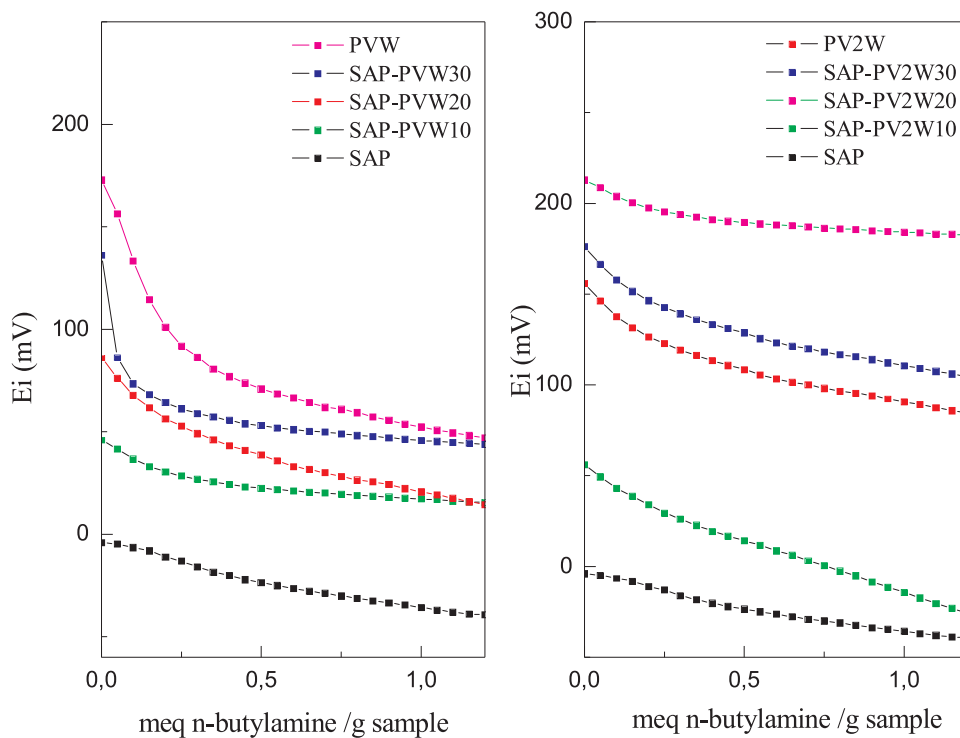


Fig. 6. Potentiometric titration with n-butylamine of: a) SAP, PVW and SAP-PVWX, X = 10, 20 and 30%w/w, b) SAP, PV2W and SAP-PV2WX, X = 10, 20 and 30%w/w.

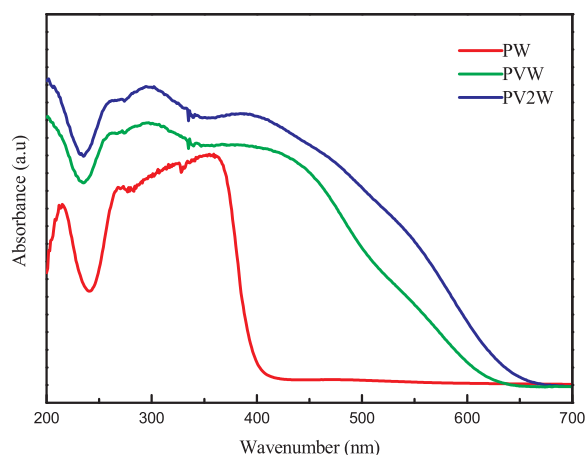


Fig. 7. Uv–vis DRS spectra of PW, PVW and PV2W.

mV), compared with bulk PV2W ($E_i = 213$ mV). The acid strength and the number of sites determined by this technique increase slightly with increasing amount of POTV in the samples.

The UV–vis DRS spectrum of bulk TPA presents a band at 212 nm and another broad band that extends from 250 to 450 nm [74] assigned to the charge transfer from bridging or terminal O 2p to W 5d (W–O–W and W–Od, respectively).

The DRS spectra of PVW and PV2W show the absorption threshold onset continuously shifted to the visible region when the number of

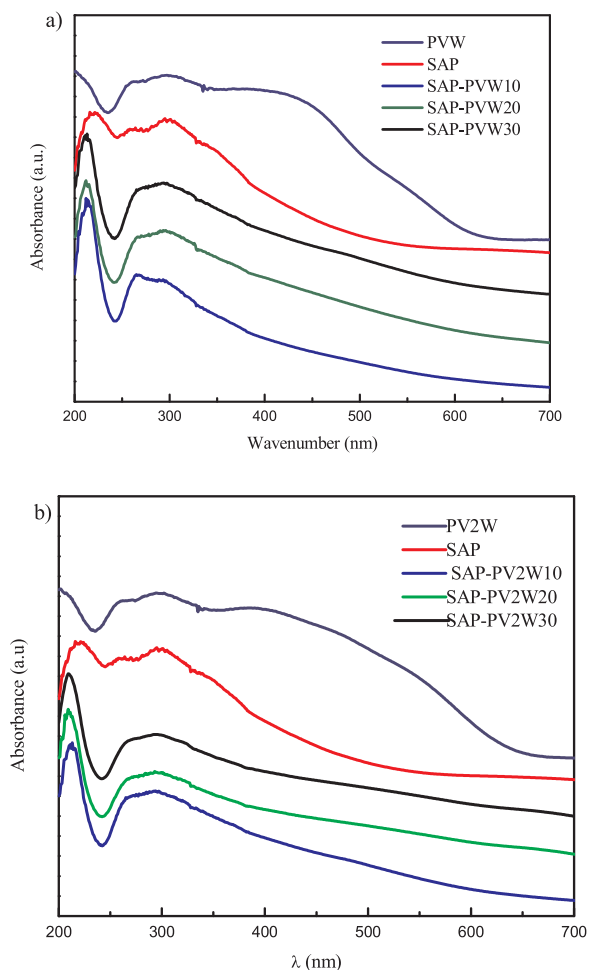


Fig. 8. Uv–vis DRS spectra of the synthesized hybrid materials: a) SAP, PVW and SAP-PVWX; b) SAP, PV2W and SAP-PV2WX, X = 10, 20 and 30%w/w.

Table 2

The absorption edge energy of PVW, PV2W and the PAACA-POTV hybrid materials.

Sample	E_b (eV)
PW	3.02
PVW	1.86
PV2W	1.81
PAACA-PVW30	2.25
PAACA-PV2W30	2.13
PAACA-PVW20	2.34
PAACA-PV2W20	2.23
PAACA-PVW10	2.45
PAACA-PV2W10	2.29

vanadium atom per anion increases (Fig. 7) in agreement with previous reports [75,76].

The UV–vis DRS spectra of the synthesized hybrid materials (PAACA-PVWX and PAACA-PV2WX) show the charge transfer bands previously mentioned (Fig. 8a and b, respectively) superimposed with those of the PAACA. The intensity of the bands increases with the increment of POTV in the hybrid material.

The absorption edge energy (E_g) in the UV–vis spectrum reflects the energy required for ligand-to-metal charge transfer (LMCT) [55,75,76]. It was reported that POM reduction potential increases with decreasing absorption edge energy [77].

The POMs that are stronger oxidizing agents present absorption edges at longer wavelength (lower energy), and reduction potentials at more positive voltages.

The E_g of the PW, PVW and PV2W (Table 2) decreases in parallel with the increment of the number of vanadium atom in the Keggin anion. On the other hand, the hybrid materials (PAACA-PVWX and PAACA-PV2WX) show absorption edge energy higher than the parent POTV (PVW and PV2W respectively), which slowly decreases with the increment of POTV content in the material (Table 2).

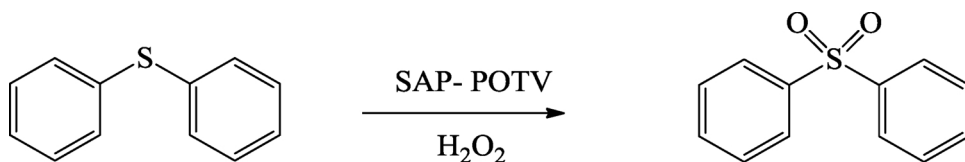
3.2. Catalytic studies

First, the catalytic activity of PW, PVW, and PV2W was evaluated in the diphenyl sulfide oxidation (Scheme 2) under homogeneous conditions. The blank experiment (Table 3, entry 1) was carried out without catalyst, using an excess of H_2O_2 (10 mmol, 35% w/v), and 5 ml of acetonitrile as reaction solvent at 25 °C. In these conditions, the conversion was 5% at 24 h, increasing considerably when PVW and PV2W were used (Table 3, entries 3 and 4), showing 100% of sulfide conversion at 3 h, with 100% of sulfone selectivity.

Under the same reaction conditions, using PW as catalysts, 98% of sulfide conversion with a 90% of selectivity to sulfoxide was reached (Table 3, entry 2). So, the synthesized materials (PVW and PV2W) showed better catalytic performance than PW for the studied reaction. However, they are very soluble in the reaction system, making their isolation and reuse an exceedingly difficult labor.

Then, with the purpose of evaluating the catalytic performance of the PAACA-PVWX and PAACA-PV2WX materials, the oxidation of DPS to the corresponding sulfone in heterogeneous conditions was carried out under the experimental conditions previously used for PVW and PV2W, using the weight of PAACA-PVWX (or PAACA-PV2WX) containing 0.01 mmol of PVW (or PV2W). First, we evaluated the activity of PAACA as catalyst, and we found that it was negligible. The conversion of DPS using PAACA (under the same experimental condition) was 5%. This value was similar to the obtained without catalyst (Table 3, entry 1).

We evaluated the H_2O_2 decomposition during different catalytic tests. For this purpose, 0.01 mmol of the catalyst, 10 mmol of H_2O_2 , and 5 ml of acetonitrile were added in a test tube. After 24 h at 25 °C, the decomposition of H_2O_2 was determined using yodometric titration. The



Scheme 2. Mild oxidation of diphenyl sulfide (DPS).

Table 3

Selective oxidation of diphenyl sulfide to diphenyl sulfone using PW, PVW and PV2W as catalysts in homogeneous conditions.^a

Entry	Catalysts	Sulfide Conversion % ^b	Sulfoxide Selectivity % ^c	Sulfone Selectivity % ^d
1	None ^e	5	100	–
2	PW	98	90	10
3	PVW	100	–	100
4	PV2W	100	–	100

^a Reactions were performed by reactivity of sulfide 1 mmol and 1 ml 35%w/v H₂O₂ in acetonitrile for 3 h at 25 °C temperature.

^b Determined by GC on the crude reaction mixture.

^c Sulfoxide Selectivity = sulfoxide/(sulfoxide + sulfone).

^d Sulfone Selectivity = sulfone/(sulfoxide + sulfone).

^e Blank experiment, 24 h.

Table 4

Selective oxidation of diphenyl sulfide to diphenyl sulfone using PAACA-PVWX and PAACA-PV2WX, X = 10, 20 and 30%w/w, as catalysts in heterogeneous conditions.^a

Entry	Catalyst	Sulfide Conversion % ^b	Sulfoxide Selectivity % ^c	Sulfone Selectivity % ^d
1	PAACA-PVW10	6	20	80
2	PAACA-PVW20	30	18	82
3	PAACA-PVW30	45	17	83
4	PAACA-PV2W10	20	33	67
5	PAACA-PV2W20	35	15	85
6	PAACA-PV2W30	54	14	86

^a Reactions were performed by reacting sulfide 1 mmol, 1 ml 35%w/v H₂O₂ in acetonitrile (5 ml) for 3 h, catalyst 1% mmol and 25 °C temperature.

^b Determined by GC on the crude reaction mixture.

^c Sulfoxide Selectivity = sulfoxide/(sulfoxide + sulfone).

^d Sulfone Selectivity = sulfone/(sulfoxide + sulfone).

values obtained were in the range 12–15% (they were reported in the supplementary information, Table S2). Additionally, the values did not depend on the type (PVW or PV2W) and content of polyoxotungstovanadate in the hybrid material.

The obtained results (Table 4) show that the conversion and selectivity achieved using PAACA-PVW and PAACA-PV2W hybrid materials were lower than those of the parent POTV in homogeneous conditions. However, the main benefit of these catalysts is they are insoluble in the reaction mixture system. On the other hand, the conversion increase with the increment of the POTV percentage. As was mentioned before, the oxidant capacity of the hybrid materials (PAACA-PVWX and PAACA-PV2WX) increased with the increment of the POTV content. Additionally, their acidity increased in the same order: PAACA-PVW10 < PAACA-PVW20 < PAACA-PVW30 (the same behavior was exhibited by the PAACA-PV2WX samples). A. Shaabani et al. reported that the sulfide oxidation using H₂O₂ solution was assisted by Brønsted acidity and that acidity influences the formation rate of peroxy complexes [78,79]. Taking into the account these reports and our previous results [68], we can suggest that the catalytic activity of

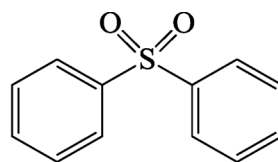


Table 5

Selective oxidation of diphenyl sulfide to diphenyl sulfone using PAACA-PVWX and PAACA-PV2WX, X = 10, 20 and 30%w/w, as catalysts in heterogeneous conditions.^a

Entry	Catalyst	Time (h)	Sulfide Conversion % ^b	Sulfoxide Selectivity % ^c	Sulfone Selectivity % ^d
1	PAACA-PVW10	5	13	35	65
		7	13	3	97
		24	29	12	88
2	PAACA-PVW20	5	30	15	85
		7	32	11	89
		24	42	12	88
3	PAACA-PVW30	5	70	–	100
		7	84	–	100
		24	93	–	100
4	PAACA-PV2W10	5	26	31	69
		7	28	–	100
		24	41	–	100
5	PAACA-PV2W20	5	52	–	100
		7	64	–	100
		24	100	–	100
6	PAACA-PV2W30	5	82	10	90
		7	90	6	94
		24	100	–	100

^a Reactions were performed by reacting 1 mmol sulfide, 1 ml 35%w/v H₂O₂ in acetonitrile (5 ml), 0.01 mmol catalyst and 25 °C temperature at 5, 7 and 24 h.

^b Determined by GC on the crude reaction mixture.

^c Sulfoxide Selectivity = sulfoxide/(sulfoxide + sulfone).

^d Sulfone Selectivity = sulfone/(sulfoxide + sulfone).

the samples is strongly affected by their oxidant capacity and acidity, which increases in parallel with the POTV content.

The catalysts with 30% w/w of bulk PVW and PV2W (PAACA-PVW30 and PAACA-PV2W30 respectively) showed the best catalytic performance in the selective oxidation of diphenyl sulfide to the corresponding sulfone. Then, the conversion of DPS and the selectivity to sulfone achieved using longer reaction times were studied. From the obtained results (Table 5), we can see that the complete conversion of DPS to sulfone only was achieved after 24 h using PAACA-PV2W20 and PAACA-PV2W30 catalysts (Table 5, entries 5 and 6, respectively). At the same reaction time, using PAACA-PVW30 as catalysts, excellent conversion and selectivity were also obtained (Table 5, entry 3). On the other hand, after only 7 h of reaction very good conversion (84% and 90%, respectively) and excellent selectivity (96% and 94%, respectively) were achieved using PAACA-PVW30 and PAACA-PV2W30 as catalysts (Table 5, entries 3 and 6).

After the reaction ended, the catalysts (PAACA-PVW30 and PAACA-PV2W30) were separated by filtration and reused using the optimized conditions. Fig. 9 shows three consecutive catalytic cycles in the selective oxidation of DPS to sulfone as a function of reaction time. The conversion results reached are similar to the ones obtained in the first use, showing no important loss of catalytic activity after three cycles. With the object to appreciate the possible POTV solubilization, the PAACA-PVW30 sample was placed in contact with pure acetonitrile for 24 h and filtered. The acetonitrile was employed as solvent in a reaction without incorporate the PAACA-PVW30 catalyst. Using this solvent and after 20 h of reaction, the DPS conversion was 17%, similar to the value obtained in the blank experiment (Table 3, entry 1).

Finally, when we use an excess of aqueous H₂O₂, the reaction is highly selective and proceeds in high yield to sulfone, providing an

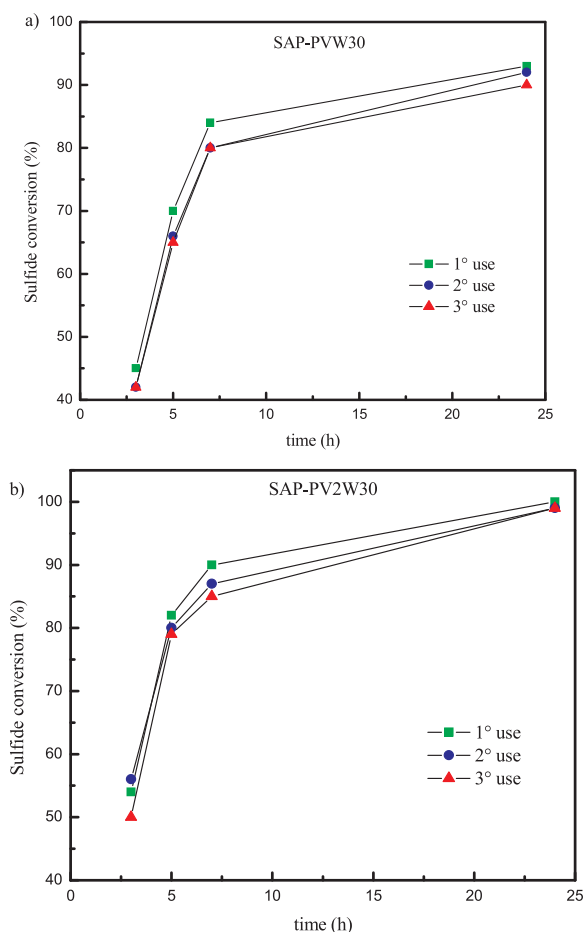


Fig. 9. Use and reuse of SAP-PVW30 (a) and SAP-PV2W30 (b) at 25 °C for sulfide conversion vs. time.

excellent synthesis method for such compounds.

Encouraged by the above-mentioned results, we used the same reaction conditions in the oxidation of 4,4'-diamino diphenyl sulfide to obtain dapson. The reaction conditions used were: 1 mmol of sulfide, 0.01 mmol of PAACA-PV2W30, 1 ml 35% w/v H₂O₂, acetonitrile as solvent (5 mL) and 25 °C. After 24 h, sulfide conversion was 65% with a 78% of selectivity to dapson.

4. Conclusions

Polyoxotungstovanadates with Keggin structure were synthesized and their structure was investigated by diverse techniques. In accordance to FT-IR and ³¹P-NMR results, the principals species present in the catalysts PVW, PV2W and the hybrid materials PAACA-PVWX and PAACA-PV2WX (X = 10, 20 and 30% w/w) are [PVW₁₁O₄₀]⁻⁴ and [PV₂W₁₀O₄₀]⁻⁵, respectively. Conform to XRD results, these species are highly dispersed in the polymer or appear as noncrystalline phases.

With DTA-TGA results, we could determine that PAACA-POTV materials do not experiment any notable chemical change up to 200 °C, being able to be used as catalysts in the oxidation reaction studied. Additionally, the PAACA-POTV samples exhibit strong acid sites, whose number increases as the POTV content in them is higher.

These Keggin-type POTVs were used as catalysts for the selective oxidation of diphenyl sulfide to diphenyl sulfone using a green oxidant agent (aqueous H₂O₂ 35% w/v). The replacement of W atoms by V enhances their catalytic activity with respect to commercial PW.

With the purpose of recovering the catalyst with easiness after the reaction and developing an eco-friendly procedure, the POTVs were included in a novel support, a superabsorbent polymer, synthesized by

the polymerization of AA and AM as former monomers, MBA as the cross-linking agent and APS as the polymerization initiator. The hybrid materials were reused without loss of their catalytic activity after three reaction cycles. This indicates that PVW and PV2W are strongly attached to the support. The main advantages of this process are the operational simplicity, the clearness of reaction and the very good yields attained. This process can be extended to other sulfides.

The catalyst with better performance for diphenyl sulfone was chosen for the oxidation of 4,4'-diamino diphenyl sulfide to obtain dapson. The catalyst PAACA-PV2W30 showed high conversion and selectivity values, providing an excellent, easy and clean synthesis method for such compound.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.mcat.2018.07.016>.

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