



## Mo-based Keggin heteropolyacids as catalysts in the green and selective oxidation of diphenyl sulfide

Valeria Palermo, Gustavo P. Romanelli, Patricia G. Vázquez\*

Centre of Research and Development of Applied Sciences "Dr. Jorge J. Ronco" (CINDECA), CONICET-CCT-La Plata, National University of La Plata (UNLP), 47 N° 257, B1900AJK La Plata, Argentina

### ARTICLE INFO

#### Article history:

Received 21 December 2012  
Received in revised form 28 February 2013  
Accepted 1 March 2013  
Available online 14 March 2013

#### Keywords:

Green selective oxidation  
Diphenyl sulfide  
Supported heteropolyacid  
Keggin heteropolyacid

### ABSTRACT

Heteropolyacids are used as redox catalysts due to their bifunctional properties. Some advantages over conventional catalysts, such as selectivity, easy isolation and reuse, are worth noting. In homogeneous conditions their isolation and recycling can be harder, so that they are supported for their use as heterogeneous catalysts.

In this work, we compare the catalytic activity of different heteropolyacids with Keggin structure, supported on pure and functionalized silica (with 3-aminopropyltrimethoxysilane).  $H_6PMo_{11}BO_{40}$ ,  $H_6PMo_{11}BiO_{40}$ ,  $H_6PMo_{11}LaO_{40}$ , and  $H_6PMo_{11}YO_{40}$  were synthesized, supported and characterized by several physicochemical techniques. Highly selective results were obtained in the selective oxidation of diphenyl sulfide to diphenyl sulfoxide or diphenyl sulfone. Besides, these catalysts can be reused. The above-mentioned reaction is useful due to the importance of these compounds as intermediates in the synthesis of biologically significant molecules.

© 2013 Elsevier B.V. All rights reserved.

### 1. Introduction

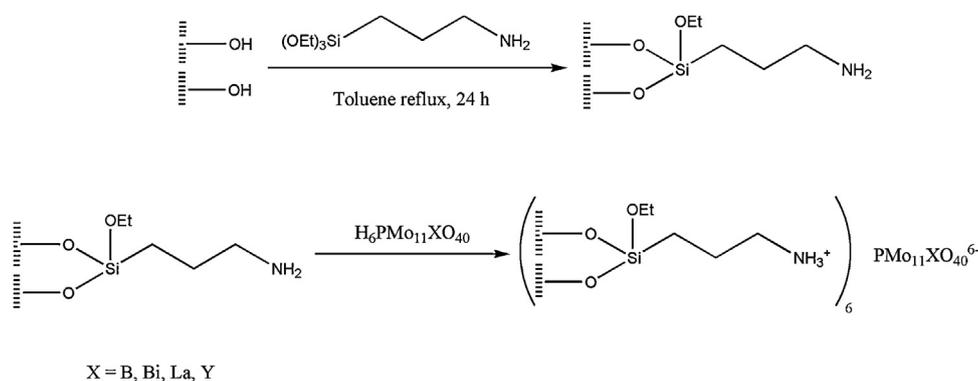
Heteropolyacids are well-known compounds with complex structural characteristics. Besides their relatively high acid strength, they have particularly favorable technological features such as easy recovery and environmentally safe handling. On the other hand, there is a special interest in those that form a basic Keggin-type structure [1,2]. The growing demand for new functional materials to be used in advanced nanoscale technologies makes the control of the wide range of properties of transition metal compounds an increasingly attractive goal. In this respect, by varying the environment of transition metal complexes, the guest–host interactions involved is an efficient means to finely tune their properties [3]. One of the most striking abilities of polyoxoanion building blocks, particularly for lacunary polyoxoanion clusters, is that they can act as multidentate inorganic ligands to accommodate transition-metal or rare-earth cations between the polyoxoanion clusters [4]. Heteropolyacid (HPA) compounds with Keggin structure are polynuclear complexes principally constituted by a close-packed framework of 12 molybdenum-oxygen octahedral  $MoO_6$  surrounding a central  $PO_4$  tetrahedron [3]. They operate either as multielectron oxidants or strong acids, with an

acid strength higher than that of classical acids [4]; their properties can be controlled by the substitution of the central heteroatom and addenda or transition-metal substituted atoms without changing the fundamental structure [5]. The HPA can be used to replace the conventional inorganic and organic acids in many liquid-phase reactions [6]. In relation to the fundamental importance of ubiquitous protonate water (the aqueous acids) in chemical and biological systems, these HPAs are very important [7,8].

Heteropolycompounds have been supported on different materials with high surface area in order to increase the activity of such compounds in surface heterogeneous reactions [9–12]. Even though the catalysts in homogeneous conditions are effective for organic compound oxidation, their isolation and reuse are difficult. Due to the need to obtain catalysts for green processes, the use of recycled catalysts is required for reducing the catalytic cost.

In recent years, inorganic/organic hybrid materials have attracted great interest as they can easily integrate the special function of organic and inorganic components. The hybrid matrix may be a polymer chain or an inorganic polymeric network, and a composite inorganic/polymer host. Based on the interaction among the different components or phases in hybrid systems, these hybrid materials can be divided into two major classes: the first is made up of the so-called physically mixed hybrids with weak interactions such as hydrogen bonding, van der Waals force or weak static effects between the organic and inorganic phases, and the second is formed by chemically bonded hybrids with covalent bonds linking the organic and inorganic parts [13,14]. The motivation for the

\* Corresponding author. Tel.: +54 221 4210711; fax: +54 221 4210711.  
E-mail addresses: [vazquez@quimica.unlp.edu.ar](mailto:vazquez@quimica.unlp.edu.ar), [pgvazquez@hotmail.com](mailto:pgvazquez@hotmail.com) (P.G. Vázquez).



**Scheme 1.** Heterogenization of HPA.

utilization of Bi, La, Y and B as doped elements of heteropolyacids is due to different reasons in each case. From our first studies on Keggin structures we have always tried to obtain different properties in one compound. In this research we use Bi and Mo together because of their very good activity in oxidation reactions [15].

In relation to La it is interesting to obtain a heteropolyoxocompound with high-quality interaction between silica and lanthane oxide, that is, with good dispersion. Yttrium, rarely found in nature, usually occurs in two states. The use of yttrium is still growing, in fact due to its good properties to produce catalysts. Finally, B is very similar to Al, an element that we studied and reported in different papers (see our references), but in this case we are trying to improve our results.

On the other hand,  $H_2O_2$  is one of the oxidants frequently used in fine chemicals synthesis, as an option to the conventional ones, due to its effective oxygen content, low cost, safety in storage and operation. The use of  $H_2O_2$  leads to a cleaner technology because its reaction produces only  $H_2O$  as by-product [13].

The selective catalysis of sulfides to sulfoxides and sulfones has been a challenge for many years, owing to the importance of these compounds as intermediates in organic synthesis and their potential fungicidal activity. There are several reagents available for these key transformations, but they are conventionally achieved using stoichiometric amounts of both organic and inorganic reagents, for example, nitric acid and chromic acid, among others [6]. However, these reagents cause environmental pollution and corrosion problems, which can be avoided by using catalysts based on supported HPA. Sulfoxides are important as an activating group in organic synthesis; they have been utilized extensively in carbon bond-forming reactions as building block [16], especially as chiral auxiliaries [17], and they play key roles in the activation of enzymes [18]. The use of sulfones in organic synthesis has become a classic strategy in the synthesis of many complex molecules.

The influence of silica-supported molybdenum catalysts on the reaction mechanisms, and also on the improvement of the required parameters for specific reactions of economic importance, has been studied. The decrease of acid catalytic activity with the formation of heteropoly blue ( $Mo(VI) \rightarrow Mo(V)$ ) in electrophilic reactions has also been investigated [1]. Studies about  $MoO_3$  catalysts supported on silica showed the presence of phosphosilicic acid and its primary catalytic role in such a system [19].

The general objective of this work is the synthesis and characterization of different HPAs with Keggin structure from molybdophosphoric acid (MPA), where Mo is the addenda atom and different B, Bi, La and Y elements incorporate into the primary structure. These HPAs were supported on silica and functionalized silica (with 3-aminopropyltrimethoxysilane), using an equilibrium impregnation technique in all cases. The impregnation step consists of different experimental conditions in order to obtain an active

stabilized phase on the supports during reaction in a liquid medium. A detailed analysis of the nature of species present both in solids and in impregnating solutions was carried out. Also, the synthesized catalysts were tested in the selective diphenyl sulfide oxidation, using  $H_2O_2$  as oxidant and ethanol as solvent, to determine the redox characteristics of the obtained catalysts. In addition, these results were compared with those provided by different techniques such as FTIR and potentiometric titration, among others.

## 2. Experimental

### 2.1. Catalyst preparation

#### 2.1.1. Silica preparation via sol–gel technique

Tetraethoxysilane (TEOS) (102 mL), absolute ethanol (99%) (42 mL), and glacial acetic acid (30 mL), in a molar ratio equal to 1:1.6:1.1, were mixed in a glove box under nitrogen atmosphere at room temperature. The mixture was removed from the controlled atmosphere and another part of absolute ethanol (90 mL) was added, and then sol–gelation took place. Finally, wet gel was aged in the same medium until dry silica particles were obtained. These particles were dried at  $40^\circ C$  and this solid was named S.

#### 2.1.2. Preparation of functionalized silica

The S solid (4 g) was refluxed with toluene (128 mL) for 1 h. Then, 3-aminopropyltrimethoxysilane (APS) (6.40 mL) was added and stirred under reflux conditions for 24 h (Scheme 1). The solid was filtered, washed in a Soxhlet apparatus with diethyl ether and dichloromethane and dried at  $40^\circ C$  according to Ref. [20]. The solid was named  $NH_2-S$ .

#### 2.1.3. Synthesis of heteropolyacids

$H_6PMo_{11}BO_{40}$  (PMoB),  $H_6PMo_{11}BiO_{40}$  (PMoBi),  $H_6PMo_{11}LaO_{40}$  (PMoLa), and  $H_6PMo_{11}YO_{40}$  (PMoY) were prepared by the hydrothermal synthesis method [21]. The following HPA synthesis procedure was used: a stoichiometric mixture of  $MoO_3$ , the corresponding metal oxide, as raw precursor in each case, and  $H_3PO_4$  (85%, w/v) was suspended in 120 mL of distilled water. The mixture was stirred for 3 h at  $75^\circ C$ . After cooling down to room temperature and removal of insolubles, the heteropolyacid solution was evaporated and dried at  $40^\circ C$ . Colorful crystals were obtained.

#### 2.1.4. Preparation of silica-supported catalysts

Catalysts were obtained by the equilibrium adsorption technique. The impregnated solutions were prepared by dissolution of the corresponding HPA (150 mg) in absolute ethanol (3.50 mL), obtaining 23% (w/w) in the final catalyst for each HPA. The HPA amounts added were: PMoB: 0.086 mmol; PMoBi: 0.077 mmol;

PMoLa: 0.080 mmol, and PMoY: 0.082 mmol. The first step in the impregnation technique was to contact the HPA solution with the support, S and/or NH<sub>2</sub>-S (500 mg), with H<sub>2</sub>O (0.50 mL). The impregnated solids were left without stirring for 24 h, to help the diffusion of HPA into the supports. Then they were shaken for 24 h. Finally, the impregnating solutions were separated from the solids and dried at 20 °C for 12 h. The nomenclature of the new catalysts is:

- when S was used as support, they were named PMoB-S, PMoBi-S, PMoLa-S, and PMoY-S;
- when NH<sub>2</sub>-S was used as support, they were named PMoB-NH<sub>2</sub>-S, PMoBi-NH<sub>2</sub>-S, PMoLa-NH<sub>2</sub>-S, and PMoY-NH<sub>2</sub>-S.

On the other hand, and with the only objective of comparing the catalytic behavior, PMoY was impregnated on NH<sub>2</sub>-S using H<sub>2</sub>O<sub>2</sub> (35%, w/v) instead of water. The catalyst obtained was labeled PMoY-NH<sub>2</sub>-S<sub>(p)</sub>. This test was made to confirm that water or hydrogen peroxide does not produce any changes in the catalytic behavior of the final material.

The modifications of the amount of HPA in each case were evaluated by quantitative element analysis and acidic properties.

## 2.2. Catalyst characterization

### 2.2.1. Quantitative element analysis

The composition of experimental bulk HPA was determined by means of the inductively coupled plasma atomic emission spectroscopy (ICP-AES) technique using a Shimadzu 1000 III.

### 2.2.2. UV-visible spectroscopy

Subsequent to the contact with the support, the impregnated solution was analyzed by ultraviolet spectroscopy (UV), using a Perkin Elmer Lambda 35 UV-vis double beam spectrophotometer, in the range 200–1100 nm.

### 2.2.3. Textural properties

The specific surface area ( $S_{\text{BET}}$ ), pore volume, and the mean pore diameter of the supported catalysts were determined by nitrogen adsorption/desorption technique using Micromeritics ASAP 2020 equipment at liquid-nitrogen temperature. The sample was previously degassed at 100 °C for 1 h.

### 2.2.4. Fourier transform infrared spectroscopy

Thermo Nicolet IR.200 equipment was employed, using pellets with BrK, and a measuring range of 400–4000 cm<sup>-1</sup>.

### 2.2.5. Potentiometric titration

Catalyst acidity was determined by means of potentiometric titration of a suspension of the solid in acetonitrile, using a solution of *n*-butylamine in acetonitrile (0.025 N) in a Metrohm 794 Basic Titrino apparatus with a double junction electrode.

## 2.3. Catalytic activity test

### 2.3.1. General

All reagents were purchased from Merck and Aldrich and used without further purification. All yields refer to isolated products after purification. Products were characterized by spectroscopy data (<sup>1</sup>H NMR). The NMR spectra were recorded on Bruker 200 MHz equipment. The NMR spectra were measured in CDCl<sub>3</sub> relative to TMS (0.00 ppm).

The organic phase was dried on anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered for its analysis by gas chromatography using Varian Scan 3400 cx equipment. The product distribution was quantified by a Shimadzu C-R34. Reactions were monitored by thin layer chromatography (TLC) analyses. Homogeneous reactions: (a) Bulk HPA

(12 mg), diphenyl sulfide (Aldrich, 1 mmol, 186 mg), and ethanol (Soria, 4 mL) were stirred at 25 °C. Then aqueous H<sub>2</sub>O<sub>2</sub>, 35% (w/v) (1.5 mmol, 0.15 mL), was added. The progress of the reaction was monitored by TLC. After the end point of reaction, it was treated with dichloromethane and water (2 × 3 mL). The organic phase was dried on anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated to obtain diphenyl sulfoxide.

(b) Diphenyl sulfone was obtained using bulk HPA (12 mg), diphenyl sulfide (Aldrich, 1 mmol, 186 mg), 35% (w/v) H<sub>2</sub>O<sub>2</sub> (7.5 mmol, 0.75 mL), and ethanol (Soria, 4 mL) at 50 °C.

### 2.3.2. Heterogeneous reactions

(a) Supported catalyst (50 mg), diphenyl sulfide (Aldrich, 1 mmol, 186 mg), and ethanol (Soria, 4 mL) were stirred at 25 °C. Then 35% (w/v) H<sub>2</sub>O<sub>2</sub> (1.5 mmol, 0.15 mL) was added. The progress of the reaction was monitored by TLC. After the reaction end point, the catalyst was recovered by centrifugation and washed with dichloromethane. The reaction mixture was treated with dichloromethane and water (2 × 3 mL). The organic phase was dried on anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated to obtain diphenyl sulfoxide. (b) Equally, diphenyl sulfone was obtained using 0.75 mL of H<sub>2</sub>O<sub>2</sub> 35% (w/v) at 50 °C.

The performance of the catalysts was evaluated quantitatively by the conversion of diphenyl sulfide (Conv.%), and the selectivity of diphenyl sulfoxide and diphenyl sulfone (Sel.%).

## 3. Results and discussion

### 3.1. Characterization of catalysts

Many heteropolycompounds with Keggin structure present high acidity. Therefore, they can be used to catalyze attractive reactions. For example, they can be used to replace classical acids, such as sulfuric acid, with some advantages, such as a lower corrosion and a lower production of wastes, thus leading to eco-efficient processes [22]. In the Keggin structure there are four oxygen types: O<sub>a</sub> surrounds the central tetrahedral P, and links P and Mo together; O<sub>b</sub> connects MoO<sub>6</sub> octahedra by the corners; O<sub>c</sub> shares the octahedra edges; and terminal oxygen O<sub>d</sub> is bonded to only one Mo atom. Each Keggin anion [XM<sub>12</sub>O<sub>40</sub>]<sup>3-</sup> can be inscribed into a sphere of center X and radius close to 0.52 nm [23] (radius = mean of the 12X–O<sub>d</sub> distances, and X = P in our case). M atoms are located at the corners of an octahedron cube, which are just moved from centers of the side of the associated cube.

Although the [PMo<sub>12</sub>O<sub>40</sub>]<sup>3-</sup> anion is compact, it can accommodate heteroatoms that differ greatly in size of M (Mo in our case) shown by the range of covalent radius for atoms such as 0.82 Å (B) to 1.70 Å (Bi). Then, PMoB, PMoBi, PMoLa, and PMoY can present interesting characteristics as catalysts since they can have Lewis and/or Brønsted acidity. To the best of our knowledge, their real structure has been characterized by different techniques. Table 1 shows the atomic properties of Mo, B, Bi, La, and Y as elements, which were used to replace one Mo atom in the Keggin primary or secondary structures [24].

Taking into account the atomic mass, it could be supposed that Y incorporation produces less structural modifications in the Keggin primary structure (for example, bond between O or Mo addenda), given that both Mo and Y have similar atomic mass (Table 1, entries 1 and 3). The extreme behavior is presented by B and Bi (Table 1, entries 2 and 5); they show values of 10.81, almost nine times smaller than Mo, and Bi, with 208.98, is twice higher than Mo. With respect to the ionic radius (Table 1) it might be said that 3 B atoms are necessary to replace one Mo, if not just one La can take the place of one Mo. This supposes a strong effect on the bond that is opposite to the electronegativity of doping metals. In this regard,

**Table 1**  
Atomic properties of phosphomolybdic acid doping metals.

Entry	Metal	Atomic mass	Van der Waals radius (Å)	Ionic radius (Å)	Covalent radius (Å)	Electronegativity
1	Mo	95.94	1.39	0.62	1.45	1.8
2	B	10.81	0.98	0.20	0.82	2.0
3	Y	88.91	1.80	0.93	1.48	1.2
4	La	138.91	1.87	1.15	1.69	1.1
5	Bi	208.98	1.70	1.20	1.70	1.9

**Table 2**  
Elemental analysis by ICP-AES.

Entry	HPA theoretical formula	Experimental (ICP-AES)	Theoretical
1	H <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub> ·13H <sub>2</sub> O	Mo 55.98	Mo 50.70
2	H <sub>6</sub> PMo <sub>11</sub> BO <sub>40</sub> ·14H <sub>2</sub> O	Mo 52.89 B 0.54	Mo 53.50 B 0.88
3	H <sub>6</sub> PMo <sub>11</sub> BiO <sub>40</sub> ·12H <sub>2</sub> O	Mo 48.91 Bi 9.69	Mo 47.45 Bi 9.36
4	H <sub>6</sub> PMo <sub>11</sub> LaO <sub>40</sub> ·6H <sub>2</sub> O	Mo 53.32 La 7.02	Mo 52.60 La 8.53
5	H <sub>6</sub> PMo <sub>11</sub> YO <sub>40</sub> ·12H <sub>2</sub> O	Mo 51.80 Y 4.36	Mo 51.95 Y 6.49

Bi and B have electronegativity similar to that of Mo, while La and Y present similar values. The above-mentioned properties are very important in the preparation of HPA as redox catalysts since the identification of the species present in the impregnating solutions is particularly significant. For this reason, the elemental analysis of synthesized HPA by ICP-AES was performed and is summarized in Table 2.

This confirmed that one of the Mo atoms was replaced by the corresponding elements and it is possible to obtain doped HPA. The experimental values are in accordance with the theoretical values (calculated for hydrated HPA, whose hydration number was obtained by TGA). Then, with other characterization techniques, we could compare these values and conclude about the nature of the present species.

Fig. 1 shows the FTIR spectra of the all synthesized bulk HPAs. The main characteristic features of the H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> (MPA) spectrum (marked lines in the figure) are bands at 1064 cm<sup>-1</sup> (P–O<sub>a</sub>), 964 cm<sup>-1</sup> (Mo=O<sub>d</sub>), 871 cm<sup>-1</sup> (Mo–O<sub>b</sub>–Mo), 784 cm<sup>-1</sup> (Mo–O<sub>c</sub>–Mo) [19].

When another atom is introduced in the MPA structure, the same characteristic bands appear in the spectra, which confirm the Keggin primary structure, but the difference in length of the bonds could be introducing defects into the original spectrum of MPA. Here it is important to consider the atomic properties of B, Bi, La and Y. However, small displacements take place in some bands (Table 3), in particular PMoLa and PMoY in relation to 964 cm<sup>-1</sup> (Mo=O<sub>d</sub>) and 871 cm<sup>-1</sup> (Mo–O<sub>b</sub>–Mo) bonds of the H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> spectrum.

It is possible that La, with an atomic mass of 138.91, introduces a steric factor in the Mo–O<sub>b</sub> bond, in addition to the small electronegativity of Mo, modifying the Mo=O<sub>d</sub> bond. In relation to PMoY, for the previously mentioned bonds, the atomic mass is very close to that of Mo, but the electronegativity is smaller than that of Mo (1.2) although the splitting shown for Mo–O<sub>b</sub>–Mo could be due

**Table 3**  
FTIR bands of bulk synthesized HPA.

Entry	HPA	P–O <sub>a</sub>	Mo=O <sub>d</sub>	Mo–O <sub>b</sub> –Mo	Mo–O <sub>c</sub> –Mo
1	PMoB	1066	963	868	785
2	PMoBi	1064	965	871	789
3	PMoLa	1062	961	900	808
4	PMoY	1063	961	900, 876 <sup>a</sup>	803

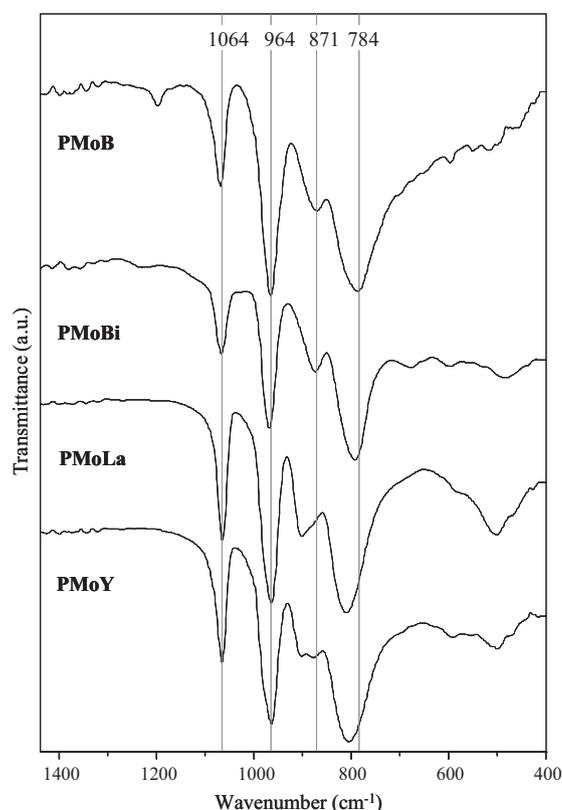
<sup>a</sup> This band is split in two.

to different reasons during the incorporation of Y into the primary structure.

They are usually attributed to vibrations of the bridges between “inter” (Mo–O<sub>b</sub>–Mo) and “intra” (Mo–O<sub>c</sub>–Mo) groups (Mo<sub>3</sub>O<sub>13</sub>). Therefore, for the assignment of each of the bands to two vibration bridges it would be reasonable to consider these two groups as pairs of vibrations of bridge building. Nevertheless, in order to simplify, the two frequencies for a vibration-isolated bridge could be considered, although this is not completely exact.

For a better definition of the species resulting from the interaction of both heteropolyacids with the impregnated support in equilibrium, they were characterized by FTIR. In the spectra of supported HPA some acid bands are overlapped to those of the support. The characteristic spectrum of silica shows bands at 1000, 800, and 470 cm<sup>-1</sup>; there are other bands at 3400 and 1620 cm<sup>-1</sup> attributed to the stretching and bending of OH groups, respectively [7]. In relation to functionalized silica, the main differences are: the N–H stretching band (3300–2600 cm<sup>-1</sup>) broad peak overlapped with the silanol stretching bands of silica and –CH<sub>2</sub>– groups.

The small shoulders at the 3000–2750 cm<sup>-1</sup> region can be assigned to C–H stretching of APS. Also, the functionalizing agent used in the grafting process presents a strong band at the 1110–1050 cm<sup>-1</sup> region attributed to Si–O–C aliphatic groups, which is observed as a transmittance increase of the silica band in the functionalized support. In addition, the APS band at 790 cm<sup>-1</sup>

**Fig. 1.** FTIR spectrum of bulk HPA.

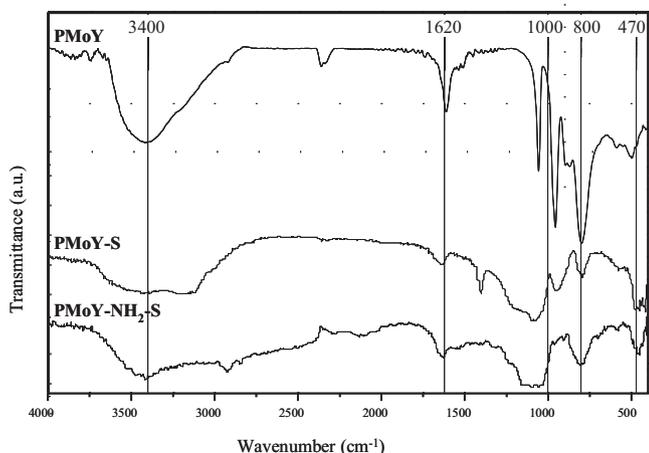


Fig. 2. FTIR spectrum of supported PMoY.

is present without overlapping and a transmittance increase at  $550\text{ cm}^{-1}$  can be seen on the silica band [25].

The FTIR spectra of bulk PMoY and supported on S and S-NH<sub>2</sub> are shown in Fig. 2 to compare the active phase–support interaction. PMoY-S shows masking in the  $1100\text{ cm}^{-1}$  zone, the band at  $951$  and  $794\text{ cm}^{-1}$  as an increase in intensity and a nonoverlapping band at  $869\text{ cm}^{-1}$ . This last band indicates a good interaction between silanols of silica and HPA protons. During the impregnation, an electrostatic interaction is generated, and the HPAs maintain the primary structure. However, when water is incorporated to the support, the Keggin structure can undergo changes and the band at  $1100\text{ cm}^{-1}$  (P–O<sub>a</sub>) could be split into two bands.

N<sub>2</sub> adsorption tests were used to make a textural characterization of the catalysts, and the results ( $S_{\text{BET}}$  (m<sup>2</sup>/g), pore volume (cm<sup>3</sup>/g), and pore size (Å)) are listed in Table 4.

For different types of silica impregnation, the textural characterization results show that impregnation causes a sharp decrease in microporosity, and therefore, in the support surface area, as in PMoB-S (Table 4, entry 2). This is due to a strong HPA diffusion during the impregnation and a small interaction with the support surface. For PMoY-S (Table 4, entry 5), the value of  $S_{\text{BET}}$  is very similar to that of silica ( $287\text{ m}^2/\text{g}$ ); the value obtained for PMoBi-S (Table 4, entry 3) is higher than that of the support. This could be because of the formation of HPA clusters on the surface, without diffusion into the silica. When NH<sub>2</sub>-S is used as support, the  $S_{\text{BET}}$  values of the catalysts are higher than those of functionalized silica. This indicates that there is a big HPA interaction between NH<sub>2</sub> groups and HPA proton. Anyway, these values are small and very close to those of pure Keggin heteropolyacids, conceivably for the reasons previously mentioned. In this point, we reported values of

Table 4  
Textural properties of catalysts.

Entry	Sample	$S_{\text{BET}}$ (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Pore size (Å)
1	S	292	0.13	18.3
2	PMoB-S	21	0.01	22.2
3	PMoBi-S	318	0.15	18.7
4	PMoLa-S	392	0.18	18.9
5	PMoY-S	287	0.13	18.7
6	NH <sub>2</sub> -S	–	–	–
7	PMoB-NH <sub>2</sub> -S	4.8	–	–
8	PMoBi-NH <sub>2</sub> -S	4.4	–	–
9	PMoLa-NH <sub>2</sub> -S	4.4	–	–
10	PMoY-NH <sub>2</sub> -S	4.7	–	–

(–) Experimental error.

Table 5  
Color of impregnated catalysts and impregnated solutions.

Entry	Supported catalyst	Color of supported catalyst	Solution after impregnation
1	PMoB-S	Green	Dark green
2	PMoBi-S	Blue	Dark green
3	PMoLa-S	White	Green
4	PMoY-S	Green	Yellowish green
5	PMoB-NH <sub>2</sub> -S	Bluish white	Colorless
6	PMoBi-NH <sub>2</sub> -S	Light blue	Colorless
7	PMoLa-NH <sub>2</sub> -S	White	Colorless
8	PMoY-NH <sub>2</sub> -S	Bluish white	Colorless

different supports (near  $4\text{ m}^2/\text{g}$ ), with the objective of obtaining a comparative grade.

Before studying the acidic properties, the colors of solids and solutions were determined and are listed in Table 5. The supports are white in both cases. But impregnated catalysts present different coloration for each HPA. This property is close to the internal redox reaction of HPA when Mo is an addenda atom and is indicative of the interaction between HPA and the surface.

For example, after the contact with S, the solution has the same color as bulk HPA, but when the HPAs were supported on functionalized silica, after the impregnation the solutions were colorless. To color solids, a potentiometric method was developed; the measured potential difference is mainly determined by the acidic environment that is around the electrode membrane [3]. In this method, the measured potential difference is mainly determined by the acidic environment around the electrode membrane. The measured electrode potential is an indicator of the surface acidic properties of the dispersed solid particles. An aliphatic amine, such as *n*-butylamine, with a basic dissociation constant of  $10^{-6}$ , allows the potentiometric titration of strong acids. It was suggested that the initial electrode potential ( $E_i$ ) indicates the maximum strength of the acid sites, and the value of meq. amine/g solid where the plateau is reached indicates the total number of acid sites present in the titrated solid [26]. Acidity of the HPA is purely Brønsted in nature. The potentiometric curves obtained by titration with *n*-butylamine of the bulk HPA are presented in Fig. 3.

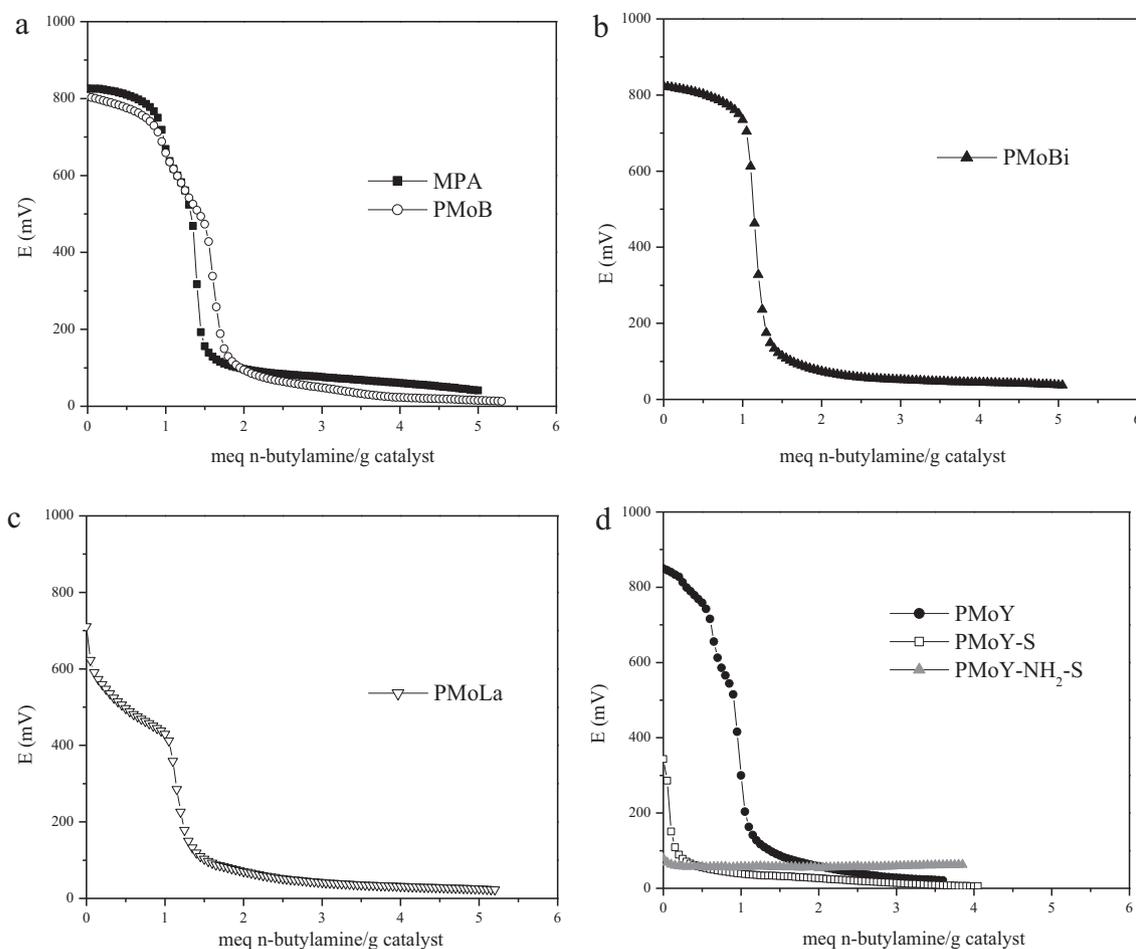
MPA, PMoBi, PMoB and PMoY show very strong acid sites, whereas PMoLa does not have any acid site; its acid strength is much lower than that of the other HPAs. The acid strength of the HPA is related to proton mobility, which in part depends on the negative charge distribution in the heteropolyanion oxygens [4].

In addition, all the supported HPAs do not present acid sites, and the acid strength is lower than that determined for bulk HPA; as an example the curves obtained for PMoY-S and PMoY-NH<sub>2</sub>-S, in comparison with the corresponding bulk PMoY, are presented in Fig. 3d. The acid strengths of bulk and supported HPAs are included in Table 6.

With regard to acidity measurements of supported HPAs, they present a higher acid strength than the support ( $74$  and  $-1\text{ mV}$  for S and NH<sub>2</sub>-S, respectively) but the number of acid sites is almost none. This behavior is related to the different interaction of HPA with silica, which was observed from the adsorption isotherms of both HPAs on the support [10]. During the contact between the

Table 6  
Acid strength ( $E_i$ ) of the catalysts.

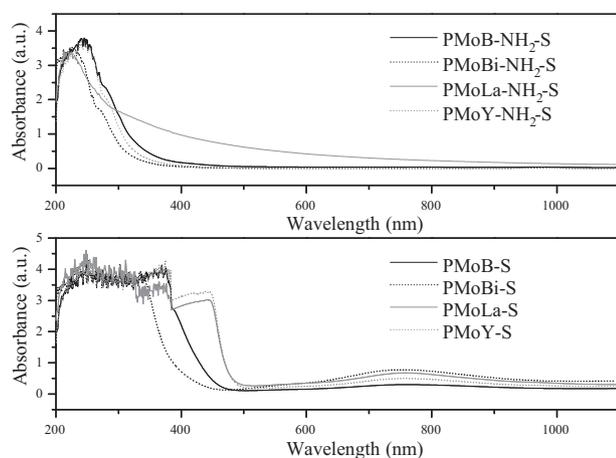
Entry	$E_i$ (mV)				
1	S	74			
2	NH <sub>2</sub> -S	-1			
3	HPA	MPA	PMoB	PMoBi	PMoLa
4	Bulk	826	806	823	711
5	HPA-S	444	478	313	168
6	HPA-NH <sub>2</sub> -S	67	36	27	45
					PMoY
					850
					343
					79



**Fig. 3.** Potentiometric titration curves of bulk HPA. (a) MPA and PMoB; (b) PMoBi; (c) PMoLa; (d) PMoY bulk and supported (PMoY-S and PMo-NH<sub>2</sub>-S).

solution and S, a proton transfer to the silanol groups and an electrostatic interaction of the  $[\text{PMo}_{11}\text{Mo}_{40}]^{3-}$  anion with the protonated silanols take place. In short, the protons are less anchored to the support for the HPA-S catalyst than for HPA-NH<sub>2</sub>-S, due to the weak interaction of HPA and low adsorbed concentration [8]. The supported HPAs present a decrease of the acid strength and the acid sites due to the interaction with the silica. This effect is stronger when functionalized silica is used (Table 6).

Fig. 4 shows UV-visible spectra of the solutions between the HPA solution and the support after 72 h. The band attributed to



**Fig. 4.** UV-visible spectra of solutions after contact with the solid.

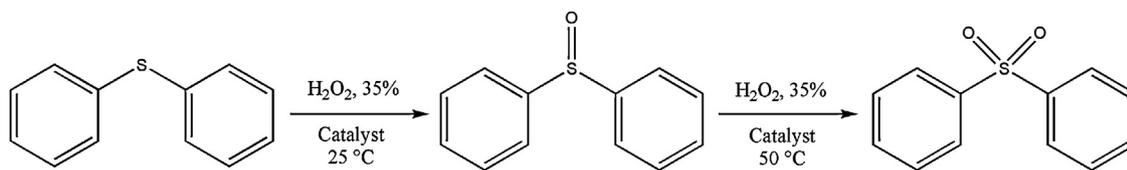
oxygen-metal transfers at 210–230 nm can be seen in all the spectra. Also in S impregnation, another band that extends from 240 up to 545 nm is observed. In S-supported catalysts the band near 600 nm is assigned to the heteropoly blue of Mo species, and this HPA structure changes the color of both the solid and the solution. In addition, this indicates Mo in octahedral position in the Keggin structure. The HPA solution has different colors after the contact with silica and functionalized silica, and it is possible that the initial species no longer exist, which is indicative of very interesting redox properties for their performance as catalysts.

### 3.2. Catalytic test

Initially, the catalytic performance of the different bulk synthesized heteropolyacids was evaluated in a homogeneous oxidation reaction. The oxidation of diphenyl sulfide with aqueous hydrogen peroxide (35%, w/v) was selected as the model reaction (Scheme 2). Ethanol was chosen as reaction solvent because it gives a homogeneous phase with the reagents and it is a nontoxic and safe solvent.

We first screened the selective oxidation of diphenyl sulfide to diphenyl sulfoxide using the different catalysts (Table 7).

The blank experiment was performed in the absence of the catalyst using an almost stoichiometric amount of aqueous H<sub>2</sub>O<sub>2</sub> (35%, w/v; 0.15 mL, 1.5 mmol). Under these conditions, the reaction conversion was very low (5% for 7 h), at 25 °C (Table 7, entry 1), but when the HPA is added, the conversion increases to values close to 60%. Under these conditions, PMoB and PMoY showed the best performance. When PMoB was used (Table 7, entry 3), a conversion of 64% was observed at 7 h, with 100% of sulfoxide selectivity.



**Scheme 2.** Selective oxidation of diphenyl sulfide.

**Table 7**

Selective oxidation of diphenyl sulfide to diphenyl sulfoxide employing different synthesized HPA catalysis in homogeneous conditions.<sup>a</sup>

Entry	Catalyst	Sulfide conversion (%) <sup>b</sup>	Sulfoxide selectivity (%) <sup>b</sup>	Sulfone selectivity (%) <sup>b</sup>
1	None	5	100	–
2	MPA	58	89	11
3	PMoB	64	100	–
4	PMoBi	68	90	10
5	PMoLa	73	94	6
6	PMoY	60	100	–

<sup>a</sup> Reactions were performed by reacting sulfide 1 mmol and 35% (w/v) H<sub>2</sub>O<sub>2</sub> (0.15 mL, 1.5 mmol) in ethanol 96% (4 mL) for 7 h. Catalyst, 12 mg and temperature, 25 °C.

<sup>b</sup> The conversion and selectivity (%) were determined by GC analysis.

Similarly, PMoY showed a conversion and selectivity of 60% and 100%, respectively, in this time period (Table 7, entry 6). Under the same reaction conditions, commercial MPA only gives a sulfoxide selectivity of 89% (Table 7, entry 2). In all experiments performed, the new synthesized catalyst showed more activity and selectivity in the diphenyl sulfide oxidation to sulfoxide than the corresponding commercial MPA.

Similarly, we performed the selective oxidation of diphenyl sulfide to diphenyl sulfone using an excess of H<sub>2</sub>O<sub>2</sub> (35%, w/v; 0.7 mL, 7 mmol) at 50 °C. Under these conditions it is possible to obtain diphenyl sulfone selectively and the results at different reaction times are summarized in Table 8. PMoY presented the best performance in short reaction times.

When this catalyst is used (Table 8, entry 5), a conversion of 76% is observed at 0.5 h with a 63% of sulfone selectivity. All the catalysts, except PMoLa, showed 100% of sulfone selectivity after 8 h (Table 8, entries 1–5). Even though the HPAs show a good performance in this reaction, the bulk HPAs are completely soluble

**Table 8**

Selective oxidation of diphenyl sulfide to diphenyl sulfone employing different synthesized HPA catalysis in homogeneous conditions.<sup>a</sup>

Entry	Catalyst	Sulfide conversion (%) <sup>b</sup>	Sulfoxide selectivity (%) <sup>b</sup>	Sulfone selectivity (%) <sup>b</sup>
1	MPA	73	90	10
		100 <sup>c</sup>	30	70
		100 <sup>d</sup>	0	100
2	PMoB	62	58	42
		100 <sup>c</sup>	33	67
		100 <sup>d</sup>	0	100
3	PMoBi	100	100	0
		100 <sup>c</sup>	15	85
		100 <sup>d</sup>	0	100
4	PMoLa	77	84	16
		100 <sup>c</sup>	38	62
		100 <sup>d</sup>	9	91
5	PMoY	76	37	63
		100 <sup>c</sup>	23	77
		100 <sup>d</sup>	0	100

<sup>a</sup> Reactions were performed by reacting sulfide 1 mmol and 35% (w/v) H<sub>2</sub>O<sub>2</sub> (0.7 mL, 7.0 mmol) in ethanol 96% (4 mL) for 0.5 h. Catalyst, 12 mg and temperature, 50 °C.

<sup>b</sup> The conversion and selectivity (%) were determined by GC analysis.

<sup>c</sup> Reaction time 4 h.

<sup>d</sup> Reaction time 8 h.

**Table 9**

Selective oxidation of diphenyl sulfide to diphenyl sulfoxide employing the different synthesized HPA supported on silica.<sup>a</sup>

Entry	Catalyst	Sulfide conversion (%) <sup>b</sup>	Sulfoxide selectivity (%) <sup>b</sup>	Sulfone Selectivity (%) <sup>b</sup>
1	PMoB–S	69	94	6
2	PMoBi–S	50	90	10
3	PMoY–S	79	95	5
4	PMoY–S <sup>c</sup>	45	95	5

<sup>a</sup> Reactions were performed by reacting sulfide 1 mmol and 35% (w/v) H<sub>2</sub>O<sub>2</sub> (0.15 mL, 1.5 mmol) in ethanol 96% (4 mL) for 10 h. Catalyst, 50 mg and temperature, 25 °C.

<sup>b</sup> The conversion and selectivity (%) were determined by GC analysis.

<sup>c</sup> Catalyst reuse.

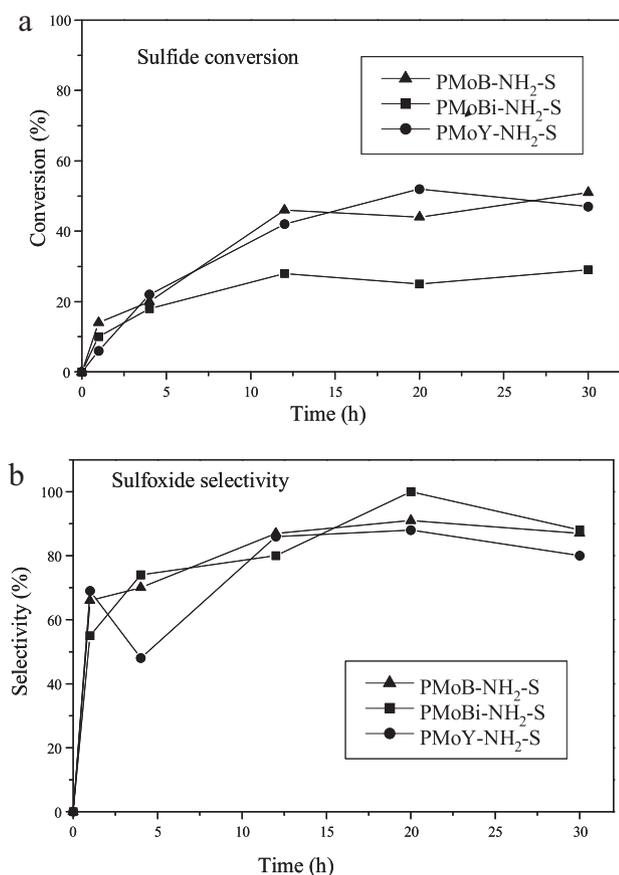
in the reaction medium, and their isolation and reuse are difficult. In order to carry out the reaction in heterogeneous conditions, some more active HPAs were supported on silica. Table 9 lists the results obtained using PMoB, PMoBi and PMoY supported on silica (PMoB–S, PMoBi–S, and PMoY–S) in the selective diphenyl sulfide oxidation to diphenyl sulfoxide at 25 °C.

Silica-supported MPA was studied previously in the selective oxidation of sulfide to sulfones [27]. The yttrium catalyst supported on silica (PMoY) shows the best performance. When this catalyst is used under the selective diphenyl sulfide oxidation to sulfoxide conditions, a conversion of 79% is observed at 10 h, with a 95% of sulfoxide selectivity (Table 9, entry 3). After the reaction ended, the catalyst was isolated by centrifugation and reused under the same conditions. However, a lower conversion than in the first use was obtained (Table 9, entry 4), due to the leaching of HPA from the silica support in the reaction media.

To avoid the leaching of HPA, amino-functionalized silica was used as support. These catalysts were tested in the diphenyl sulfide oxidation at 25 °C employing a nearly stoichiometric amount of aqueous 35% H<sub>2</sub>O<sub>2</sub> (0.15 mL, 1.5 mmol), for 1 mmol of substrate. Fig. 5a shows diphenyl sulfide conversion as a function of time of three representative catalysts: PMoB–NH<sub>2</sub>–S, PMoBi–NH<sub>2</sub>–S, and PMoY–NH<sub>2</sub>–S. In the three cases, the catalytic activity decreases compared with the use of bulk catalyst; these catalysts have the advantage of being insoluble in the mixture reaction.

The reaction time required for reaching the maximum conversion was 20 h, after that, sulfide conversion remained constant. The best two catalysts for the reaction performed were PMoY–NH<sub>2</sub>–S and PMoB–NH<sub>2</sub>–S, contrary to the use of PMoBi–NH<sub>2</sub>–S that gives lower conversion. For example, PMoY–NH<sub>2</sub>–S showed the best performance (52%, 20 h) and PMoBi–NH<sub>2</sub>–S gave only 27% at 10 h (Fig. 5a). With regard to the selectivity toward diphenyl sulfoxide, the three catalysts presented similar results. The highest values are achieved at 20 h of reaction, and selectivity decreases due to diphenyl sulfone formation (Fig. 5b).

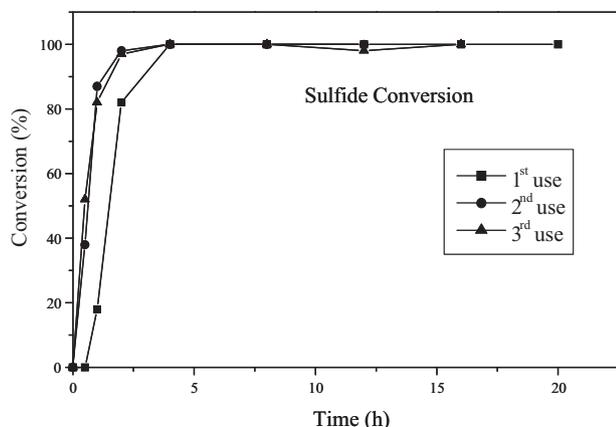
With the objective of obtaining diphenyl sulfone selectivity, the catalytic activity of selected HPAs was tested at 50 °C using an excess of aqueous H<sub>2</sub>O<sub>2</sub>. The best activity was obtained for PMoB–NH<sub>2</sub>–S and PMoY–NH<sub>2</sub>–S, in short times (results not shown). In addition, PMoY–NH<sub>2</sub>–S presented the best performance for diphenyl sulfone selectivity.



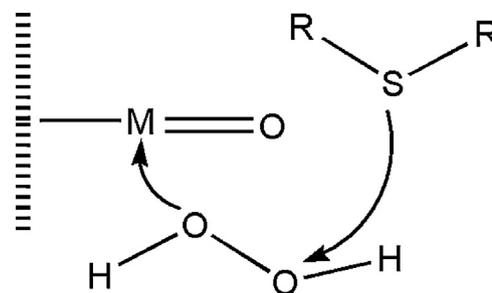
**Fig. 5.** (a) Sulfide conversion vs. time, at 25 °C, using different HPA supported on functionalized silica. (b) Sulfoxide selectivity vs. time, at 50 °C, using different HPA supported on functionalized silica.

Due to the need to obtain a catalyst for green processes, the use of a recycled catalyst is required for reducing the catalytic cost. PMoY-NH<sub>2</sub>-S was selected to prove reusability under the same reaction conditions. When the reaction was completed, the catalyst (insoluble) was filtered, dried in vacuum (20 °C), and reused. The catalyst was used and reused for three cycles with similar activity. Fig. 6 presents the conversion of diphenyl sulfide as a time function for the use and reuses, and no appreciable loss of activity is shown after three cycles.

The catalyst prepared using hydrogen peroxide during the impregnation, PMoY-NH<sub>2</sub>-S<sub>(P)</sub>, was tested in the diphenyl sulfide



**Fig. 6.** Use and reuse of PMoY-NH<sub>2</sub>-S, at 50 °C, for sulfide conversion vs. time.



**Scheme 3.** Plausible activation of hydrogen peroxide for HPA.

oxidation to diphenyl sulfone at 50 °C using an excess of aqueous H<sub>2</sub>O<sub>2</sub>. The results are similar to that obtained with PMoY-NH<sub>2</sub>-S under the same conditions: 100% sulfide conversion is reached at 4 h, for both catalysts. However, sulfone selectivity is slightly higher for PMoY-NH<sub>2</sub>-S than for PMoY-NH<sub>2</sub>-S<sub>(P)</sub> at 4 h (53% and 35%, respectively), 100% of selectivity being achieved at 12 h for both catalysts. PMoY-NH<sub>2</sub>-S<sub>(P)</sub> was reused and no appreciable loss of activity is shown after three cycles, as in the case where PMoY-NH<sub>2</sub>-S was employed.

A plausible mechanism of this reaction involves the formation of peroxy-molibdate species and the subsequent nucleophilic attack of the sulfur atom in the sulfide on the peroxy species. Indeed, it is known that thioethers are oxidized to sulfoxides by electrophilic oxidants. Mechanistically, it is believed that the electrophilicity of the peroxide oxygen of H<sub>2</sub>O<sub>2</sub> is increased by an oxometal group (M=O<sub>d</sub>) in the HPA (Scheme 3) [28].

#### 4. Conclusions

Four new HPAs with Keggin structure, based on MPA, were synthesized and their structure was investigated by diverse techniques. These Keggin-type HPAs were used as catalysts in the diphenyl sulfide oxidation to diphenyl sulfoxide or diphenyl sulfone, with the eco-friendly H<sub>2</sub>O<sub>2</sub> as oxidant. The replacement of one Mo by another atom in the Keggin structure enhances the catalytic activity of HPA with respect to commercial MPA, due to different properties of the doping atoms, such as electronegativity.

With the purpose of recovering the catalyst more easily after the reaction and developing a green process, the HPAs were supported on silica and amino-functionalized silica, by the equilibrium adsorption technique.

The supported HPAs on amino-functionalized silica were reused without loss of their catalytic activity after three reaction cycles. This indicates the HPA is strongly attached to this support. The main advantages of this procedure are the operational simplicity, the cleanness of reaction, and the very good yields attained. This process can be extended to other aryl-alkyl sulfides. Using an excess of aqueous H<sub>2</sub>O<sub>2</sub>, the reaction is highly selective and proceeds in high yield to sulfone, providing an excellent synthesis method of such compounds.

PMoY, chosen for its performance in the reaction system, was impregnated on NH<sub>2</sub>-S using H<sub>2</sub>O<sub>2</sub> (PMoY-NH<sub>2</sub>-S<sub>(P)</sub>) and was tested in the diphenyl sulfide oxidation to sulfone, just to compare the behavior of HPA during impregnation. Although the results from the studied reaction do not show a great improvement, this new method of impregnation is being investigated by our group.

#### Acknowledgments

The authors thank E. Soto and D. Peña for their experimental contribution for the measurements of S<sub>BET</sub> and, GC respectively; and CONICET and UNLP for their financial support.

## References

- [1] B. Török, Á. Molnár, N. Balogh, I. Kiricsi, I. Pálkó, L.I. Horváth, *Appl. Catal. A: Gen.* 158 (1997) L17–L25.
- [2] J.F. Keggin, *Proc. R. Soc. Lond. A* 144 (1934) 75–100.
- [3] G. Romanelli, P. Vázquez, N. Quaranta, L. Pizzio, J. Autino, M. Blanco, C. Cáceres, *Appl. Catal. A: Gen.* 261 (2004) 163–170.
- [4] G.P. Romanelli, J.C. Autino, M.N. Blanco, L.R. Pizzio, *Appl. Catal. A: Gen.* 295 (2005) 209–215.
- [5] C. Hu, M. Hashimoto, T. Okuhara, M. Misono, *J. Catal.* 143 (1993) 437–448.
- [6] A.G. Sathicq, G.P. Romanelli, V. Palermo, P.G. Vázquez, H.J. Thomas, *Tetrahedron Lett.* 49 (2008) 1441–1444.
- [7] P. Vázquez, L. Pizzio, C. Cáceres, M. Blanco, H. Thomas, E. Alesso, L. Finkielstein, B. Lantaño, G. Moltrasio, J. Aguirre, *J. Mol. Catal. A: Chem.* 161 (2000) 223–232.
- [8] P. Vázquez, L. Pizzio, G. Romanelli, J. Autino, C. Cáceres, M. Blanco, *Appl. Catal. A: Gen.* 235 (2002) 233–240.
- [9] G.I. Kapustin, T.R. Brueva, A.L. Klyachko, M.N. Timofeeva, S.M. Kulikov, I.V. Kozhevnikov, *Kinet. Katal.* 31 (1991) 896–898.
- [10] P.G. Vázquez, M.N. Blanco, C.V. Cáceres, *Catal. Lett.* 60 (1999) 205–215.
- [11] L.R. Pizzio, C.V. Cáceres, M.N. Blanco, *Appl. Catal. A: Gen.* 167 (1998) 283–294.
- [12] L.R. Pizzio, C.V. Cáceres, M.N. Blanco, *J. Colloid Interface Sci.* 190 (1997) 318–326.
- [13] F. Bonadies, F. De Angelis, L. Locati, A. Scettri, *Tetrahedron Lett.* 37 (1996) 7129–7130.
- [14] K. Kaczorowska, Z. Kolarska, K. Mitka, P. Kowalski, *Tetrahedron* 61 (2005) 8315–8327.
- [15] V. Palermo, A.G. Sathicq, P.G. Vázquez, H.J. Thomas, G.P. Romanelli, *React. Kinet. Mech. Catal.* 104 (2011) 181–195.
- [16] B.M. Trost, *Chem. Rev.* 78 (1978) 363–382.
- [17] M.C. Carreño, *Chem. Rev.* 95 (1995) 1717–1760.
- [18] B. Karimi, M. Ghoreishi-Nezhad, J.H. Clark, *Org. Lett.* 7 (2005) 625–628.
- [19] C. Rocchiccioli-Deltcheff, M. Amirouche, M. Che, J.M. Tatibouët, M. Fournier, *J. Catal.* 125 (1990) 292–310.
- [20] A. Tarlani, M. Abedini, A. Nemat, M. Khabaz, M.M. Amini, *J. Colloid Interface Sci.* 303 (2006) 32–38.
- [21] P. Villabril, G. Romanelli, P. Vázquez, C. Cáceres, *Appl. Catal. A: Gen.* 270 (2004) 101–111.
- [22] V.M. Fuchs, L.R. Pizzio, M.N. Blanco, *Catal. Today* 133–135 (2008) 181–186.
- [23] C. Rocchiccioli-Deltcheff, M. Fournier, R. Franck, R. Thouvenot, *Inorg. Chem.* 22 (1983) 207–216.
- [24] <http://www.lennotech.com/espanol/tabla-periodica.htm> (November 2012).
- [25] L. Pizzio, G. Romanelli, P. Vázquez, J. Autino, M. Blanco, C. Cáceres, *Appl. Catal. A: Gen.* 308 (2006) 153–160.
- [26] S.G. Casuscelli, M.E. Crivello, C.F. Perez, G. Ghione, E.R. Herrero, L.R. Pizzio, P.G. Vázquez, C.V. Cáceres, M.N. Blanco, *Appl. Catal. A: Gen.* 274 (2004) 115–122.
- [27] V. Palermo, G.P. Romanelli, P.G. Vázquez, *Phosphorus, Sulfur Silicon Relat. Elem.* 184 (2009) 3258–3268.
- [28] A.L. Maciucă, C.E. Ciocan, E. Dumitriu, F. Fajula, V. Hulea, *Catal. Today* 138 (2008) 33.