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Author: Romina Frenzel Ángel G. Sathicq Mirta N. Blanco  
Gustavo P. Romanelli Luis R. Pizzio



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**Carbon-supported metal-modified lacunary tungstosilicic  
polyoxometallates used as catalysts in the selective oxidation of  
sulfides**

**Romina Frenzel, Ángel G. Sathicq, Mirta N. Blanco, Gustavo P. Romanelli\*, Luis R. Pizzio\***

Centro de Investigación y Desarrollo en Ciencias Aplicadas “Dr. Jorge J. Ronco” (CINDECA),  
CCT-La Plata-CONICET, Departamento de Química, Facultad de Ciencias Exactas, Universidad  
Nacional de La Plata, 47 N° 257 (B1900AJK) La Plata

Corresponding authors:

Dr. Luis R. Pizzio and Gustavo P. Romanelli,

Centro de Investigación y Desarrollo en Ciencias Aplicadas “Dr. Jorge J. Ronco” (CINDECA),  
CCT-LaPlata-CONICET, Facultad de Ciencias Exactas, Universidad Nacional de La Plata,  
47 N° 257 (B1900AJK) La Plata, Argentina.

e-mail: [lpizzio@quimica.unlp.edu.ar](mailto:lpizzio@quimica.unlp.edu.ar) and [gpr@quimica.unlp.edu.ar](mailto:gpr@quimica.unlp.edu.ar)

Graphical abstract

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Highlights

Metal modified lacunary tungstosilicic polyoxometallates supported on carbon

Catalytic selective oxidation of sulfides to sulfoxides and sulfones

$[\text{SiW}_{11}\text{O}_{39}]^{8-}$  was modified with transition metal ions where  $M = \text{Mn}^{2+}, \text{Fe}^{2+}, \text{Cu}^{2+}$  or  $\text{Co}^{2+}$

The catalysts can be reused without appreciable loss of the catalytic activity

The reaction is useful due to status of compounds in biological molecules synthesis

## Abstract

Lacunary tungstosilicic polyoxometallates modified with transition metal ions  $[\text{SiW}_{11}\text{O}_{39}\text{M}(\text{H}_2\text{O})]^{6-}$ , where  $M = \text{Mn}^{2+}, \text{Fe}^{2+}, \text{Co}^{2+}$  or  $\text{Cu}^{2+}$ , were synthesized and supported on activated carbon to obtain the SiW11MC catalysts. The samples were characterized by FT-IR, XRD,  $\text{N}_2$  adsorption–desorption measurements, and the acidic properties were determined using the isopropanol dehydration test reaction.

The activity and selectivity of the catalysts were evaluated in the selective oxidation of a series of sulfides to sulfoxides or sulfone. The reaction was carried out in acetonitrile as solvent using  $\text{H}_2\text{O}_2$  35% p/v as a clean oxidant. The conversion values decreased in the following order:  $\text{SiW11MnC} > \text{SiW11FeC} > \text{SiW11CuC} > \text{SiW11CoC}$ . The catalysts were reused without appreciable loss of their catalytic activity. It was found that the activity of the catalysts decreases in parallel with the increment in the reduction temperature values. The most easily reducible catalyst displayed the highest conversion values. We found a convenient and selective procedure for oxidizing sulfides to sulfoxides or sulfones using aqueous hydrogen peroxide and a catalytic amount of lacunary tungstosilicic polyoxometallates supported on carbon at low

temperatures (20–50 °C) in a reasonably short reaction time.

*Keywords:* Supported metal-substituted polyoxometallates, carbon, sulfide oxidation, hydrogen peroxide

## 1. Introduction

The development of new catalytic systems for selective organic synthesis is one of the challenging tasks in Organic Chemistry. In recent years, the search of ecofriendly benign chemical methodologies has received much attention from chemistry communities, because they are essential for the conservation of the global ecosystem. From this viewpoint, in the last two decades, very useful procedures involving catalysis and hydrogen peroxide, as oxidant, have been developed. They promote the efficient organic substrate oxidation, due to their low cost, effective oxygen content, safety in storage and operation, and mainly the ecofriendly character of hydrogen peroxide [1–3].

Catalysis using heteropolyacids and related compounds is a field of increasing importance worldwide. Numerous developments are being carried out in industrial processes and basic research. Heteropolyacids present a very strong acidity and redox properties, which can be changed by varying the chemical composition of the heteropolyanion. Different transformations catalyzed by heteropolyacids in heterogeneous and homogeneous phases have been reviewed [4–7]. Recently, our research group has used Keggin and Wells-Dawson heteropolyacids/aqueous hydrogen peroxide systems, in a series of oxidation processes, including phenol [8], alcohol [9], amine [10], sulfide [11], and 1,4-dihydropyridine [12] oxidation.

Transition metal-modified lacunary heteropolycompounds with Keggin structure, obtained by modification of the  $[\text{PW}_{11}\text{O}_{39}]^{7-}$  lacunary phase with ions of the transition metals Ni (II), Fe (III), Co (II), Zn (II), Mn (II) or Cu (II) have been used as catalysts in the oxidation of cyclohexane with aqueous  $\text{H}_2\text{O}_2$  [13], in methyl isobutyrate and cyclohexene with oxygen [14], and in the oxidation of 2-(methylthio)-benzothiazole with aqueous  $\text{H}_2\text{O}_2$  [15]. However, transition metal-modified lacunary heteropolycompounds with Keggin structure, obtained by modification of the  $[\text{SiW}_{11}\text{O}_{39}]^{8-}$  lacunary phase with ions of the transition metals, have been little studied in catalytic oxidation processes.

Meanwhile, sulfoxides and sulfones are important intermediates in organic chemistry due to their application in basic and applied research, especially because they are versatile intermediates for the preparation of biologically important products [16], including therapeutic agents such as antiulcer, antibacterial, antifungal, antiatherosclerotic, antihypertensive and cardiogenic agents as well as psychotropics and vasodilators [3, 17-18]. Omeprazole and dapsone are two typical examples of the extensive application in the pharmaceutical industry. Omeprazole (one of the most widely prescribed drugs internationally) is a proton pump inhibitor used in the treatment of dyspepsia, peptic ulcer disease, and gastroesophageal and laryngopharyngeal reflux [19], and

dapsone, an antibacterial most commonly used for the treatment of leprae infections and in the treatment of malaria [20] (Figure 1).

(Figure 1)

The most appropriate method for the preparation of sulfoxide and sulfone compounds is the selective oxidation of the corresponding sulfide. In general, the system formed by the oxidant/catalyst is the same for the selective oxidation of sulfides to sulfoxides as that of sulfones. The only change is often the more drastic reaction conditions required for obtaining sulfones. Hydrogen peroxide may be used as an electrophilic reagent for the direct selective oxidation of sulfides to sulfoxides or sulfones. However, the rate of reaction can be greatly improved by the use of a catalyst [3]. Some of the most recent catalysts are: silica-vanadia [21], oxalic acid dihydrate [22], metalloporphyrin [23], *p*-toluenesulfonic acid [24], sulfamic acid [25], titanosilicates [26], heteropolyacids [27], and many others.

The objective of this paper is to study both the use of carbon-supported transition metal-modified lacunary tungstosilicic polyoxometallates as catalysts in the selective oxidation of sulfides to sulfoxides or sulfones (Scheme 1) and the effect of the metal introduced in the heteropolyacid structure, on the activity and selectivity on the reaction test. A relation between the substrate structure and conversion rate was also found.

(Scheme 1)

## 2. Experimental

### 2.1. Catalyst synthesis

### 2.1.1. Transition metal-modified lacunary tungstosilicic polyoxometallate (TMPOM) synthesis

The TMPOM ions  $[\text{SiW}_{11}\text{O}_{39}\text{M}]^{6-}$ , ( $\text{M} = \text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Co}^{2+}$ ) were synthesized according to the literature data [28–30]. An aqueous solution of  $\text{H}_4\text{SiW}_{12}\text{O}_{40}\cdot 23\text{H}_2\text{O}$  was alkalized with aqueous  $\text{NaHCO}_3$  solution up to a pH value of 5.0–5.5, which resulted in the formation of the lacunary heteropolyanion  $[\text{SiW}_{11}\text{O}_{39}]^{8-}$ . In order to introduce the transition metal ion into the octahedral lacuna, the obtained solution of  $[\text{SiW}_{11}\text{O}_{39}]^{8-}$  and an aqueous solution of the transition metal salt were mixed and stirred at 60–90°C. The sodium salts of the lacunary heteropolycompounds were obtained by solvent evaporation and recrystallization from water. They were dried at 70°C before their characterization by thermal and physicochemical techniques.

### 2.1.2. Supported catalyst synthesis

The support used was a commercial activated carbon ground to a mean particle size of 1 mm, previously washed with 0.1 N solutions of NaOH and HCl, and then treated with a  $\text{HNO}_3$  30% solution under heating to reflux for 2 h. It has a surface area of 806  $\text{m}^2/\text{g}$ , and a mean pore diameter below 2 nm. The carbon was impregnated using the incipient wetness method, with  $[\text{SiW}_{11}\text{O}_{39}\text{M}]^{6-}$  water solutions (0.14 M), in order to add  $1.0 \cdot 10^{-4}$  mol of the lacunary heteropolycompounds per gram of carbon. The catalysts were kept at room temperature till dryness and then thermally treated at 70 °C for 24 h. They will be named SiW11MC ( $\text{M} = \text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Co}^{2+}$ ). A fraction of the solids obtained were washed with ethanol, acetonitrile or toluene, for 24 h. For this leaching experiment, 1 g of solid was placed in contact with 4 mL of solvent at 20 °C under constant stirring for a selected time.

The tungsten concentration in the solutions, after leaching, was determined by atomic absorption spectrometry. The calibration curve method was used, with standards prepared in the

laboratory. An IL Model 457 spectrophotometer, with single channel and double beam, and monochromator with a 330 mm focal distance, was used. The light source was a hollow monochromator lamp. The analysis was carried out at wavelength 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).

## 2.2. Catalyst characterization

### 2.2.1 FT-IR spectroscopy

Fourier transform infrared spectroscopy (FT-IR) of  $[\text{SiW}_{11}\text{O}_{39}\text{M}]^{6-}$  sodium salts and catalysts dried at 70 °C for 24 h was obtained in the 400–4000  $\text{cm}^{-1}$  wavenumber range using Bruker IFS 66 FT-IR spectrometer.

### 2.2.2 X-ray diffraction

X-ray diffraction (XRD) patterns were recorded on the same samples that had been analyzed by FT-IR. The equipment used to this end was Philips PW-1732 with built-in recorder, using Cu  $K\alpha$  radiation, nickel filter, 30 mA and 40 kV in the high-voltage source, and scanning angle between 5 and 60° of  $2\theta$  at a scanning rate of 1° per min.

### 2.2.3. SEM analysis

The distribution of  $[\text{SiW}_{11}\text{O}_{39}\text{M}]^{6-}$  anions along the width of the carbon granules was measured with a Philips Model 505 scanning electron microscope with an energy dispersive X-ray analysis (EDAX) system, following a technique previously reported [31, 32].

### 2.2.4. Isopropanol decomposition

The isopropanol dehydration test reaction was carried out in a conventional flow fixed-bed reactor at atmospheric pressure and 180 °C. The gas carrier was helium and the isopropanol volumetric flow was 0.126  $\text{cm}^3/\text{min}$  in a total flow of 50  $\text{cm}^3/\text{min}$ . The reaction products were

quantified by gas chromatography, using a thermal conductivity detector. The specific isopropanol conversion ( $CS_{\text{PROP}}$ ) was calculated under differential conversion conditions (conversions lower than 10%) and expressed as mol propene/mol SiW<sub>11</sub>M. s

### *2.2.5 Temperature programmed reduction*

Temperature programmed reduction (TPR) of the samples dried at 70 °C (100 mg, 60 to 100 mesh) was obtained using a mixture of H<sub>2</sub> (5%) in Ar flowing at 90 mL/min. The heating rate was kept at 10 °C/min until reaching a temperature of 1000 °C. The amount of H<sub>2</sub> consumed during reduction was determined using a thermal conductivity detector.

## **2.3. Catalytic test**

### *General remarks*

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

### *Sample analysis*

Samples were withdrawn from the organic phase at 15-minute intervals. Each volume sample was approximately 20 µL and it was diluted with 1–2 mL of acetonitrile, the concentrations were calculated for the determination of the corresponding areas. The capillary column was a 30 m Chromopack CP Sil 8 CB, 0.32 mm in diameter.

### *General procedure for the oxidation of sulfide to sulfoxide*

A solution of sulfide (1 mmol) and catalyst (100 mg), in acetonitrile (9 mL), was added to H<sub>2</sub>O<sub>2</sub> 35% (w/v) (2 mmol). The mixture was stirred at 20 °C for a time period (see Tables 1 and 2). The solvent was evaporated and then H<sub>2</sub>O (5 mL) was added. The substrate was extracted with toluene (2 x mL) and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>; filtration and evaporation afforded the corresponding sulfoxides. The solid crude sulfoxides were purified by recrystallization to afford the pure sulfoxides.

#### *General procedure for the oxidation of sulfide to sulfone*

A solution of sulfide (1 mmol) and catalyst (100 mg), in acetonitrile (9 mL), was added to H<sub>2</sub>O<sub>2</sub> 35% (w/v) (10 mmol). The mixture was stirred at 50 °C for a time period (see Tables 1 and 2). The solvent was evaporated and then H<sub>2</sub>O (5 mL) was added. The substrate was extracted with toluene (2 x mL) and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>; filtration and evaporation afforded the corresponding sulfoxides. The crude solids were purified by recrystallization to afford the pure sulfones.

#### *Electronic 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” modulus available in HyperChem 5.0. Each molecular structure was firstly preoptimized with the Molecular Mechanics Force Field (MM+) procedure, and the resulting geometry was further refined by For Peer Review Only means of the semiempirical method PM3 (Parametric Method-3). A gradient norm limit of 0.01 kcal Å<sup>-1</sup> was chosen.

#### *Electronic impact mass spectra of the representative compounds*

Diphenyl sulfoxide: EIMS, m/z (Relative intensity): 202 ( $M^+$ , 83%), 185 (18%), 154 (73%), 109 (90%), 97 (48%), 77 (78%), 65 (59%), 51 (100%), 39 (32%).

Diphenyl sulfone: EIMS, m/z (Relative intensity): 218 ( $M^+$ , 36%), 153 (7%), 125 (100%), 97 (12%), 77 (37%), 51 (23%).

Di-n-butyl sulfoxide: EIMS, m/z (Relative intensity): 162 ( $M^+$ , 5%), 145 (11%), 106 (32%), 89 (45%), 57 (58%), 41 (98%), 29 (100%).

Benzyl phenyl sulfoxide: EIMS, m/z (Relative intensity): 216 ( $M^+$ ) (10%), 182 (16%), 165 (2%), 125 (5%), 91 (100%), 77 (11%), 65 (18%).

Di-n-butyl sulfone: EIMS, m/z (Relative intensity): 178 ( $M^+$ , 3%), 149 (2%), 123 (32%), 81 (4%), 57 (100%), 41 (52%), 29 (56%).

Ethyl phenyl sulfone: EIMS, m/z (Relative intensity): 170 ( $M^+$ , 28%), 142 (18%), 141 (23%), 125 (8%), 94 (56%), 78 (71%), 77 (100%), 51 (55%).

Benzyl phenyl sulfone: EIMS, m/z (Relative intensity): 232 ( $M^+$ , 4%), 167 (2%), 165 (2%), 152 (15%), 91 (100%), 77 (11%), 65 (17%), 51 (13%).

Di-benzyl sulfone: EIMS, m/z (Relative intensity): 182 ( $M^+$ , 10%), 91 (100%), 65 (24%), 39 (11%).

Phenyl methyl sulfone: EIMS, m/z (Relative intensity): 156 ( $M^+$ , 29%), 141 (27%), 94 (33%), 77 (100%), 51 (8%), 39 (9%).

Methyl p-tolyl sulfone: EIMS, m/z (Relative intensity): 170 ( $M^+$ , 28%), 155 (30%), 107 (22%), 91 (100%), 77 (7%), 65 (22%), 39 (11%).

1,1-Dioxide-2,3,4,5-tetrahydrothiophene (sulfolane): EIMS, m/z (Relative intensity): 120 ( $M^+$ , 44%), 92 (14%), 56 (85%), 55 (69%), 41 (100%), 28 (60%).

Phenyl vinyl sulfone: EIMS, m/z (Relative intensity): 168 ( $M^+$ , 18%), 125 (100%), 77 (64%), 51 (27%), 27 (6%).

4,4'-Diaminodiphenyl sulfone (dapsone): EIMS, m/z (Relative intensity): 248 ( $M^+$ , 83%), 184 (8%), 140 (62%), 108 (100%), 92 (37%), 65 (48%), 39 (18%).

2-(Methylthio)-benzothiazole sulfoxide: EIMS, m/z (Relative intensity): 197 (62%)  $M^+$ ; 182 (78); 153 (60); 151 (100); 150 (64); 134 (42%); 123 (15); 108 (25); 90 (26); 50 (30); 39 (98).

2-(Methylthio)-benzothiazole sulfone: EIMS, m/z (Relative intensity): m/z (I %): 197 (18)  $M^+$ ; 150 (100); 134 (42); 108 (20); 90 (25); 50 (24); 39 (74).

### 3. Results and discussion

#### 3.1. Catalyst characterization

The characteristics of XRD patterns of  $SiW_{11}MC$  samples were similar to those of the original carbon, so neither the diffraction lines of the  $Na_6[SiW_{11}O_{39}M]$  salts, nor those of other crystalline phases were detected. On the other hand, according to the results obtained by energy dispersive X-ray analysis (EDAX), a uniform distribution of the modified lacunary Keggin anions along the width of the carbon particles was obtained. This indicates that the species present onto the support surface are highly dispersed as a noncrystalline form, owing to the interaction with the support.

The FT-IR spectrum of  $Na_8[SiW_{11}O_{39}]$  showed the main bands of the lacunar anion placed at 1008, 959, 882, 869, 794, and 720  $cm^{-1}$  (Figure 2a). The spectrum of  $Na_5[SiW_{11}O_{39}Mn]$  (Figure 2b) displayed bands at 1002, 959, 899, 810, 701, and 541  $cm^{-1}$ . They are in agreement with those reported by Rocchiccioli et al. [33] and are considered typical of the transition metal-modified lacunary heteropolycompounds [33]. The FT-IR spectra of the other  $Na_6[SiW_{11}O_{39}M]$  salts ( $M = Fe^{2+}$ ,  $Cu^{2+}$ , or  $Co^{2+}$ ) displayed the same features.

On the other hand, the FT-IR spectra of the  $SiW_{11}MC$  ( $M = Mn^{2+}$ ,  $Fe^{2+}$ ,  $Cu^{2+}$ , and  $Co^{2+}$ ) showed the characteristic bands of the  $[SiW_{11}O_{39}M]^{6-}$  anion superimposed to those of the carbon used as support. These results confirm that the structure of the metal-modified lacunary

heteropolycompounds remains unaltered after the interaction with carbon that takes place during the impregnation.

According to the DTA studies, the thermal decomposition of sodium  $[\text{SiW}_{11}\text{O}_{39}\text{M}]^{6-}$  takes place at temperatures in the range 450–490 °C. The exothermic peaks assigned to  $\text{Na}_6[\text{SiW}_{11}\text{O}_{39}\text{Mn}]$  and  $\text{Na}_6[\text{SiW}_{11}\text{O}_{39}\text{Fe}]$  decomposition were observed at 485 and 478 °C, respectively. These salts are thermally slightly more stable than  $\text{Na}_6[\text{SiW}_{11}\text{O}_{39}\text{Cu}]$  and  $\text{Na}_6[\text{SiW}_{11}\text{O}_{39}\text{Co}]$ , which showed the exothermic peak at 469 and 458 °C, respectively. The dehydration of the salts occurs at temperatures below 150 °C. Their DTA diagrams showed a broad endothermic peak with a maximum at 60–70 °C, which was reflected in the TGA diagram as the appearance of continuous weight loss.

In the DTA diagrams of the  $\text{SiW}_{11}\text{MC}$  samples, an endothermic peak with a maximum at around 70 °C was observed. It was similar to that displayed by the support and ascribed to water evolution. A wide exothermic signal with a maximum in the range 470–500 °C, assigned to  $[\text{SiW}_{11}\text{O}_{39}\text{M}]^{6-}$  decomposition, was observed. The decomposition temperature of transition metal-modified lacunary tungstosilicic polyoxometallates was slightly enhanced as a result of their interaction with the functional groups present on the support surface [34].

The TPR pattern of  $\text{Na}_8\text{SiW}_{11}\text{O}_{39}$  showed two peaks with maxima at 691 and 917 °C (Figure 3). They appeared at temperatures higher than the decomposition temperature of the  $[\text{SiW}_{11}\text{O}_{39}]^{8-}$  anion and were assigned to the reduction of the species resulting from lacunary anion decomposition. The same peaks, shifted to higher temperatures, were present in the patterns of  $\text{Na}_6[\text{SiW}_{11}\text{O}_{39}\text{Mn}]$  (711 and 917 °C),  $\text{Na}_6[\text{SiW}_{11}\text{O}_{39}\text{Fe}]$  (722 and 935 °C),  $\text{Na}_6[\text{SiW}_{11}\text{O}_{39}\text{Cu}]$  (731 and 948 °C), and  $\text{Na}_6[\text{SiW}_{11}\text{O}_{39}\text{Co}]$  (742 and 972 °C). Due to the introduction of M in the octahedral lacuna, the reduction of the species resulting from  $[\text{SiW}_{11}\text{O}_{39}\text{M}]^{6-}$  decomposition takes place at slightly higher temperatures. These species may be

the constituent oxides of the decomposed salts. Gamelas et al. [35] have found  $\text{WO}_3$  as the main component of the decomposition products of potassium salts of transition metal-modified lacunary heteropolycompounds.

On the other hand, the TPR patterns of the  $\text{SiW}_{11}\text{MnC}$ ,  $\text{SiW}_{11}\text{FeC}$ ,  $\text{SiW}_{11}\text{CuC}$ , and  $\text{SiW}_{11}\text{CoC}$  samples (Figure 4) showed a strong and wide peak with a maximum in the range 660–720 °C, overlapping the wide band of the support (480–750 °C). Taking into account the DTA results, they appeared at temperature values higher than the decomposition temperature of the  $[\text{SiW}_{11}\text{O}_{39}\text{M}]^{6-}$  anion in the  $\text{SiW}_{11}\text{MC}$  samples. We can suggest that as result of the interaction of the transition metal-modified lacunary tungstosilicic polyoxometallates with the functional groups present on the support surface, the reduction of  $[\text{SiW}_{11}\text{O}_{39}\text{M}]^{6-}$  anion decomposition products takes place almost at the same temperature and only reduction peak in the TGR patterns was displayed. For these samples, the reduction temperature ( $\text{TPR}_{\text{SiW}_{11}\text{MC}}$ ) slightly increased according to the following order:  $\text{SiW}_{11}\text{MnC}$  (662 °C) <  $\text{SiW}_{11}\text{FeC}$  (681 °C) <  $\text{SiW}_{11}\text{CuC}$  (697 °C) <  $\text{SiW}_{11}\text{CoC}$  (711 °C).

Isopropanol dehydration proceeds quickly on acidic sites [36] and has been used [37, 38] as a test reaction for comparing the acidity of different catalysts. At temperatures lower than 300 °C, isopropanol decomposition can form either propene and water (dehydration) or acetone and hydrogen (dehydrogenation).

The results of isopropanol dehydration ( $\text{CS}_{\text{PROP}}$ ) catalyzed by  $\text{SiW}_{11}\text{MC}$  samples are shown in Table 1. We found that isopropanol decomposes to propene and only traces of diisopropylether were detected by means of GCMS. According to these results, the acidity of the samples decreases in the following order:  $\text{SiW}_{11}\text{MnC}$  >  $\text{SiW}_{11}\text{FeC}$  >  $\text{SiW}_{11}\text{CuC}$  >  $\text{SiW}_{11}\text{CoC}$ .

### 3.2. Catalytic activity

**Effect of the nature of the transition metal on the catalytic activity of SiW11MC samples**

Table 1 shows the obtained results for methyl *p*-tolyl sulfide conversion and selectivity to the corresponding sulfoxide and sulfone using the prepared transition metal-modified lacunary tungstosilicic polyoxometallates supported on carbon (SiW11MnC, SiW11FeC, SiW11CuC and SiW11CoC). The experimental conditions were: 100 mg of catalyst, 1 mmol of substrate, 10 mmol of H<sub>2</sub>O<sub>2</sub> (35 % (w/v)) and 9 mL of acetonitrile; reaction time and temperature of 60 min and 40°C, respectively. In these conditions, the corresponding sulfoxide and sulfone were obtained with a high selectivity (98%–99%), free of other secondary products. The blank experiment was performed in the absence of the catalyst using an excess of aqueous H<sub>2</sub>O<sub>2</sub> (35% (w/v), 10 mmol), and acetonitrile (9 mL) as reaction solvent. Under these conditions, the reaction conversion was very low (10% at 60 min and 40 °C, Table 1, entry 1).

The complete conversion of methyl *p*-tolyl sulfide was obtained in 60 min using SiW11MnC as catalyst (Table 1, entry 2). The conversion values reached using the other SiW11MC samples were slightly lower (Table 1, entries 2–5) and decreased in the following order: SiW11MnC > SiW11FeC > SiW11CuC > SiW11CoC. This order was opposite to that found for the TPR<sub>SiW11MC</sub> values. In other words, the activity of the catalysts decreases in parallel with the increment of the TPR<sub>SiW11MC</sub> values. So, the most easily reducible catalyst displayed the highest conversion values.

Palermo et al. reported [39] that the oxidation of diphenyl sulfide catalyzed by Mo-based Keggin heteropolyacids takes place through the formation of peroxo-molybdate species and the subsequent nucleophilic attack of the sulfur atom in the sulfide on the peroxo species. Maciuca et al. suggested that the electrophilicity of the peroxide oxygen of H<sub>2</sub>O<sub>2</sub> is increased by an oxometal group (M=O) in the heteropolycompound [40].

Additionally, the influence of acidity on the formation rate of peroxo complexes has been reported [41] as well as the fact that the selective oxidation of sulfides to sulfoxides or sulfones in the presence of aqueous  $\text{H}_2\text{O}_2$  is promoted by Brønsted acidity [42]. Taking into account that the acidity of the SiW11MC samples decreases in the same way as the catalytic activity and previous reports [41, 42], we can suggest that both the easiness of reduction and the acidity strongly affect the catalytic activity of the SiW11MC samples.

On the other hand, the selectivity of the catalysts to sulfone was sensitive to the type of cation used in the modification of the lacunary tungstosilicic polyoxometallate and it decreased in parallel with the conversion decrease (80%, 75%, 70 and 65%, respectively, for sulfone production).

The possible mechanism for the oxidation of methyl *p*-tolyl sulfide to the corresponding sulfoxide or sulfone using  $\text{H}_2\text{O}_2$  in the presence of SiW11MC catalysts is outlined in Scheme 3. The interaction of hydrogen peroxide with transition metal-modified lacunary tungstosilicic polyoxometallate generates an electrophilic intermediate (peroxo oxygen/TMPOM), which produces an electrophilic attack on the sulfur atom in the sulfide, generating the corresponding sulfoxide (Scheme 2). The mechanism for the oxidation of the sulfoxide to the corresponding sulfone is different. First, it involves the formation of a TMPOM-sulfoxide intermediate through the nucleophilic attack on the tungsten atom in the TMPOM by the oxygen of the sulfoxide, and then the nucleophilic attack of the sulfur atom in TMPOM-sulfoxide by  $\text{H}_2\text{O}_2$  via an  $\text{S}_\text{N}2$  mechanism [43-45] (Scheme 2).

Scheme 2. Proposed mechanism for the oxidation of methyl *p*-tolyl sulfide to the corresponding sulfoxide and sulfone with aqueous hydrogen peroxide in the presence of polyoxometallates

The selective oxidation of methyl-p-tolyl sulfide to the corresponding sulfoxide, in homogeneous and heterogeneous system, using aqueous hydrogen peroxide, catalyzed by heteropolyacids or related compounds such as:  $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$  [46],  $\text{H}_5\text{PMo}_{11}\text{Al}_{0.5}\text{V}_{0.5}\text{O}_{40}$  [8],  $\text{PyHPMo}_{11}\text{VO}_{40}$  [47],  $[\text{TBA}]_4[\text{Al}_4(\text{H}_2\text{O})_{10}(\beta\text{-AsW}_9\text{O}_{33}\text{H}_2)_2]_4$  [48],  $[\text{TBA}]_4[\gamma\text{-SiW}_{10}\text{O}_{36}(\text{PhPO})_2]$  [49],  $[\text{TBA}]_4[\gamma\text{-HPW}_{10}\text{V}_2\text{O}_{40}]$  [50],  $\text{H}_3[\text{PW}_{12}\text{O}_{40}]$ -polyacrylamide based ammonium salt [51], and  $[\gamma\text{-1,2-H}_2\text{SiW}_{10}\text{V}_2\text{O}_{40}]$  [52], were reported in the literature.

In all the above mentioned examples the reaction yields were high and very similar to those obtained using the methodology reported in this work. However our SIW11MC catalysts have some advantages for example: easy preparation, no moisture sensitive and very low toxicity of the catalyst. Additionally, they could be used and easily recycled several times, without appreciable loss of their catalytic activity.

### **Effect of the solvent on the reaction activity**

Then, with the most active catalyst, SiW11MnC, we decided to study the effect of solvent and catalyst reusability for the oxidation of methyl p-tolyl sulfide (Table 2). The reaction was attempted with different solvents, such as ethanol, acetonitrile, and toluene. Complete substrate conversion was obtained using ethanol and acetonitrile (Table 2, entries 1 and 2). However, when toluene was used as solvent, two phases were observed due to aqueous hydrogen peroxide insolubility in toluene, and methyl p-tolyl sulfide conversion was significantly lower (Table 2, entry 3).

The catalyst was recovered by filtration, washed with the reaction solvent, dried in vacuum at 40 °C and reused. The conversion remained practically constant when acetonitrile or toluene was used as solvent. However, in the case of ethanol the conversion was remarkably

lower (Table 2, entry 1). This was in agreement with the leaching experiments that showed that only when the catalysts were extracted with ethanol, an important loss of the  $[\text{SiW}_{11}\text{O}_{39}\text{Mn}]^{6-}$  lacunary anion (almost 22% of the original amount) took place.

For the  $\text{SiW}_{11}\text{MnC}$  catalyst, an additional test was performed in order to evaluate the possible catalyst solubilization. The sample was refluxed in acetonitrile at 40 °C for 2 h, filtered and dried in vacuum till constant weight. The activity of the so-treated catalyst was the same as that of the fresh catalyst. The refluxed acetonitrile was used as solvent for attempting the reaction without adding the catalyst. After 1 h a conversion similar to that of the blank experiment (10%), was obtained.

### **Effect of the reaction conditions on the selectivity**

The reaction conditions were optimized using methyl p-tolyl sulfide as substrate at 20°C. The results of the study of the oxidation reaction of methyl p-tolyl sulfide with the use of  $\text{SiW}_{11}\text{MnC}$  as catalyst are summarized in Table 3. A conversion of 15% was obtained in the absence of the catalyst at 20 °C, in a time period of 10 h using 10 mmol of 35% (w/v) hydrogen peroxide (Table 3, entry 1). However, when  $\text{SiW}_{11}\text{MnC}$  catalyst was added (Table 3, entry 2), the reaction took place efficiently obtaining a conversion of 75% with a 95% selectivity of the corresponding sulfoxide in 10 h. Then, the effect of  $\text{H}_2\text{O}_2$  amount on conversion and selectivity was studied using four different  $\text{H}_2\text{O}_2$  amounts: 1, 2, 5 and 10 mmol (Table 3, entries 2–5). When 2, 5 and 10 mmol were used, a conversion of 100 % was obtained in 7, 5 and 4 h, respectively; however, sulfoxide selectivity was very good only when 2 mmol of  $\text{H}_2\text{O}_2$  was used (conversion 100%, sulfoxide selectivity 91%), (Table 3, entry 3). This condition was considered as optimal for the selective synthesis of sulfoxides.

In order to continue with the study of the reaction optimization, the effect of temperature on the conversion and selectivity of methyl p-tolyl sulfide was analyzed using  $\text{H}_2\text{O}_2$  in excess

(10 mmol) (Table 3, entries 5–8). As can be observed, at 20 °C, the reaction reached 100% of methyl p-tolyl sulfide conversion, but the selectivity to sulfone was only 68% (Table 3, entry 5). An increase of the reaction temperature improved the selectivity to sulfone values. For example, at 50 °C and for 3 h, 100% selectivity to methyl p-tolyl sulfone was achieved (Table 3, entry 8).

Once the reaction conditions for the selective oxidation of sulfides to sulfoxides and sulfones had been optimized, the reaction was extended to other different substrates. Diaryl (Table 4, entries 1, 2 and 12), aryl-alkyl (Table 4, entries 3–6 and 10), dialkyl (Table 4, entries 7 and 8) and more complex sulfides (Table 4, entries 9, 11) were used as starting materials. In Table 4, the third column shows the results obtained for the selective oxidation of these sulfides to the corresponding sulfoxides. All the reactions were run within a reasonable short reaction time and the sulfoxides were obtained in excellent yields (92%–59%), and only traces of sulfones and other secondary products were detected. Therefore, the reaction condition is selective to the transformation of sulfides to sulfoxides. For example, in Table 4 (entries 5 and 10), it can be seen that the hydroxyl and the formyl groups were not significantly affected under these reaction conditions. On the other hand, the sulfide 4,4'-diamino-diphenyl sulfide (Table 4, entry 12) can be oxidized to the corresponding sulfoxide or sulfone under the suitable reaction conditions with good yields. For this substrate, low amounts of several secondary unidentified compounds were detected by TLC. The optimized conditions were: 1 mmol of sulfide, 0.2 mL of 35 % p/V H<sub>2</sub>O<sub>2</sub>, 100 mg of SiW<sub>11</sub>MnC catalyst, 9 mL of acetonitrile, 20 °C, during a time period depending on the substrate structure. The procedure allows obtaining dapsone (a leader drug for leprose) with good yields (71%, Table 4, entry 12). Finally, the selective oxidation of sulfide to the corresponding sulfone was obtained with excellent yields (Table 4), in short time periods (2–4 h) by increasing the reaction temperature from 20 to 50 °C.

### Reaction chemoselectivity

In order to determine the chemoselectivity of the SiW11MnC catalyst under the previously mentioned reaction conditions, some competitive reactions were studied. Thus, the competitive oxidation of sulfides in the presence of benzylic alcohol, benzaldehyde, benzonitrile, cyclohexene and methyl- p-tolyl sulfoxide were checked (Scheme 3). These experiment show that the method is applicable for the chemoselective oxidation of sulfides to sulfoxides in the presence of the previously mentioned functional groups and can be considered as a useful practical method for the oxidation of sulfides to sulfoxides without appreciable oxidation of other functional groups. The optimal reaction conditions for the chemoselective oxidation of sulfides were: 1 mmol of sulfide, 1 mmol of the other substrate, 0.2 mL of 35 % p/V H<sub>2</sub>O<sub>2</sub>, 100 mg of SiW11MnC catalyst, 9 mL of acetonitrile, 20 °C, after 7 h under continuous stirring.

### Sulfide reactivity study

Recently, we found that there is a relationship between sulfide oxidation facility and the sulfur atom charge obtained by a computational method [46]. For this reason, we explored again the reactivity of the different sulfides tested in the present work, using a semi-empirical method. The relationship between the electron densities of the sulfur atoms, which were estimated by Hyperchem release 5, and the oxidative facility of the sulfur-containing compounds was analyzed. The electron densities on the sulfur atom of the 12 sulfides, which varied between -0.078 and 0.168, are shown in Figure 4.

Figure 4 shows a relationship between the substrate reactivity, evaluated as the reaction time for a 100% conversion of sulfide, and the electron densities on the sulfur atom. From the results obtained, it could be observed that dialkyl sulfides (-0.031, -0.047 and -0.078) are more reactive than alkyl-aryl sulfides (0.076–0.097), and alkyl-aryl sulfides are more reactive than diaryl sulfides (0.165 and 0.220). This different reactivity is associated with the electronic density on

the sulfur, since a higher electronic density on this atom facilitates the electrophilic attack of the electrophilic intermediate peroxy oxygen/TMPOM.

Finally, in order to explore a possible reaction mechanism, an additional experiment was performed using a radical inhibitor such as *t*-butanol. The experimental conditions were: 1 mmol of methyl *p*-tolyl sulfide, 0.2 mL of H<sub>2</sub>O<sub>2</sub> (35% w/v), 100 mg of SiW11MnC, 8 mL of acetonitrile and 1 mL of *t*-butanol; reaction for 7 h at 20°C. In these conditions, the conversion of methyl *p*-tolyl sulfide (100%) and the selectivity of sulfoxide (91%) obtained were similar to those reached without a radical inhibitor. This result indicates that the reaction does not take place via a free radical path and it is in agreement with the suggested mechanism.

#### 4. Conclusions

The sodium salts of metal-modified lacunary tungstosilicic polyoxometallates [SiW<sub>11</sub>O<sub>39</sub>M(H<sub>2</sub>O)]<sup>6-</sup>, where M= Mn<sup>2+</sup>, Fe<sup>2+</sup>, Co<sup>2+</sup> or Cu<sup>2+</sup>, were successfully prepared and supported on activated carbon to obtain the SiW11MC catalysts.

The [SiW<sub>11</sub>O<sub>39</sub>M]<sup>6-</sup> anions are the main species present in SiW11MC materials and they are uniformly distributed along the width of the carbon particles. As a result of their interaction with the support surface groups, the [SiW<sub>11</sub>O<sub>39</sub>M]<sup>6-</sup> anion temperature decomposition was slightly enhanced.

The activity and selectivity of the catalysts were evaluated in the selective oxidation of methyl *p*-tolyl sulfide to the corresponding sulfoxides or sulfones. The reaction was carried out in acetonitrile as solvent using H<sub>2</sub>O<sub>2</sub> 35% p/v as a clean oxidant. The conversion values decreased in the following order: SiW11MnC > SiW11FeC > SiW11CuC > SiW11CoC, and it was found that the activity of the catalysts decreases in parallel with the increment in the reduction temperature (TPR<sub>SiW11MC</sub>) values. The most easily reducible catalyst displayed the highest conversion values.

In this research we found a convenient and selective procedure for oxidizing sulfides to sulfoxides, using 35% (w/v) aqueous hydrogen peroxide and a catalytic amount of lacunary tungstosilicic polyoxometallates supported on carbon. The reaction for sulfoxide preparation was carried out at room temperature (20 °C), in a reasonably short reaction time.

Meanwhile, the selective oxidation of sulfides to sulfones required a temperature of 50 °C and aqueous hydrogen peroxide in excess. Under this condition, excellent yields of sulfone were obtained.

The different reactivity of sulfides is associated with the electronic density on the sulfur atom, since a higher electronic density on this atom facilitates the attack by the electrophilic form of the hydrogen peroxide/catalyst system.

Using carbon-supported lacunary tungstosilicic polyoxometallates as catalysts, the heterogeneous liquid-phase sulfoxidation of methyl p-tolyl sulfide takes place without significant loss of the active phase, facilitating the separation and reuse. The use of aqueous hydrogen peroxide gives only water as a byproduct, contributing to the field of clean technologies.

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[1] S. S. Kim, G. Rajagopal, *Synth. Commun.* 34 (2004) 2237-2243.

[2] D. Choudhary, S. Paul, R. Gupta, J. H. Clark, *Green Chem.* 8 (2006) 479-482.

[3] A. Hasaninejad, M. Zolfigol, G. Chehardoli, M. Mokhlesi, *J. Serb. Chem. Soc.* 75 (2010) 307–316.

[4] G. Yadav, *Catal. Surveys from Asia* 9 (2005) 117-137.

- [5] I. V. Kozhevnikov, *J. Mol. Catal. A: Chem.* 262 (2007) 86-92.
- [6] M. Misono, I. Ono, G. Koyano, A. Aoshima, M. Misono, I. Ono, G. Koyano, A. Aoshimam, *Pure Appl. Chem.* 72 (2000) 1305-1311.
- [7] L.R. Pizzio, P.G. Vázquez, C.V. Cáceres, M.N. Blanco, *Appl. Catal. A: Gen.* 256 (2003) 125-139.
- [8] G. Romanelli, D. Bennardi, V. Palermo, P. Vázquez, P. Tundo, *Lett. Org. Chem.* 4 (2007) 544-549.
- [9] V. Palermo, P. Villabrille, P. Vázquez, P. Tundo, C. Cáceres, G. Romanelli, *J. Chem. Sci.* 125 (2013) 1375-1383.
- [10] P. Tundo, G. Romanelli, P. Vázquez, P. Loris, F. Aricó, *Synlett* 7 (2008) 667-670.
- [11] V. Palermo, A. Sathicq, P. Vázquez, H. Thomas, G. Romanelli, *Reaction kinetics, mechanisms and catalysis* 104 (2011) 181-195.
- [12] L. Sánchez, G. Sathicq, G. Baronetti, H. Thomas, G. Romanelli, *Catal. Lett.* 144 (2014) 172-180.
- [13] M.M.Q. Simoes, C.M.M. Conceiao, J.A.F. Gamelas, P.M.D.N. Domínguez, A.M.V. Cavaleiro, J.A.S. Cavaleiro, A.J.V. Ferrer-Correira, R.A.W. Johnstone, *J. Mol. Catal. A.: Chem.* 144 (1999) 461-468.
- [14] S. Ellis, I.V. Kozhevnikov, *J. Mol. Catal. A: Chem.* 187 (2002) 227-235.
- [15] Romina Frenzel, Gustavo P. Romanelli, Mirta N. Blanco, Luis R. Pizzio, *J. Chem. Sci.* 127 (2015) 123-132.
- [16] F. Liu, Z. Fu, Y. Liu, Ch. Lu, Y. Wu, F. Xie, Z. Ye, X. Zhon, D. Yin, *Ind. Eng. Chem. Res.* 49 (2010) 2533-2536 and references cited therein.
- [17] I. Fernández, N. Khair, *Chem. Rev.* 103 (2003) 3651-3706 and references cited therein.
- [18] A. M. Khenkin, R. Neumann, *J. Am. Chem. Soc.* 124 (2002) 4198-4199.

- [19] M. Vaz-Da-Silva, A.I. Loureiro, T. Nunes, J. Maia, S. Tavares, A. Falcão, P. Silveira, L. Almeida, P. Soares-Da-Silva, *Clin Drug Investig* 25 (2005) 391–399.
- [20] Y. Isabel Zhu, Matthew J. Stiller, *J. Am. Acad. Dermatol.* 45 (2001) 420–434.
- [21] F. Gregori, I. Nobili, F. Bigi, R. Maggi, G. Predieri, G. Sartori. *J. Mol. Catal. A: Chem.* 286 (2008) 124–127.
- [22] M. Mokhtary, M. Qandalee, M. R. Niaki, *E-Journal of Chemistry* 9 (2012) 863-868.
- [23] S. Zakavi, A. Abasi, A. R. Pourali, S. Talebzadeh, *Bull. Korean Chem. Soc.* 33 (2012) 35-38.
- [24] A. Rostami, F. Hassanian, A. Ghorbani-Choghamarani, S. Saadati, *Phosphorus, Sulfur, and Silicon and the Related Elements* 188 (2013) 833-838.
- [25] H. Jafari, A. Rostami, F. Ahmad-Jangi, A. Ghorbani-Choghamarani, *Synth. Commun.* 42 (2012) 3150-315.
- [26] Y. Kon, T. Yokoi, M. Yoshioka, Y. Uesaka, H. Kujira, K. Sato, T. Tatsumi, *Tetrahedron Lett.* 54 (2013) 4918-4921.
- [27] M. Rahimizadeh, G. Rajabzadeh, S. Khatami, H. Eshghi, A. Shiri, *J. Mol. Catal. A: Chem.* 323 (2010) 59–64.
- [28] A. Tézé, G. Hervé, *Inorg. Synth.* 27 (1990) 85-96.
- [29] A. Tézé, G. Hervé, *J. Inorg. Nucl. Chem.* 39 (1977) 2151.-2154.
- [30] A. Tézé, G. Hervé, *Inorg. Synth.* 27 (1990) 96-104.
- [31]. L.R. Pizzio, P.G. Vázquez, C.V. Cáceres, M.N. Blanco, *Adsorp. Sci. Technol.* 13 (1996) 165-176.
- [32] H. Viturro, R. Bonetto, L.R. Pizzio, P.G. Vázquez, M. Sánchez, G. Alvarez, *X-ray Spectrom.* 24 (1995) 3-8.
- [33] C. Rocchiccioli-Deltcheff, R. Thouvenot, *C.R. Acad. S. Paris* 278 (1974) 857-860.
- [34] G.K.M. Abotsi, A.W. Scaroni, *Carbon* 28 (1990) 79-84.

- [35] J.A. Gamelas, F.A.S. Couto, M.C.N. Trovão, A.M.V. Cavaleiro, J.A.S. Cavaleiro, J.D. Pedrosa de Jesús, *Thermochim. Acta* 326 (1999) 165-173.
- [36]. J.R. Sohn, H.J. Jang, *J. Mol. Catal.* 64 (1991) 349-360.
- [37]. M.E. Chimienti, L.R. Pizzio, C.V. Cáceres, M.N. Blanco, *Appl. Catal. A: General*, 208 (2001) 7-19.
- [38]. L.R. Pizzio, M.N. Blanco, *App. Catal. A: General* 255 (2003) 265-277.
- [39]. V. Palermo, G.P. Romanelli, P.G. Vazquez, *J. Mol. Catal. A: Chem.*, 373 (2013) 142-150.
- [40] A.L. Maciuca, C.E. Ciocan, E. Dumitriu, F. Fajula, V. Hulea, *Catal. Today* 138 (2008) 33-37.
- [41] Y. Ishii, K. Yamawaki, T. Ura, H. Yamada, T. Yoshida, M. Ogawa, *J. Org. Chem.* 53 (1988) 3581-3593.
- [42] A. Shaabani, A.H. Rezayan, *Catal. Comm.* 8 (2007) 1112-1116.
- [43] A.L. Maciuca, C.E. Ciocan, E. Dumitriu, F. Fajula, V. Hulea, *Catal. Today*, 138 (2008) 33-37.
- [44] A. Chellamani, S. Harikengaram, *J. Mol. Catal. A: Chem* 247 (2006) 260-267.
- [45] J.R Lindsay Smith, B.C. Gilbert, A. Mairata i Payeras, J. Murray, T.R. Lowdon, J. Oakes, R. Pons i Prats, P.H. Walton, *J. Mol. Catal. A: Chem* 251 (2006) 114-122.
- [46]. V. Palermo, A. Sathicq, P. Vázquez, G. Romanelli, *Phosphorus, Sulfur Silicon Relat. Elem.*: 189 (2014) 1-10.
- [47] G. Romanelli, P. Villabrilie, C. Cáceres, P. Vázquez, P. Tundo, *Catal. Commun.* 12 (2011) 726-730
- [48] M. Carraro, S. Bassil-Bassen, A. Soraru, S. Berardi, A. Suchopar, U. Kortz, M. Bonchio, *Chem. Commun.* 49 (2013) 7914-7916.
- [49] M. Carraro, L. Sandei, A. Sartorel, G. Scorrano, M. Bonchio. *Org. Lett.* 8 (17) (2006) 3671-3674.

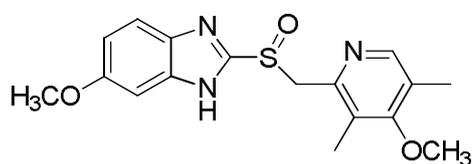
[50] T. Yamaura, K. Kamata, K. Yamaguchi, N. Mizuno, *Catal. Today* 203 (2013) 76-80.

[51] Y. Yamada, H. Tabata, M. Ichinohe, H. Takahashi, S. Ikegami, *Tetrahedron* 60 (2004) 4087-4096.

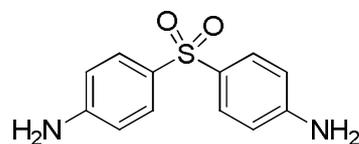
[52] J. Kasai, Y. Nakagawa, S. Uchida, K. Yamaguchi, N. Mizuno, *Chemistry–A European Journal* 12 (2006) 4176-4184.

Figures

**Figure 1.** Bioactives sulfoxides and sulfones

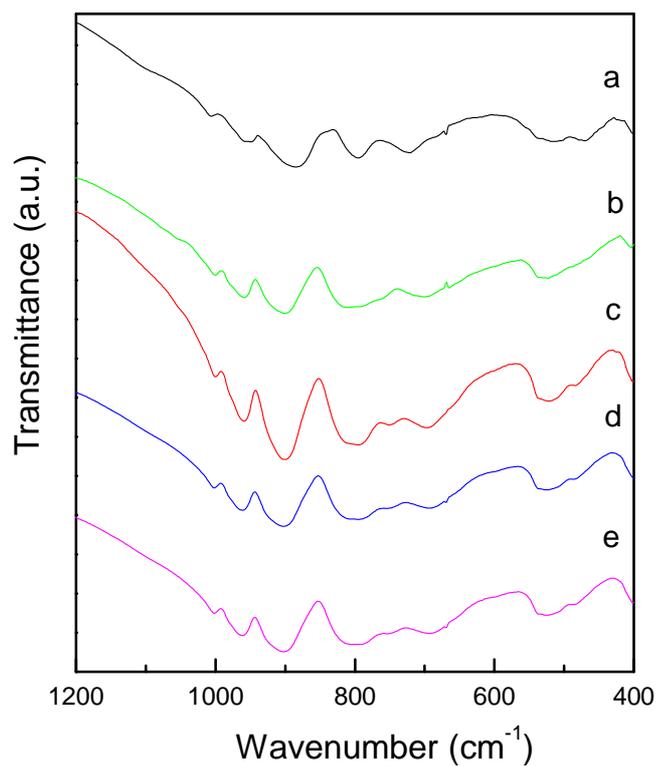


Omeprazole

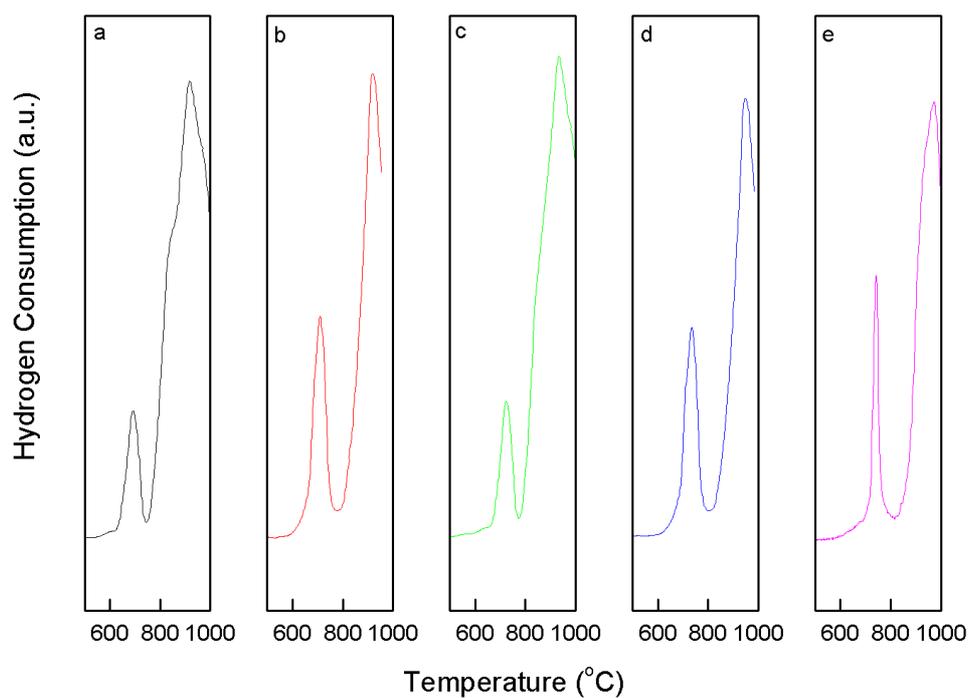


Dapsone

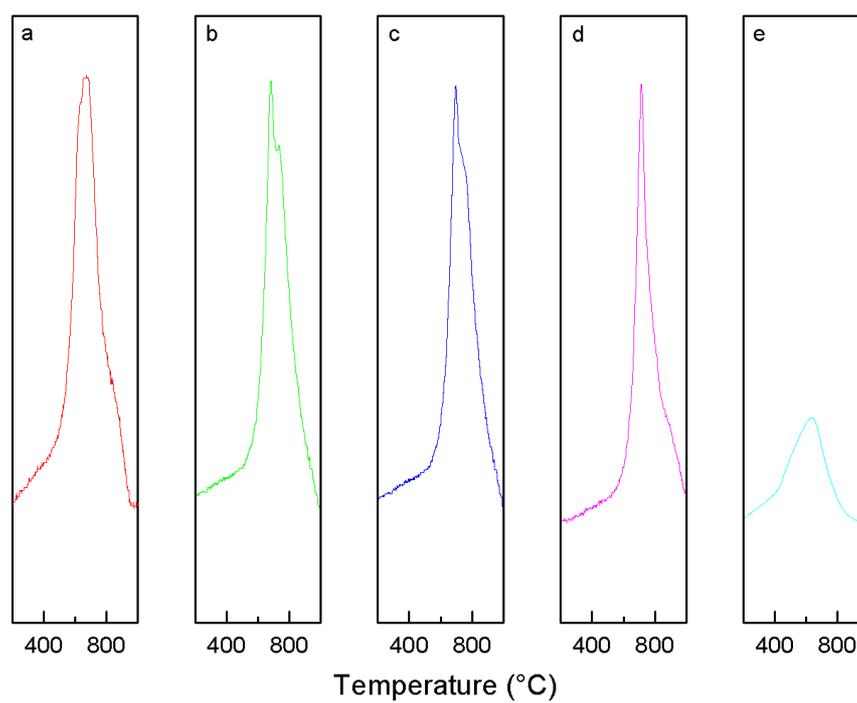
**Figure 2.** FT-IR spectra of the  $\text{Na}_8\text{SiW}_{11}\text{O}_{39}$  (a) Transition metal-modified lacunary tungstosilicic polyoxometallates salt  $\text{Na}_6[\text{SiW}_{11}\text{O}_{39}\text{M}]^{6-}$ , with  $\text{M} = \text{Mn}^{2+}$  (b),  $\text{Fe}^{2+}$  (c),  $\text{Cu}^{2+}$  (d), or  $\text{Co}^{2+}$  (e).



**Figure 3.** TPR patterns of  $\text{Na}_8\text{SiW}_{11}\text{O}_{39}$  (a) and of lacunary tungstosilicic polyoxometallate salt  $\text{Na}_6[\text{SiW}_{11}\text{O}_{39}\text{M}]^{6-}$ , with  $\text{M} = \text{Mn}^{2+}$  (b),  $\text{Fe}^{2+}$  (c),  $\text{Cu}^{2+}$  (d), or  $\text{Co}^{2+}$  (e).

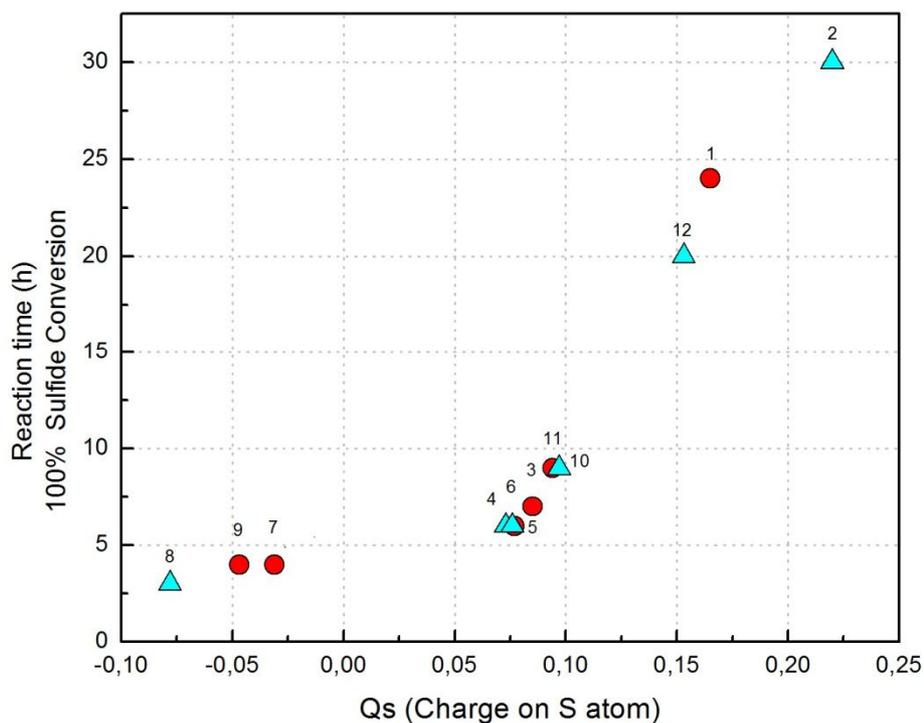


**Figure 4.** TPR patterns of SiW11MnC (a), SiW11FeC (b), SiW11CuC (c), SiW11CoC (d), and the carbon support.

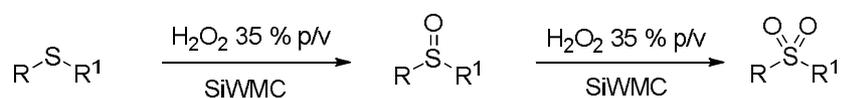


**Figure 5.** Reaction time for 100% conversion of sulfide vs.  $Q_s$  (charge on sulfur atom in the corresponding sulfide)<sup>a</sup>.

<sup>a</sup>Number 1-12 corresponding to the different sulfides (see Table 4).

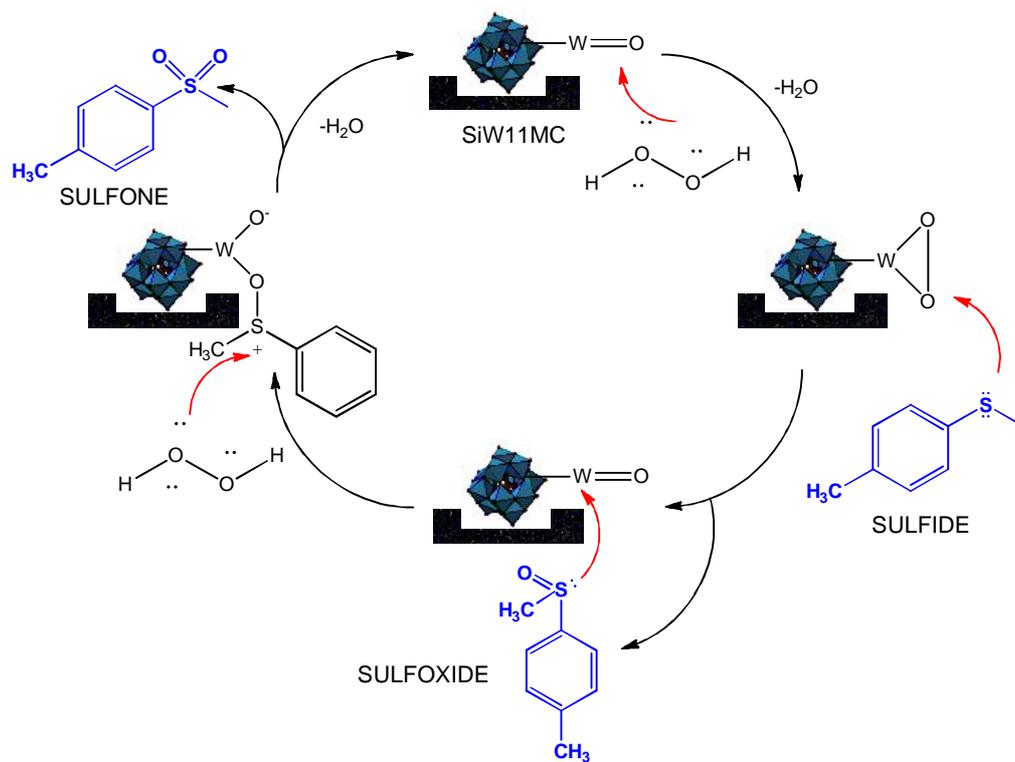


**Scheme 1.** Selective oxidation de sulfide to sulfoxide or sulfone

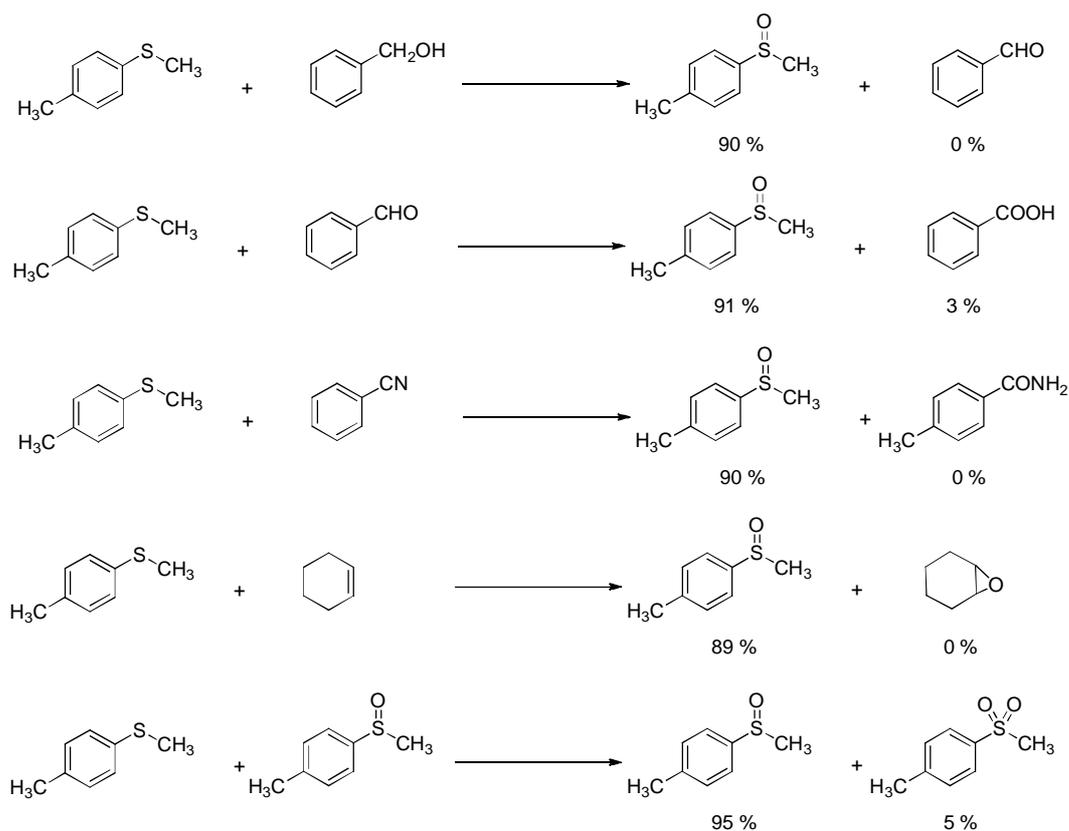


M = Mn, Fe, Co, Cu

**Scheme 2.** Proposed mechanism for the oxidation of metil p-tolyl sulfide to the corresponding sulfoxide and sulfone with aqueous hydrogen peroxide in the presence of polyoxometalates



Reaction condition for the selective oxidation of sulphide to sulfone: 1 mmol de sulfide, 1 mL of 35 % p/V H<sub>2</sub>O<sub>2</sub>, 100 mg catalyst of SiW11MnC, 9 ml of acetonitrile, 50 °C, stir.

**Scheme 3.** Chemoselectivity in the sulfoxide synthesis

Reaction condition: 1 mmol de sulfide, 1 mmol of the second substrate (see the corresponding equation in the scheme), 0.2 mL of 35 % p/V H<sub>2</sub>O<sub>2</sub>, 100 mg catalyst of SiW11MnC, 9 ml of acetonitrile, at 20 °C, after 7 h.

Tables

**Table 1.** Conversion and selectivity of the SiW11MC samples in the methyl p-tolylsulfide

Entry	Catalyst	CS <sub>PROP</sub> (s <sup>-1</sup> )	Conversion (%)	Sulfoxide selectivity (%)	Sulfone selectivity (%)
1	None	-	10	100	-
2	SiW11MnC	0.24	100	20	80
3	SiW11FeC	0.20	95	25	75
5	SiW11CuC	0.14	85	30	70

5	SiW11CoC	0.12	83	35	65
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Experimental conditions: 100 mg catalyst, 1 mmol of methyl p-tolyl sulfide, 10 mmol of H<sub>2</sub>O<sub>2</sub> (35 % w/v) and 9 ml of acetonitrile; reaction for 60 min at 40°C.

CS<sub>PROP</sub> = mol propene/mol SiW<sub>11</sub>M. s

**Table 2.** Screening of solvent and catalyst reuse in methyl p-tolylsulfide oxidation at 40 °C

Entry	Solvent	Conversion (%)	Conversion (%) First reuse
1	Ethanol	100	75
2	Acetonitrile	100	100 (100,100) <sup>a</sup>
3	Toluene <sup>b</sup>	55	54

Experimental conditions: 100 mg catalyst of SiW11MnC, 1 mmol of methyl p-tolyl sulfide, 10 mmol of H<sub>2</sub>O<sub>2</sub> (35 % w/v) and 9 ml solvent; reaction for 60 min at 40°C.

<sup>a</sup> Second and third reuse

<sup>b</sup>Two phases were observed due to aqueous hydrogen peroxide insolubility in toluene.

**Table 3.** Optimization of the reaction conditions for the selective synthesis of sulfoxide and sulfone.

Entry	H <sub>2</sub> O <sub>2</sub> (mL)	Time (h.)	Temp. (° C)	Conversion (%)	Sulfoxide selectivity (%)	Sulfone Selectivity (%)
1	0.1 <sup>a</sup>	10	20	15	100	-
2	0.1	10	20	70	95	5
3	0.2	7	20	100	91	9
4	0.5	5	20	100	51	49

<b>5</b>	1	4	20	100	32	68
<b>6</b>	1	1	40	100	20	80
<b>7</b>	1	2	50	100	2	98
<b>8</b>	1	3	50	100	0	100

Experimental conditions: 100 mg catalyst of SiW11MnC, 1 mmol of methyl p-tolyl sulfide, and 9 ml of acetonitrile.

<sup>a</sup> Without catalyst

**Table 4.** Oxidation of sulfide (1.0 mmol) to the corresponding sulfoxide and sulfones using H<sub>2</sub>O<sub>2</sub> 35 % p/v in the presence of SiWMnC as catalyst

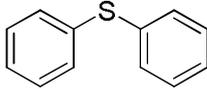
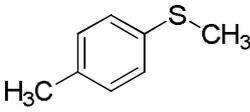
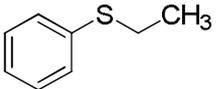
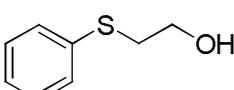
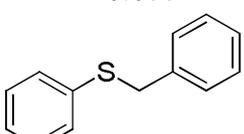
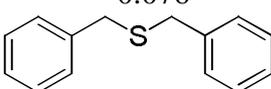
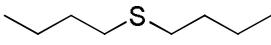
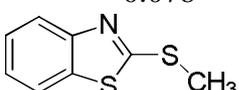
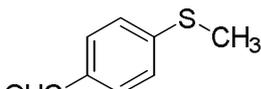
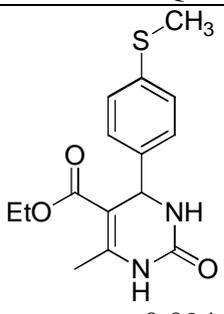
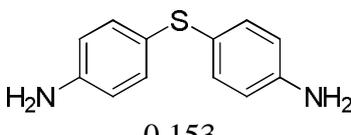
Entry	Substrate Qs	Yields (%) Sulfoxide /time (h)	Yields (%) Sulfone /time (h)
1	 0.165	91(24)	93(4)
2	 0.220	87(30)	92(4)
3	 0.085	92(7)	90(3)
4	 0.073	90(6)	94(3)
5	 0.077	85(6)	93(3)
6	 0.076	89(6)	92(3)
7	 -0.031	80(4)	85(2)
8	 -0.078	81(3)	90(2)
9	 -0.047	77(4)	82(3)
10	 0.097	77(9)	84(3)

Table 4 continuation

Entry	Substrate Q <sub>s</sub>	Yields (%) Sulfoxide /time (h)	Yields (%) Sulfone /time (h)
11		81(9)	84(3)
12	 0.094 0.153	59(20)	71(3)

Reaction condition for the selective oxidation of sulfide to sulfoxide: 1 mmol de sulfide, 0.2 mL of 35 % p/V H<sub>2</sub>O<sub>2</sub>, 100 mg catalyst of SiW<sub>11</sub>MnC, 9 ml of acetonitrile, 20 °C, stir.

