Structural and Compositional Effect of Heteropolyoxoanions [NiMo$_{6-x}$W$_x$O$_{24}$H$_6$]$^{4-}$ on the Catalytic Activity of Clean Selective Oxidation of Diphenylsulfide

Mercedes Muñoz[a], María G. Egusquiza[a], Irma L. Botto[b] and Carmen I. Cabello[a,*]

[a]*Centro de Investigación y Desarrollo en Ciencias Aplicadas, Dr. J. J. Ronco, Cindeca-Conicet CCT La Plata- UNLP, 47 Nº 257, (1900) La Plata, Argentina.*

[b]*Centro de Química Inorgánica, Cequinor-Conicet CCT La Plata-UNLP, 47 and 115, (1900) La Plata, Argentina.*

Abstract: Diphenyilsulfide oxidation by H$_2$O$_2$ as oxidant was studied through the structural effect of the isomorphous W-Mo systems, Anderson type, with [Ni(II)Mo(VI)$_{6-x}$W(VI)$_x$O$_{24}$H$_6$]$^{4-}$ composition. These phases were proved as alternative catalysts instead of W and Mo conventional systems. The characterization of the substituted phases was carried out by different physico-chemical techniques (AAS, DRS, micro-Raman, XRD, TPR). The catalytic evaluation for the phase NiW$_6$ revealed that the process was selective to the sulfone formation (selectivity ~ 81-88 %) while the Ni-Mo bi-metallic system (NiMo$_6$) was only selective to the sulfoxide production (selectivity 98 %). The activity was 90 % at 60 and 180 min for the NiMo$_6$ and NiW$_6$ respectively, whereas the substituted phases presented intermediate values. The observed differences can be related to the strength of the bridge bonds (Mo-O…Ni and W-O…Ni) associated to the higher electronegativity and ionic potential of Mo with respect to W. Hence, the W-O bond is more reactive by the inductive effect of Ni, which produces a higher oxidation of diphenyilsulfide to give sulfone, considering the electronic mobility in the redox processes.

Keywords: Clean oxidation, Diphenylsulfone, Diphenylsulfoxide, Hydrogen peroxide, Selective oxidation, W and Mo heteropolymetalates.

INTRODUCTION

Anderson-type heteropolyoxoanions, identified by the general formula [XM$_6$O$_{24}$H$_6$]$^{n-}$, are included in an important class of complex anions which have received great attention due to their potential applications [1, 2]. The synthesis and characterization of this type of materials constitute an increasingly attractive subject of investigation in the catalysis field [3]. The species for which M =Mo^{VI} or W^{VI} and X is a transition metal such as Co$^{II/III}$ or Ni^{II}, have been used as both bulk or γ-Al$_2$O$_3$ supported catalysts [4]. Such species easily become bi or trimetallic mixed oxides (XO/MoO$_3$, XO/WO$_3$, XO/Mo$_{1-x}$W$_x$O$_3$), molybdates and metallic tungstates (XMoO$_4$, XWO$_4$) under soft thermal treatments, generating well-known catalysts in industrial oxidations and hydrodesulfurization processes [5-7].

The present work deals with the analysis of the chemical properties of ammonium salt, whose substituted planar heteropolyanion is [Ni^{II}Mo$^{VI}_{6-x}$W$^{VI}_x$O$_{24}$H$_6$]$^{4-}$ (expressed in a simplified form as [NiMo$_{6-x}$W$_x$]). Correlation of the properties with the catalytic behavior is intended in the oxidation reaction of the diphenyilsulfide to obtain sulfoxide/sulfone using hydrogen peroxide as clean oxidant. The test selected, of major interest in the oxidative desulphurization (ODS) field, is considered a promising alternative to the intensive

desulphurization of fuel oil, diesel and H-Bio [8, 9]. In comparison with the conventional hydrodesulphurization process (HDS), the ODS can be conducted under less aggressive conditions using simple oxygen carriers such as the hydrogen peroxide, which allows working under pressure and room temperature generating water as residue.

In an oxidative process, the bivalent sulphur of dibenzothiophene DBT can be oxidized through a redox catalyst by an electrophilic addition of oxygen, leading to the production of sulfoxides or sulfones. These products have physical and chemical properties that facilitate separation. The great importance of the process in the chemical industry should be highlighted [10].

Commonly used catalysts in this type of reactions are basically mixed oxides of transition metals with greater molecular mass such as Mo, which can be supported in (Al$_2$O$_3$), though the use of heteropolyoxoanion and heteropolyacid salts has also been reported [9].

Recent works on the study and application of heteropolyoxo compounds carried out in our laboratory showed that both synthetic heteropolyoxo-composites of the [Al$_{13}$]-/(X Mo$_6$O$_{24}$)/XWO$_n$ (X =Al, Co, Cr, V, P) type and heteropoly-fosfotungstates complexes of the M$_4$[PW$_9$O$_{34}$]$_2^{10-}$ (M = Co^{II}, Zn^{II}, Mn^{II} and Cu^{II}) type markedly increase the oxidation velocity of diphenyilsulfide (DPS). Heteropolyoxocomposites containing Mo showed good outputs of sulfones, while complex heteropolytungstates-based systems showed better production of sulfoxides [11].

*Address correspondence to this author at the CIC PBA Researcher, Facultad de Ingeniería, UNLP; Tel: +54-221-4210711; Fax: +54-221-4210711; E-mail: ccabello@quimica.unlp.edu.ar
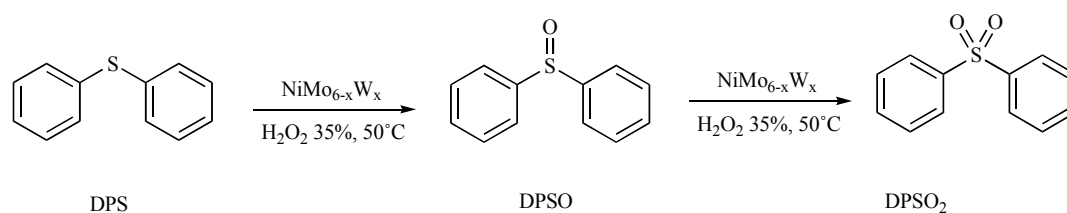
Scheme (1). Selective oxidation reaction of DPS to $DPSO_2$ in presence of hydrogen peroxide as oxidant.

Table 1. Elementary Analysis for [$NiMo_{6-x}W_x$], values Expressed in (%) w/w. M_t: Theoretical value, M_e: Experimental Value

M (%)	x=0	x=1	x=2	x=3	x=4	x=5	x=6
Ni_t	5.0	4.6	4.3	4.1	3.9	3.4	3.4
Ni_e	5.1	4.9	4.4	4.1	4.0	3.5	3.5
Mo_t	48.5	37.6	28.1	19.8	12.5	5.7	-
Mo_e	47.0	35.9	27.2	18.6	12.9	5.9	-
W_t	-	14.4	27.0	38.0	47.8	53.4	64.4
W_e	-	14.7	27.6	38.8	47.2	53.8	64.9

In the framework of a general work dealing with the synthesis and application of new materials, the aim of the present work is to explore the catalytic behavior in ODS of Anderson-type heteropolymetalates, in which a gradual substitution of Mo by W has been performed. The phases formed are members of a solid solution composed of [$Ni^{II}Mo^{VI}_{6-x}W^{VI}_x$]. Preparation of the phases was done by reaction in solution and their characterization was carried out by physicochemical techniques such as DRX, DRS, TPR, micro-Raman spectroscopy. Some chemical properties have been evaluated and compared according to those reported in literature [12].

The catalytic reaction of oxidation of diphenyilsulfide was conducted in batch, according to the Scheme (**1**).

EXPERIMENTAL

The synthesis of $(NH_4)_4[Ni^{II}Mo^{VI}_{6-x}W^{VI}_xO_{24}H_6].5H_2O$, (x = 0,1,2,3,4,5,6), was conducted by slowly adding nitrate solutions on solutions of ammonium heptamolybdate and $NaWO_4.2H_2O$, stoichiometric mixed at 80 ºC. Polycrystalline precipitates, whose color changed from light blue to light green according to the W/Mo reaction, were obtained. The chemical analyses of Ni, Mo and W, were conducted by atomic absorption from the decomposition of the samples in the acid medium and subsequent dilution, with a Varian SpectraA-30 equipment. Diffuse Reflectance (DRS) spectra were recorded with a Perkin Elmer, Lambda 35 equipment with an integrating sphere for diffuse reflectance measuring. The range covered was 200-900 nm, using $BaSO_4$ as reference. The X-ray diffraction diagrams (DRX data not shown in the present work) were obtained with a Philips PW 1714 equipment using CuKα radiation and a Ni filter (range 2Θ 5° -70°). The diagrams of Temperature Programmed Reduction TPR, were recorded with a Chembet 3000 equipped with a reactor fed with a 10 % H_2 reducing agent in N_2 (100 $cm^3.min^{-1}$) from 20 to 900 ºC; the heating rate was 5 ºC min^{-1}. Raman spectra were collected on powder samples at room temperature in the back-scattering geometry with an in Via Renishaw spectrometer equipped with an air-cooled CCD detector and super-Notch filters. The emission line at 488.0 nm from an Ar^+ ion laser was focused on the sample under a Leica DLML microscope using a 20x objective. Five 20s accumulations were acquired for each sample with a power of the incident beam on the sample of about 5 mW. The spectral resolution was 2 cm^{-1} and the spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer.

The catalytic test was carried out in a batch reactor with magnetic stirring at 800 rpm during the course of the reaction using 50 mg of the catalyst in 4 ml of ethanol, 1 ml of hydrogen peroxide, 33 % w/v, and 1 ml of diphenylsulfide (DPS) at 50°C. Aliquots were taken at different times of the reaction, up to 4 h. The reaction was followed-up by thin-layer chromatography (TLC) and gas chromatography (GC). Aliquots of 0.2 ml of the reaction mixture were withdrawn at different times of the reaction. Each sample was extracted with dichloromethane/ water (1ml/ 1ml), and the organic phase was dried with Na_2SO_4 anhydrous. The organic phase was analyzed by GC on a VARIAN S*tart 3400cx* chromatograph equipped with a Chrompack column CP-sil 5 CB (30 m) and FID detector. The GC conditions were: initial temperature of 50 ºC, ramp to 210 ºC (rate of 20 ºC/min, T constant for one min), and a second ramp to 240 ºC (rate of 10 ºC/min, T constant for 5 min). With this method the corresponding retention times were: 11.1, 13.9 and 14.5 min for diphenylsulfide (DPS), diphenylsulfoxide (DPSO), and diphenylsulfone ($DPSO_2$) respectively. The reaction sample compositions were determined by an area normalization method. From these values, the DPS conversion and selectivity values were obtained in function of time.

RESULTS AND DISCUSSION

Table **1** shows the results from the chemical analysis of the different phases conducted by AAS. The values obtained
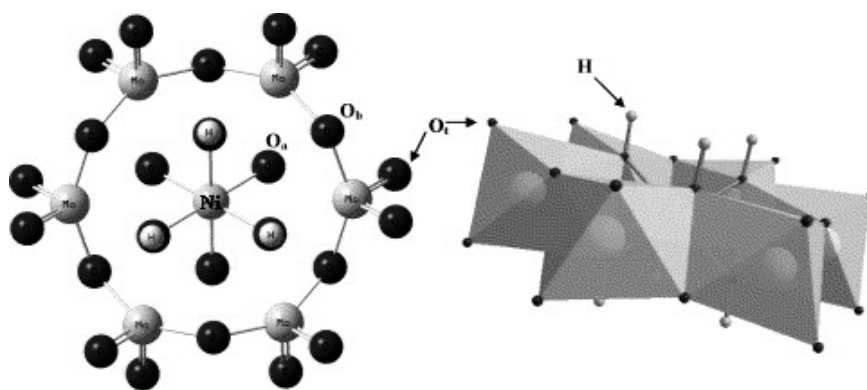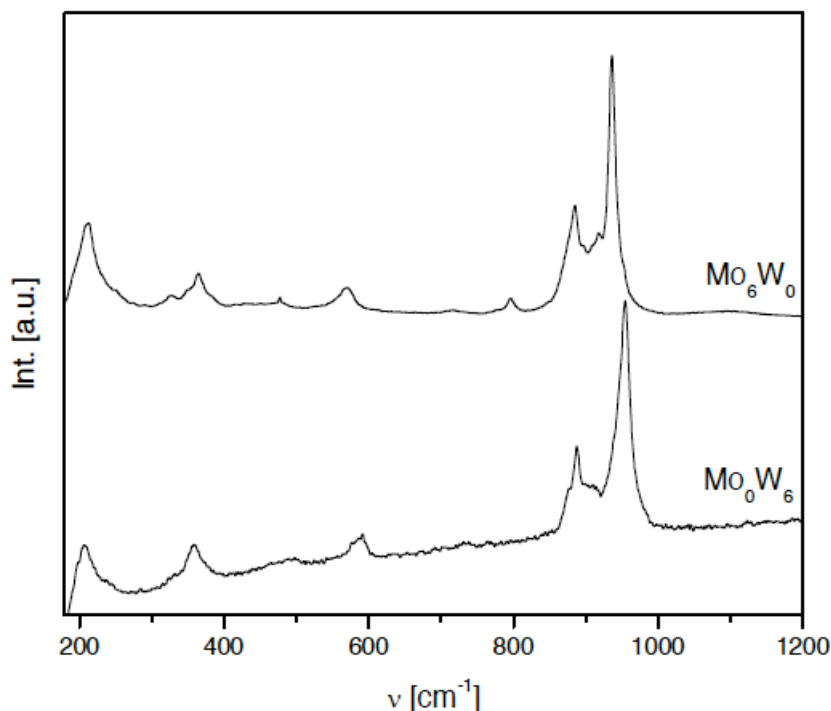
Fig. (1). Anderson-type structure [NiMo$_6$O$_{24}$].

Fig. (2). Comparative Raman spectra between NiMo$_{6-x}$W$_x$ (x= 0 and 6) bimetallic phases.

and the nominal values (x) are in good agreement and within the method error (±10 %, relative to the element).

The Anderson-type structure, showed in Fig. (**1**), is characterized by the presence of M-O-M/X bridges (with O$_a$ and O$_b$ type oxygens) and terminal groups M-O$_{2t}$ (with O$_t$ oxygens), which can operate as individual molecular units and constitute the active site of the catalyst.

The strength of these terminal bonds not only depends on the M element but is also sensitive to the type of heteroatom X in the center of the structure.

Figs. (**2**, **3** and **4**) show the comparative micro Raman spectra of the bimetallic phases (Fig. **2**, x= 0 and 6), and those of the trimetallic ones (Fig. **3**: x= 1 and 5, and Fig. **4**: x= 2, 3 and 4). All of them show the typical lines of an Anderson-type phase [XM$_6$O$_{24}$H$_6$] [5].

In this sense, Vibrational spectroscopy (FTIR and Raman) constitutes a useful tool to assess the effect of potential substitution. As an example, the Raman spectrum of phase [NiMo$_6$] presents the intense line of the symmetric mode (v$_s$)Mo-O$_{2t}$ at 936 cm^{-1}, while for the phase [NiW$_6$] the corresponding mode is located at 955 cm^{-1}, indicating a greater proximity between W and O$_t$. On the other hand, the lines corresponding to the antisymmetric modes (v$_{as}$)M-O$_{2t}$ and those corresponding to the bridges, (M-O-M) and (M-O-Ni) undergo shiftings which are illustrated in Table **2**.

The symmetric modes allow a clearer appreciation of the effect of the substitution. The general trend indicates that the modes associated with the bonds that include only M and O, such as the terminals or M-O-M bridges, shift gradually at higher frequencies, with increasing amounts of W, while the M-O-Ni modes, associated with nickel, shift at lower frequencies with increasing W, showing a difference of 10 cm^{-1} between the final members of the series (ring bonds strengthening and heteroatom bonds weakening).
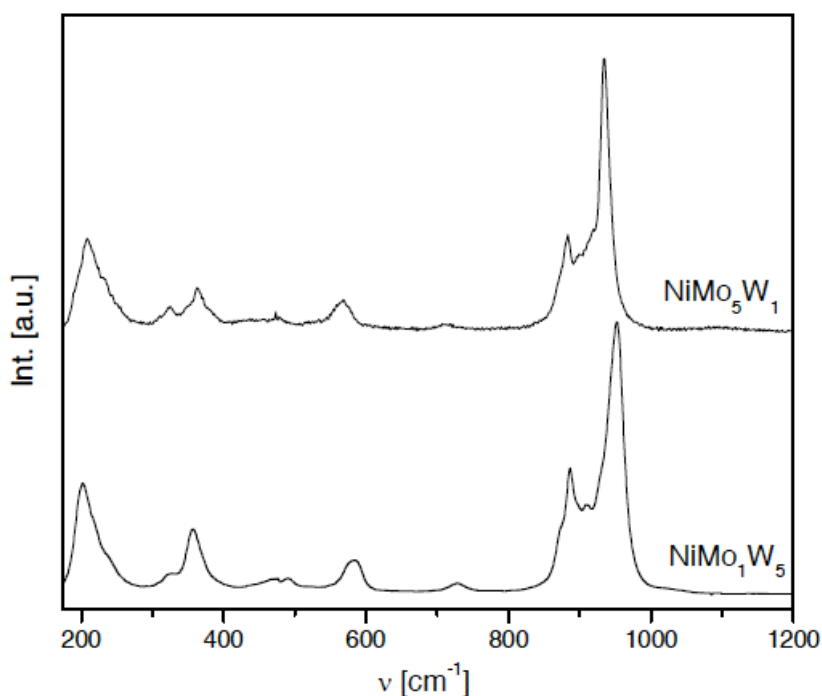
Fig. (3). Comparative Raman spectra between NiMo$_{6-x}$W$_x$ (x= 1 and 5) trimetallic phases.
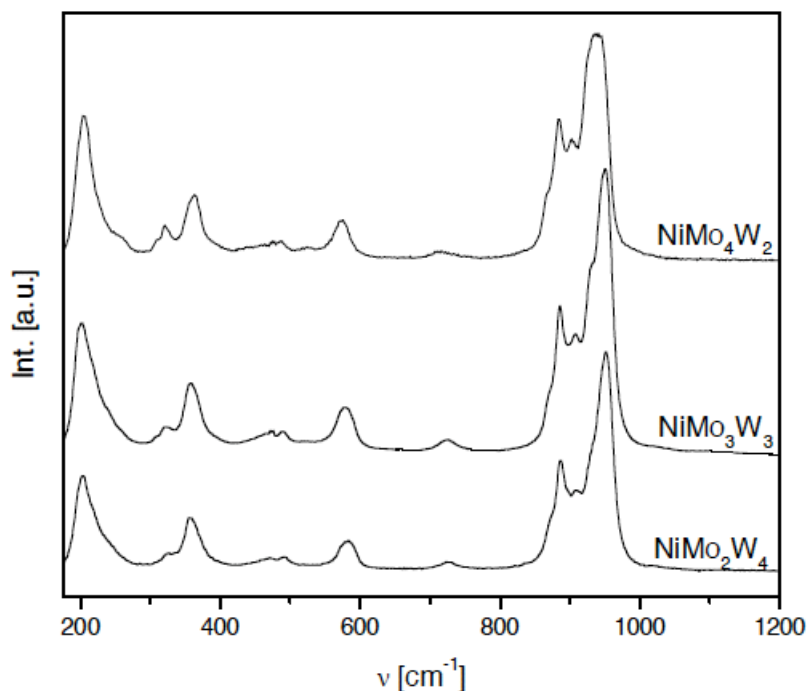
**Fig. (4).** Comparative Raman spectra between NiMo$_{6-x}$W$_x$ (x= 2, 3 and 4) trimetallic phases.

Fig. (**5**) shows diffuse reflectance spectra (DRS) of the studied phases. The substituted phases show similar spectra, while the bimetallic phases, on the extremes of the series (*a* and *g*), show spectra whose difference is revealed both in the degree of definition and in the position of the bands. In effect, in the spectrum of the phase NiW$_6$ (curve *g*) it is possible to clearly assign the intense band of the charge transference LMCT W(VI) ←O^{2-} at 261 nm, while the one analo-

gous to the Mo(VI) (curve *a*), is wider and shows a maximum value of approximately 273 nm. At greater wavelength, the first of the three bands of d-d transition may be assigned to Ni(II) in octahedral environment (^{3}A$_{2g}$ → (1°)^{3}T$_{1g}$(P), (2°)^{3}T1g, and (3°)^{3}T$_{2g}$ respectively), which is observed at 400 nm, in the spectrum (*g*) of the phase NiW$_6$, not in the spectrum (*a*) corresponding to NiMo$_6$. The second band of transition for Ni(II) is not clear, and it can be observed in all the

Table 2. Assignments for Main Raman Lines for the Phases [NiMo$_{6-x}$W$_x$].

Phase	ν_sM-O$_{2t}$	ν_{as}M-O$_{2t}$	νM-O-M	νM-O-Ni
NiMo$_6$	936	887	570	364
NiMo$_5$W$_1$	935	883	569	363
NiMo$_4$W$_2$	940	884	574	362
NiMo$_3$W$_3$	951	886	576	358
NiMo$_2$W$_4$	952	887	582	357
NiMo$_1$W$_5$	953	888	585	357
NiW$_6$	955	891	590	354
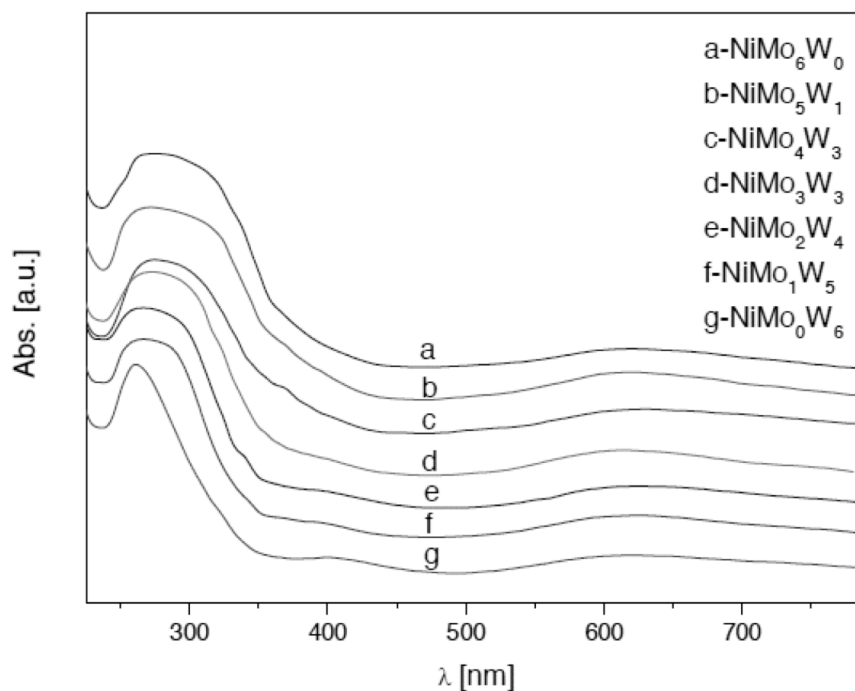
Fig. (5). Comparative diffuse reflectance spectra for the series [NiMo$_{6-x}$W$_x$] with X = 0,1, 2, 3, 4, 5 and 6.

species at approximately 620 nm. The equipment used does not allow observing the third band over 900 nm [12].

With increasing content of W, the second band of d-d Ni(II) transition shows a slight shift to higher frequencies. In this sense, it is possible to associate this effect with the greater length of the W-O bond in the W-O-Ni with respect to Mo-O-Ni bridges, which generates a higher availability of oxygen towards the central Ni atom, originating stronger Ni-O bonds in the compounds with higher content of W. This effect is inductively observed towards the terminal oxygen, revealing comparatively spectroscopic differences between the species containing Mo and W, taking into account the results of micro-Raman and DRS analyses.

Also, due to the properties above mentioned, the first d-d band of transition is better observed in NiW$_6$.

Fig. (**6**) illustrates the diagrams of temperature programmed reduction of the studied phases. This technique

constitutes a useful tool in the study of catalysts, since it allows analyzing the redox behavior of the individual metallic species in the polymetallic matrix.

Differences in the behavior of the phases are more clearly observed for the bimetallic phases (NiMo$_6$ and NiW$_6$). The TPR diagram of NiMo$_6$ is typical for the oxidic compounds with Mo, showing two regions associated with the reduction stages Mo(VI)-Mo(IV) and Mo(IV)-Mo° which depend on the characteristics of the heteroatom [13, 14]. The reduction behaviour of intermediate phases can be attributed to the stability of Mo- and W-oxides, which are segregated from the NiMO$_4$ (M=Mo, W), at a temperature in the range of 500-600 °C. On the other hand, the Mo(VI)-Mo(IV)-Mo° reduction process occurs at a lower temperature than the W(VI)-W° one. Therefore, the observed trend with a shifting of reduction signals in position and intensity can be assigned to the simultaneous presence of different oxide phases. In previous works, formation of Mo$_4$O$_{11}$; MoO$_2$ and NiMoO$_4$
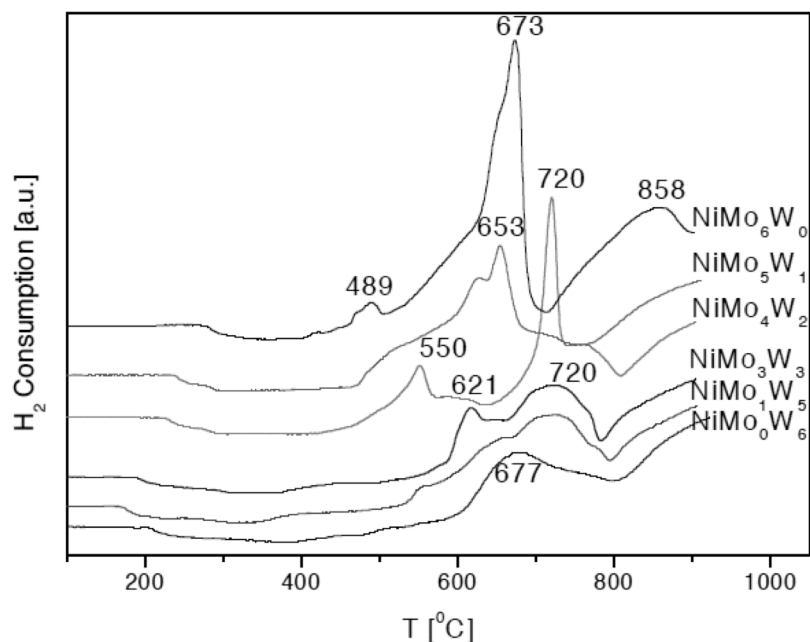
Fig. (6). Comparative TPR diagram for the series [NiMo$_{6-x}$W$_x$] con X = 0, 1, 2, 3, 4, 5 and 6.
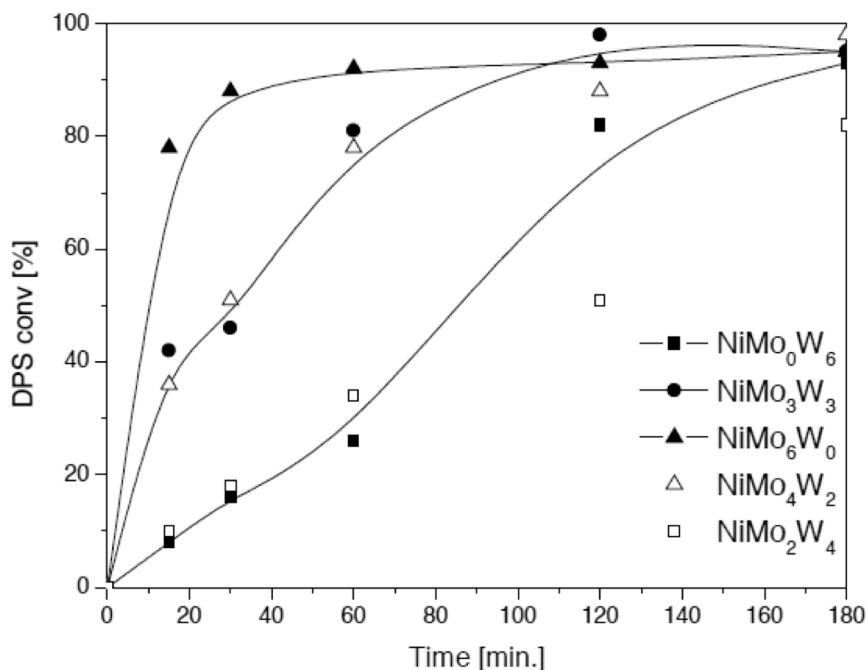
Fig. (7). Conversion as a function of time for the oxidation of DPS reaction using 50 mg of catalyst ([NiMo$_{6-x}$W$_x$] with X = 0, 2, 3, 4 and 6) and H$_2$O$_2$ 1ml in 4 ml of ethanol at 50 ºC.

[13, 14] has been identified in the range between 400 to 500 ºC. The last phase decomposes from 650 ºC, coinciding with the peak of highest consumption of H$_2$.

The TPR diagram of NiW$_6$ is also typical of the oxidic species containing W(VI), with a signal in the zone between 600 and 700 ºC and another one defined in the zone of highest temperature. The behavior is similar to that observed in wolframite-type structures. In this sense, the formation of NiWO$_4$, whose thermal stability is inferred to be higher than that of the homologous phase of Mo, is confirmed. It is evi-

dent that the divalent Ni, even when affected by reduction, has an important role in the stability of W(VI) or Mo(VI) in reducing conditions.

CATALYTIC EVALUATION

Fig. (**7**) illustrates the results of the conversion of diphenylsulfide as a function of time, for the NiMo$_6$, NiMo$_3$W$_3$, and NiW$_6$ as representative phases. The results for the NiMo$_4$W$_2$ and NiMo$_2$W$_4$ are indicated with empty symbols in the figure. It is evident that the phases with greater

Table 3. **Selectivity (%) for [NiMo$_{6-x}$W$_x$] catalysts (x = 0, 2, 3, 4, 6) at 1 and 3h in the DPS oxidation, at 50 ºC, H$_2$O$_2$ 1ml and 50 mg of catalyst in 4 ml of ethanol.**

Catalyst	Selec. (%) 1h		Selec. (%) 3h	
	DPSO	DPSO$_2$	DPSO	DPSO$_2$
NiW$_6$	12	88	19	81
NiMo$_2$W$_4$	13	87	20	80
NiMo$_3$W$_3$	12	88	27	73
Ni Mo$_4$W$_2$	16	84	3	97
NiMo$_6$	98	2	98	2

DPSO: diphenylsulfoxide; **DPSO$_2$:** diphenylsulfone

proportion of W present a behavior similar to NiW$_6$, whereas the phases with greater content of Mo have an activity similar to that of NiMo$_6$.

Table **3** shows the results of the selectivity obtained by using the phases studied in the diphenylsulfide oxidative process, indicating specifically the products of the reaction. In general, the species containing greater proportion of Mo are more active, according to Fig. (**7**), but are selective for the production of sulfoxide, unlike the formation of sulfone, which is favored by the phases with a higher proportion of W.

The efficiency in the formation of sulfone can be associated to the differences in the electronegativity and ionic potential of W with respect to Mo, aspects that ensure a greater electronic mobility in NiW$_6$ and facilitate the process by using hydrogen peroxide as oxidant.

This catalytic behavior can be correlated with the DRS and Raman spectroscopic behavior, which reveals a different strength in the bond of the Mo/W-O-Ni bridges. Thus, the compounds with greater content of W present a greater availability of oxygen towards the atom of central Ni, giving place to stronger Ni-O bonds and consequently a more reactive or vulnerable W-O bond by inductive action. On the other hand, this behavior is also confirmed by the TPR technique that showed the formation of the intermediate NiWO$_4$ at a greater temperature than the homologous phase of Mo. Consequently, the Anderson phases with a high content of W are more efficient in the formation of sulfone, the final compound of oxidation.

CONCLUSIONS

The use of [NiMo$_{6-x}$W$_x$] substituted Anderson phases was proved as a catalyst in the process of oxidation of diphenylsulfide in the presence of hydrogen peroxide. The results showed that the trimetallic structural phases containing a high proportion of W, as well as the bimetallic NiW$_6$ compound, are good catalysts for the sulfone production, although the activity is reached at long periods. On the other hand, the phases containing high values of Mo are more active, but selective for the sulfoxide production. According to spectroscopic and TPR results, the differences can be attributed to the weakness of the W-O bond with respect to that of Mo-O in the structure of Ni-heteropolyanion. The electronegativity and ionic potential of Mo and W in the lattice af-

fect the electronic mobility in the Ni-O-(Mo, W) bridges, and consequently, the availability of the active sites.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflicts of interest.

ACKNOWLEDGEMENTS

REFERENCES

[1]   Pope, M.T.: *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: Berlín, **1983**.
[2]   Pope, M.T., Müller, A: *Polyoxometalate Chemistry from topology via Self-assembly to Application*, Kluwer Academic Publishers: London, **2001**.
[3]   Mizuno, N.; Misono, M. Heterogeneous Catalysis. *Chem. Rev.*, **1998**, *98* (1), 199-218.
[4]   Misono, M. Heterogeneous Catalysis by Heteropoly Compounds of Molybdenum and Tungsten. *Catal. Rev. Sci. Eng.*, **1987**, *29* (2-3), 269-302.
[5]   Cabello, C. I.; Muñoz, M.; Payen, E.; Thomas, H.J. "Influence of cobalt content on hydrotreatment catalytic activity for CoMo$_6$/γ-Al$_2$O$_3$ heteropolymetalate based catalyst". *Cata. Lett.*, **2004**, *92*(1-2), 69-73.
[6]   Cabello, C.I.; Botto, I.L.; Thomas, H. J. "Anderson type heteropolyoxomolybdates in catalysis: 1. (NH$_4$)$_3$[CoMo$_6$O$_{24}$H$_6$]·7H$_2$O/γ-Al$_2$O$_3$ as alternative of Co-Mo/γ-Al$_2$O$_3$ hydrotreating catalysts". *Appl. Catal. A: Gral.*, **2000**,*197* (1), 79-86.
[7]   Pettiti, I.; Botto, I.L.; Cabello, C.I.; Colonna, S.; Faticanti, M.; Minelli, G.; Porta, P.; Thomas, H.J. Anderson-type heteropolyoxomolybdates in catalysis: 2. EXAFS study on γ-Al$_2$O$_3$-supported Mo, Co and Ni sulfided phases as HDS catalysts. *Appl. Catal. A: Gral.*, **2001**, *220* (1-2), 113-121.
[8]   Sato, K.; Aoki, M.; Zheng, X.Q.; Noyory, R. Oxidation of sulfides to sulfoxides and sulfones with 30 % hydrogen peroxide under organic solvent- and halogen-free conditions. *Tetrahedron*, **2001**, *57* (13), 2469-2476.
[9]   Bösing, M.; Nöh, A.; Loose, I.; Krebs, B. Highly efficient catalysts in directed oxygen-transfer processes: Synthesis, Structures of Novel manganese-containing heteropolyanions, and applications in regioselective epoxidation of dienes with hydrogen peroxide, *J. Am. Chem. Soc.*, **1998**, *120* (29), 7252-7259.
[10] Patai, S.; Rappoport, Z. The synthesis of sulfones, sulfoxides and Cyclic sulphides; John Wiley: New York, **1994**.

[11]   Egusquiza, M.G.; Ben Tayeb, K.; Muñoz, M.; Romanelli, G.; Cabello, C.I.; Botto, I.L.; Thomas, H.J. Potentiality of Heteropoly-tungstates as catalysts in the selective oxidation of diphenylsulfide to diphenylsulfoxide. *J. Arg. Chem. Soc*., **2009**, *97* (1), 166-173.

[12]   Porta, P. Minelli, G. Moretti, G. Pettiti, I. Botto, I. L. Thomas, H. Anderson-type ammonium hexamolybdotungstonickelates. *J. Mater. Chem.*, **1994**, *4*(4), 541-545.

[13]   Cabello, C.I.; Botto, I.L.; Cabrerizo, F.; González, M.G.; Thomas, H.J. Al$_2$O$_3$-supported Mo $_6$-Anderson heteropoly oxomolybdates: Adsorption Studies for X= Te^{VI}, Al^{III}, Co^{III} and Ni^{II} by DRS Spectroscopy and TPR Analysis. *Ads. Sci.&Tech*., **2000**, *18*(7), 591-608.

[14]   Botto, I. L., Cabello C. I. and Thomas H. J., Reducibility and thermal behaviour of some Anderson phases. *Thermochimica Acta*, **1994**, *232*, 183-193.