POTENTIALITY OF HETEROPOLYTUNGSTATES AS CATALYSTS IN THE SELECTIVE OXIDATION OF DIPHENYLSULFIDE TO DIPHENYLSULFOXIDE

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Abstract

The activity of complex heteropolytungstates of general formula B-α-$[M^{II}_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ (1) with M= Co(II), Zn(II), Mn(II) and Cu(II) (PWM) was investigated in the selective oxidation reaction of diphenylsulfide to diphenylsulfoxide in presence of *tert*-butylhydroperoxide as oxidant. The characterization of phases was performed by X Ray Powder Diffraction, XRD. All phases resulted isomorphous although PWCu is obtained as a mixture of two structural isomers $[Cu_2(H_2O)_2PW_{10}O_{38}]^{7-}$.

The oxidation reaction was carried out in batch at 80°C using toluene as solvent and *t*-butylhydroperoxide 5-6 M in decane as oxidant for 6 h. The catalytic evaluation made by gas chromatography revealed a similar behavior with conversions of diphenylsulfide around 60% and high selectivity to diphenylsulfoxide near to 95% for most of phases studied while PWCu resulted the most active catalyst presenting a conversion of 84%. The activity rise was correlated with the increase of the oxidant character of the cluster metal(II).

Keywords: heteropolytungstates, diphenylsulfoxides, selective oxidation, tert-butyl-hydroperoxide.

Resumen

Se investigó la actividad de heteropolitungstatos complejos de fórmula general B-α-$[M^{II}_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ (PMW) con M= Co(II), Zn(II), Mn(II) y Cu(II) en la reacción de oxidación selectiva de difenilsulfuro a difenilsulfóxido en presencia de peróxido de *ter*-butilo como oxidante. La caracterización de las fases se realizó por Difracción de Polvos por Rayos X, DRX. El estudio mostró que a excepción del precursor y la fase conteniendo M^{II}_4 Cu(II), las fases con M_4 = Co(II), Zn(II) y Mn(II) son isomorfas. La fase correspondiente a Cu(II) se obtiene como componente de una mezcla conteniendo además dos isómeros estructurales de fórmula $[Cu_2(H_2O)_2PW_{10}O_{38}]^{7-}$.

La reacción de oxidación se llevó a cabo en batch a 80°C en tolueno como solvente y peróxido de *t*-butilo como oxidante, durante un período de 6 h. La evaluación catalítica realizada por cromatografía gaseosa reveló un comportamiento similar con conversiones de difenilsulfuro alrededor del 60% y una alta selectividad a difenilsulfóxido no menor al 95% para la mayoría de las fases estudiadas mientras que el sistema que contiene cobre con M(II) = Cu resultó el catalizador más activo presentando una conversión de 84%. El incremento en la actividad se correlaciona con el incremento del carácter oxidante del metal del cluster.

Palabras Claves: heteropolitungstatos, difenilsulfóxidos, oxidación selectiva, Tert-butil-hidroperóxido.

Introduction

Many "sandwich-type" heteropolytungstophosphates having the general formula B-α-$[M^{II}_4(H_2O)_2(PW_9O_{34})_2]^{10-}$, M = transition metal, are easily obtained in aqueous solution by reaction of appropriate amounts of the tri- lacunary Keggin anion B-α-$[PW_9O_{34}]^{9-}$ and transition metal ions [1,2]. The molecular structure of this type of anions was presented for the first time by Weakley et al. for the Co analogue [3]. It is based on the linkage of two lacunary Keggin sub-units B-α-$[PW_9O_{34}]^{9-}$ as it is observed in Fig. 1.

These compounds have attracted special interest from the academic point of view and from the industrial potentiality as catalysts in "cleaning" oxidative catalysis. In this context, they have recently shown interesting results in limonene epoxidation and in oxidation processes of arenes and phenols using H_2O_2 [4,5]. However, a small number of reports appeared on their possible application as catalysts for selective oxidation of sulfides to sulfoxides.

In general, the catalytic oxidation oxidation of sulfide to sulfoxide has a lower conversion rate than that observed for the sulfoxide-sulfone process; fact that made difficult the synthesis of medicines which requires less than 0.5% of sulfones in its formulation (as rabeprazole, lansoprazole, omeprazole, etc). In this sense, the sulfoxide – sulfone separation process necessary for the isolation of active species must be optimized [6,8].

On the other hand, most of the oxidative procedures reported up to now result to be aggressive from environmental point of view. This is related to the use of contaminant reagents as Cr (VI) and Mn (VII), as well as to the long reaction times. Recently, some works in which
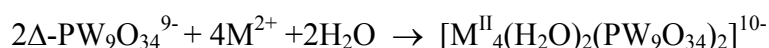
different oxygen carriers are employed have been reported. So, hydrogen peroxide allows to perform reactions in aqueous solution (in batch) and *t*-butylhydroperoxide (*t*-BuOOH) allows oxidative desulfurization reactions (ODS) in batch as well as in reactors of fixed bed [9]. Both oxidants produce "clean" residues (water and *t*-butanol) and facilitate the direct access to oxygen resulting simple in their storage and of low cost. Regarding catalysts useful in the oxidative process, they are commonly redox type. Basically they derive from precursors of transition metals oxide nature containing particularly Mo and W. Hence tungstates or molybdates are usually supported on γ-Al_2O_3 whereas W-heteropolyacids can be used without support. As example, Keggin polyoxometalates of different structural nature were applied with success in several processes of sulfide selective oxidation [10].

The objective of the present work is to explore the catalytic possibilities of the series of heteropolytungstates B-α-$[M^{II}_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ containing M(II) = Co, Cu, Mn and Zn, which are prepared, characterized and proved for the selective oxidation of sulfides. Chemical properties and catalytic activity are related.

Experimental

Synthesis of the K_{10} [$M^{II}_4(H_2O)_2(PW_9O_{34})_2$] phases

The synthesis was made by reaction in aqueous solution from a $Na_8HPW_9O_{34}.24H_2O$ precursor which was previously obtained by reaction between sodium wolframate and the H_3PO_4 acid [3]. The *$K_{10}[M^{II}_4(H_2O)_2(PW_9O_{34})_2]$* phases were obtained from the precursor and Co, Zn, Mn and Cu salts in a stoichiometric ratio by using KCl in excess according to the following reaction:

$$2\Delta\text{-}PW_9O_{34}{}^{9-} + 4M^{2+} + 2H_2O \rightarrow [M^{II}_4(H_2O)_2(PW_9O_{34})_2]^{10-}$$

The obtained solid is filtered and purified by recrystallization.

Physicochemical characterization

Physicochemical characterization was performed by (TG-DTA, TPR) Thermal Analysis, FTIR and Raman Vibrational Spectroscopy and (SEM-EDS) Electron Microscopy have been reported recently [11]. In this work, X ray powder diffraction patterns were registered by an equipment Philips-1714 (CuKα radiation, Ni filter). Also, FTIR spectra which were obtained by using a Bruker IFSS 66 FT-IR equipment (KBr pellet technique).

Catalytic activity

The reaction was carried out in a batch stirred reactor. Parameters (time reaction, catalyst/reactive and oxidant/reactive ratios) were optimized previously for this reactions using other catalyst [12,13]. The best results for the selective diphenylsulfide - diphenylsulfoxide oxidation were obtained by using 1 mmol of diphenylsulfoxide dissolved in 5 ml of toluene, 1 ml of *t*-butylhydroperoxide 5-6 M in decane as oxidant; 1 milimol % of catalyst. All runs was performed at T = 80ºC and time = 6 h. Likewise, it is interesting to remark that the inorganic phases are insoluble in the used organic solvents. The reaction advance was followed by TLC using as solvent a mixture of ethyl-acetate: hexane (1:5), then, it was quantified by GC, with a Varian Start 3400 CX, CRHOM-PACK-CP-SIL5CB, FID detector.

Results and discussion

Figure 1 shows the structures of the $[M^{II}_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ heterpolytungstates and the B-α-$PW_9O_{34}{}^{9-}$ precursor anion (hereafter PMW and PW$_9$ respectively). The structure of stable Co, Zn

and Mn heteropolytungstates is an assemblage of two PW_9 condensed lacunary-fragments through the intercalation of a M^{II} tetranuclear cluster where each MO_6 unit is octahedrally coordinated to terminal oxygen atom from two lacunary-fragments. On the other hand the MO_6 entities are condensed by edges in the metal cluster.
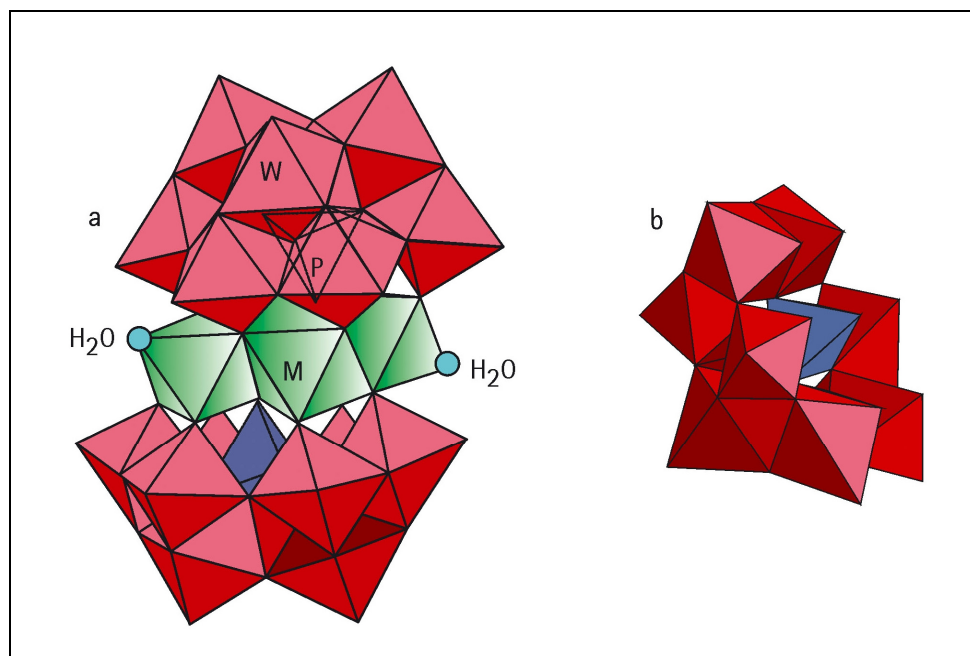

Figure 1. Polyhedral representation of (a) $[M_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ and (b) B-α- $[PW_9O_{34}]^{9-}$

In the PWCu preparation process, it was possible to observe that the species with this stoichiometry are very susceptible to environmental conditions (particularly temperature). The PWCu phase is unstable at RT decomposing partially. So, the resulting product is a mixture of the PWCu original phase and two isomers Keggin- type of formula $[PW_{10}Cu_2(H_2O)_2O_{38}]^{7-}$ (named $PW_{10}Cu_2$). In this phase, two WO_6 octahedrons are substituted by two CuO_6 polyhedra in the positions observed in Figure 2 (a and b).
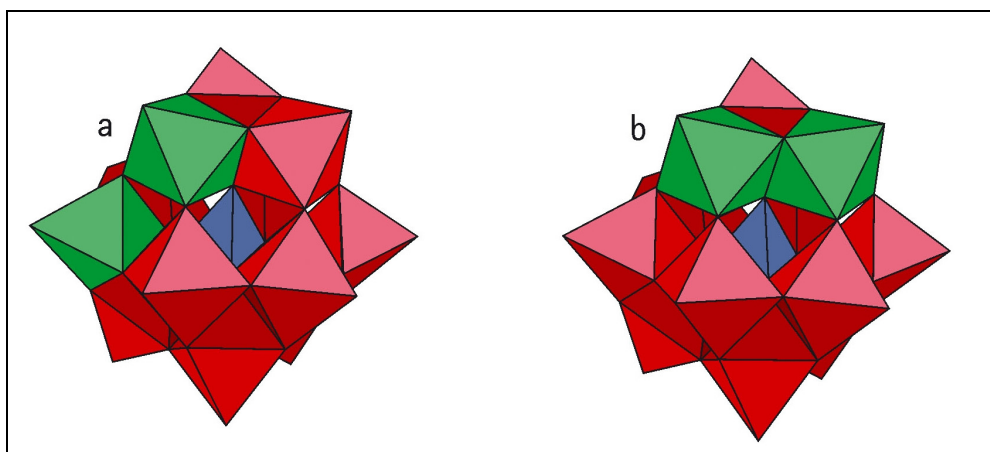

Figure 2. Polyhedral representation of (a and b) $PW_{10}Cu_2$ isomers.

On the other hand, Figure 3 shows the comparative X Ray Diffraction Powder patterns of the PWCo typical structure and the resulting Cu-phase. Co and Zn phases result isomorphous to the crystalline structure of Mn member reported in the literature (PDF 81-2062) [14]. The pattern of copper phase is poorly crystalline, some typical lines of the original phase are observed. The different behavior of the Cu member could be related to the punctual asymmetry of the CuO_6 polyhedra by Jahn-Teller effect (Cu(II) t_{2g}^6 eg^3). It is known that some Cu(II) complexes present symmetrical CuO_6 structural sites at low temperature which are distorted (tetragonal symmetry) when temperature increases. The instability of PWCu and the trend to give the two $PW_{10}Cu_2$ isomers of Figure 2 could be related to the orientation of the compressed or elongated polyhedra respect to the general symmetry of the Keggin heteropolyanion crystal structure [3].
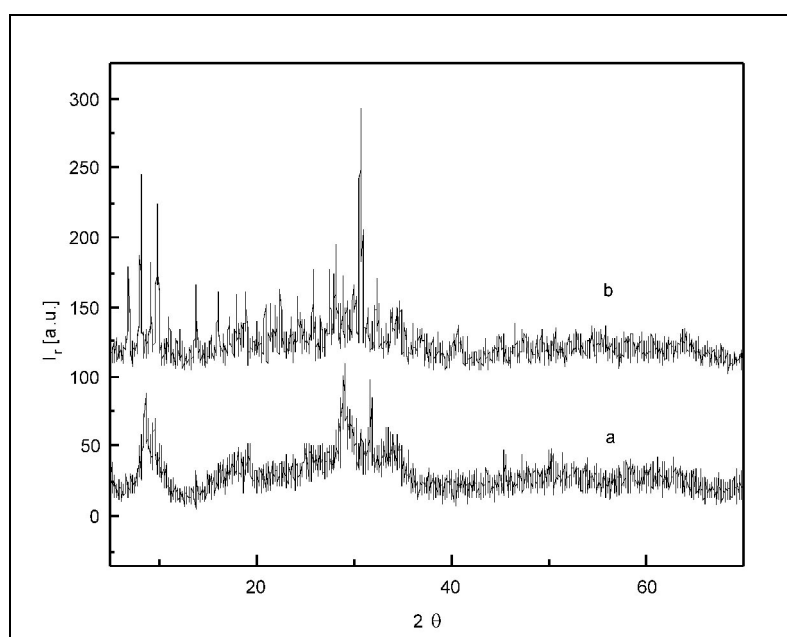

Figure 3. X Ray Powder Diffraction patterns of (a) P-W-Cu mixed phases and (b) PWCo phase.

Figure 4 shows the comparative FTIR spectra in the frequency range of 1600 to 400 cm^{-1} of (a) Precursor PW_9, (b) PWCu mixed phase and (c) PWCo typical phase. In the range between 1200 and 1000 cm^{-1} it is possible to observe that both, lacunar precursor and PWCu-mixed low symmetry species present a group of bands corresponding to P=O and P-OH groups in a distorted environment [11]. The fact that spectrum 4(b) shows four bands instead of two confirms the existence of two structural isomers $PW_{10}Cu_2$. In contrast, the PWCo spectrum 4(c) presents a single band at 1038 cm^{-1} assigned to a symmetric stretching from the phosphate group of regular tetrahedral symmetry. It has been suggested that the origin of the symmetry decrease of isomers $PW_{10}Cu_2$ and hence the thermal instability of the phase containing the Cu_4 cluster are produced by the weak interaction of CuO_6 octahedron with phosphate groups in comparison with that corresponding to the WO_6 groups. This effect is possibly caused by the Jahn-Teller distortion in axial direction typical of Cu (II) ion in octahedral coordination [15]. In this way, phosphate group loses its regular tetrahedron environment and the symmetric P=O stretching band splits. Regarding bands related to the WO_6 octahedron, it is possible to assign both W=O (940 cm^{-1}) terminal bonds and W-O-W bridges (840-750 cm^{-1}). Comparatively the bands corresponding to PWM phases suffer only a slight shift toward higher frequencies respect to the precursor [11].
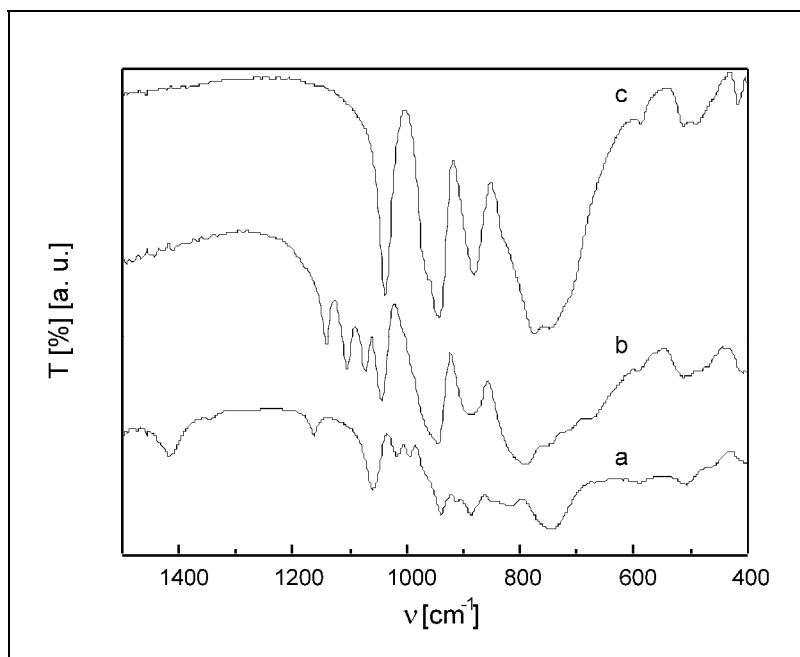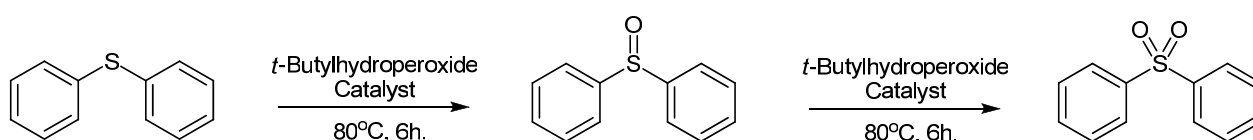
Figure 4. Comparative FTIR spectra of following samples: (a) Precursor PW$_9$; (b) P-W-Cu mixed phases and (c) PWCo phase.

Catalytic evaluation

The following scheme represents the catalytic reaction and Table 1 shows results of selective oxidation of diphenylsulfide to diphenylsulfoxide by using the different complex heteropolyanions as catalysts.

The reaction was produced with very low sulfide conversions if catalysts are not used. So, for test 1 (without catalyst), the conversion (after 6 h treatment) was only of 10% with a 100% selectivity to form sulfoxide. In presence of catalysts the conversion increases considerably, (tests 2-6) with conversion values ranged 55 and 84%. It is interesting to note that the mixture derivative of P-W-Cu was catalytically more effective, with a diphenylsulfoxide conversion of 84%. In this aspect, the species showed a similar behavior to that observed in the limonene epoxidation [5].

The comparison of results with that obtained with the PW$_9$ precursor phase suggests that the activity is related with the presence of the metal and particularly with the chemical properties. In this sense, the redox character of divalent species, the stability of its oxidation state, the chemical affinity toward the reactive and the M local symmetry play an important role to definite the following activity order PWCu > PWCo>PWZn >PWMn > PW$_9$. The reactivity is in agreement with the redox potentials for the M(II)/M reduction pair E° Cu(II)/Cu= 0,34 > E° Co(II)/Co= -0.28 V > E° Zn(II)/Zn= -0.76 V> E° Mn(II)/Mn= -1.03 V [11], pointing out the lower copper capacity to remain as divalent species. Contrary, Mn(II) only presents higher oxidation states while Co(II)-Co(III) oxidation is relatively difficult in absence of adequate environment. Zn(II) is inert to

oxidize, whereas Cu(II) is the unique species easy to reduce to monovalent ion (Cu(II)/Cu(I)= 0.16 V). On the other hand, the asymmetry of CuO_6 polyhedra by Jahn Teller effect, responsible for the PWCu instability, increases the interaction of the mixture of phases with the reactive and consequently the catalyst activity. Additionally, it is possible to suggest an increase of the Cu(I)-sulfide species according to the hard and soft Pearson' acids classification, which can favor the formation of an intermediate meta-stable phase.

Selectivity was higher than 94% for the totality of catalytically proved phases. Only small amounts of sulfones were detected (lower than 6%). Other secondary products were not detected in the reaction medium, therefore the studied process can be considered as clean and highly efficient to obtain sulfoxides.

Table 1. Catalytic activity for PW_9 and different PWM phases in the selective diphenylsulfide- to diphenylsulfoxide oxidation.

Test	Phase	Sulfide Conversion (%)	Sulfoxide Selectivity (%)	Sulfone Selectivity (%)
1	_	10	100	_
2	PW_9	55	95	5
3	PWCo	61	95	5
4	PWZn	59	95	5
5	PWMn	57	95	5
6	P-W-Cu	84	94	6

Conclusions

The synthesis and characterization of complex heteropolyoxotungstates (PWM with M= Co, Mn, Zn) lead to stable phases. The PWCu was unstable forming two Keggin isomers of $[PCu_2W_{10}]$ composition. All phases, including the precursor employed in the synthesis were proved as heterogeneous catalysts for the diphenylsulfide - diphenylsulfoxide oxidation in a clean process. The activity and selectivity can be related to the M chemical properties and in the Cu-phase particularly to the CuO_6 local symmetry associated to the electronic configuration. The possible formation of a metastable Cu(I)-S effective bond can be suggested from the chemical comparison.

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