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Application of complex heteropolytungstates in limonene epoxidation by H_2O_2 in biphasic medium

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Abstract

The synthesis of potassium salts of Cu heteropolytungstate was carried out by reaction in aqueous solution of $Na_8H[\Delta PW_9O_{34}]\cdot 19H_2O$ lacunary precursor with Cu nitrate in KCl excess. The product is a mixture of two isomers related to Keggin structure, having a composition $K_{5.5}Na_{1.5}[PW_{10}O_{38}Cu_2(H_2O)_2]\cdot 13H_2O$, which are the main phases, while the tetra-nuclear copper cluster with formula: $[K_{10}(PW_9O_{34})_2\text{-}Cu_4(H_2O)_2]\cdot 20H_2O$ was the minority phase. The characterization was carried out by means of X-ray powder diffraction analysis (XRD) and vibrational FT-IR and Raman spectroscopy. The Cu-phase mixture was used as catalyst for the epoxidation of limonene in biphasic (water–organic) reaction media using hydrogen peroxide (35% aqueous H_2O_2) as the oxygen donor. It was able to oxidize selectively limonene towards the epoxide at very high turnover numbers. In addition, similar studies were performed with both the structural related ($[K_{10}(PW_9O_{34})_2Co_4(H_2O)_2]\cdot 20H_2O$) and the lacunary precursor for comparative purposes. Some comments about the stability of copper and cobalt tetra-nuclear phases were made on the basis of topological and electronic considerations and the distortion of the metal environments was related to the catalytic behavior.

Keywords: Heteropolytungstates; Catalytic oxidations; Limonene; Hydrogen peroxide

1. Introduction

The present environmental trends have forced fine chemicals industries to re-evaluate their processes in order to reduce contaminant effluents resulting from stoichiometric oxidation processes. Therefore, it is of great interest to use effective and selective catalytic systems in combination with hydrogen peroxide as oxygen donor (clean oxidant agent) for the oxidation of organic substrates. Also, the terpene-oxygenated derivates are of great interest due to the fact that they are used in the production of fragrances and perfumes [1]. The limonene oxidation in heterogeneous conditions has been reported by Villa et al. [2] using hydrogen peroxide and tungstophosphoric acid anchored in Amberlyst IRA 900. Armendia et al. [3] have also reported the limonene oxidation to limonene oxide using the double layer hydroxides (Mg/Al) in the presence of nitrile. In the same way, Pizzio et al. have used heteropolycompounds containing W or Mo supported on carbon and alumina [4], while Corma et al. used mesoporous materials containing Ti [5] and Crivello et al. used catalysts based on hydrotalcite-type precursors [6].

Venturello et al. have reported homogeneous catalysts based on heteropolyacids working under biphasic conditions as a feasible method for epoxidation of olefins [7,8].

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Transition metallic ions have been substituted in lacunary polyoxotungstates giving place to polyoxometalates of general formula $[WMM'_2(XW_9O_{34})_2]^{12-}$ where M and M′ are manganese, cobalt, iron, zinc, nickel or copper and X might be zinc or cobalt. These compounds result in the formation of active complexes in reactions of catalytic oxidation of alkenes and alcohols [9,10]. These can be seen as a transition metals coordinated to an inorganic bond which is oxidatively stable.

In order to obtain selectively 1,2-epoxilimonene, the study was carried out by using heteropolymetalates of potential catalytic interest but with a certain structural complexity, i.e., bimetallic complexes constituted by a mixture of Cu isomers related to Keggin structure and a "sandwich"-type structure with fragments $[PW_9O_{34}]^{9-}$ [11] linked through a group or "cluster" of metallic ions, resulting in a general formula $[(PW_9O_{34})_2M_4(H_2O)_2]^{10-}$ with M = Cu(II) and Co(II) [12].

The aim of this work was the study of the catalytic reaction for the selective limonene epoxidation in a biphasic system using H_2O_2 (35%, w/w) as clean oxidant, dicloroethane as solvent and the Cu phase above mentioned as the catalyst. Likewise, both the precursor of such phases ($Na_8H[\Delta PW_9O_{34}]\cdot 19H_2O$) and the corresponding Co_4-phase were studied for comparative purposes.

2. Experimental

2.1. Synthesis of catalysts

The precursor $Na_8H[\Delta PW_9O_{34}]\cdot 19H_2O$ was synthesized from stoichiometric amounts of $Na_2WO_4\cdot 2H_2O$, phosphoric acid and acetic acid. The precipitate was treated at 80 °C for 3 days. In order to obtain the catalyst, an aqueous solution of $Cu(NO_3)_2$ was used and the precursor was added at stoichiometric amount and finally an excess of potassic salt. The solution was centrifuged and it was kept at room temperature until the precipitation of crystals occurred, and these were air-dried. The synthesis of Co derivate was carried out in a similar way by using the corresponding nitrate [13]. The catalysts obtained in this way were characterized by different techniques.

2.2. Catalyst characterization

The X-ray powder diffraction patterns obtained for pure samples were registered in a Philips-PW 1729 equipment. Cu Kα radiation (Ni filtered) was used and the register was carried out with a scanning angle between 5° and 60° at a rate of 2θ per minute.

The FT-IR spectra were obtained by using a Bruker IFSS 66 FT-IR equipment (KBr pellet technique). The number of scans was 128 and the resolution was $0.5\ cm^{-1}$.

The Raman spectra were recorded in the range of 200–1600 cm^{-1} with a Raman LabRAM Infinity microprobe (Jobin Yvon) equipped with a liquid nitrogen cooled detector and a frequency-doubled Nd:YAG laser supplying the excitation line at 532 nm. The power at the sample was below 5 mW, the resolution was $3\ cm^{-1}$ and the number scans was 10.

2.3. Catalytic reaction

The stock solution of the catalysts under study was prepared by dissolving: 0.016 mmol of polyoxometalate salt and 0.13 mmol of metiltricaprilamonium chloride (Aliquat 336) in a mixture of the same proportion H_2O/1,2-dichloroethane (5 ml, ratio 1:1). In order that the catalyst could be solubilized in the organic phase, the mixture was stirred and low heating during periods of about 1 h being evident a decolouration of the aqueous phase. Subsequently, the organic phase was separated and cooled.

The oxidation reaction was carried out in a batch-type reactor at atmospheric pressure, under vigorous stirring (800–1000 rpm) and keeping the system at 2 °C during a period of 40 h. In a typical reaction, 3.04 mmol of limonene (L) and the required amount of stock solution were dissolved in 3 ml of 1,2-dicloroethane. The reaction starts by adding peroxide 35% (w/w) (6.08 mmol), forming a biphasic system. The progression of the reaction was followed up by taking small aliquots of the organic phase and these were analysed by gaseous chromatography in a cross-linked methyl capillar column (Silicone Gum, $30\ m \times 0.53\ mm \times 2.65\ \mu m$ film thickness). The reaction products were analysed by comparison with chromatographic witnesses and by GC–mass in a Shimadzu GCMS-QP 5050A.

3. Results and discussion

3.1. Structural and spectroscopic behavior

The complex $[PW_9O_{34})_2M_4(H_2O)_2]^{10-}$ heteropolioxotungstates with M = Co (d^7), Zn (d^{10}) and Mn (d^5) divalent cations can be structurally derived from the union of two $[PW_9O_{34}]^{9-}$ fragments by means of a MO_6 tetra-nuclear cluster, giving rise to the sandwich-type structure (shown in Fig. 1) [12]. The metallic cluster, where the MO_6 groups are linked by the edges, is connected by the corners to the WO_6 and PO_4 groups of two $[PW_9O_{34}]^{9-}$ decapped Keggin phases. The disposition resembles that observed in the 2:1 laminar aluminosilicates, where a brucite-like structure is intercalated between the negative $[(Si,Al)O_4]_n$ layers [14]. Like these species, the sizes of the divalent metallic anions that allow the formation of the W-condensed structure are smaller than 0.83 Å (octahedral coordination). Although the size and charge of the copper species (0.73 Å) are adequate to adopt this structural distribution, the Cu(II) electronic configuration (d^9) hindered the formation of a shared edge octahedral cluster. In fact, the Jahn-Teller effect [15] is responsible for the CuO_6 polyhedral distortion. So, from the topological point of

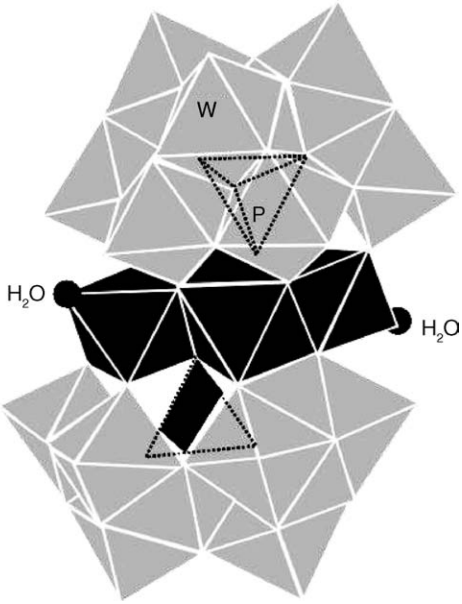

Fig. 1. Structure of $[(PW_9O_{34})_2M_4(H_2O)_2]^{10-}$ with M: Co(II), Mn(II), Zn(II) and Cu(II).

view, the octahedral condensation seems to be difficult in this case. The preparation of the copper tetra-nuclear heteropolytungstate is different from that observed for the analogue divalent species. In the reaction conditions (particularly in the re-crystallization step), the copper phase shows a great hydrolytic instability which leads to the formation of more stable condensed structures. In this structures, the copper is involved through the corner of polyhedral. Two isomers of $[PW_{10}O_{38}Cu_2(H_2O)_2]^{7-}$ composition are the major phases, although the presence of the copper tetra-nuclear heteropolytungstate phase can not be disregarded as minority phase. The mixture of phases is strongly affected by the experimental conditions (particularly time and temperature). Fig. 2 (a and b) shows the structure of the isomers which can be derived from the classic Keggin structure. In one of them two CuO_6 polyhedral are linked by the corners (a) whereas in the other isomer, the two octahedral groups are connected by the edges (b). The presence of two water molecules, bonded to the copper species, contributes to affect its local symmetry. Particularly, the combination of octahedral groups of different size and charge and the geometrical restrictions involved in the condensation lead to polyhedral strained states which are energetically more favourable from the catalytic point of view.

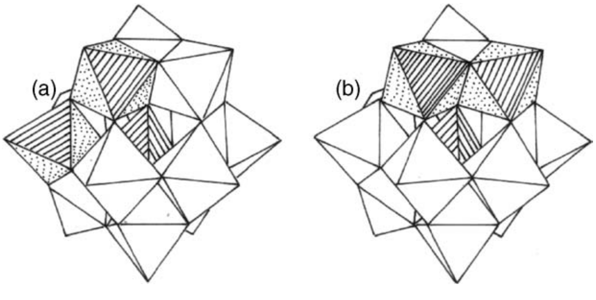

Fig. 2. Structure of isomers $[PW_{10}O_{38}Cu_2(H_2O)_2]^{7-}$: (a) connected through the corners and (b) along edges.

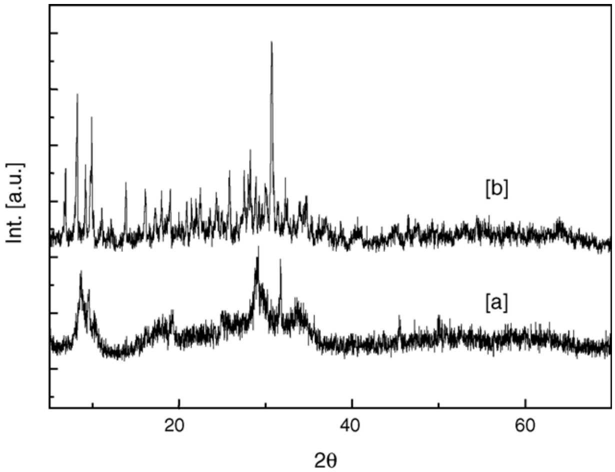

Fig. 3. XRD patterns of: (a) mixture of phases containing Cu(II) and (b) phase containing the tetra-nuclear cluster of Co(II).

The XRD characterization of the copper sample is not so clear because the mixture of phases by the hydrolysis process which is not observed in the preparation of another tetra-nuclear phases, results in amorphous products.

Fig. 3 gives the comparison between the XRD patterns of the copper sample and the cobalt tetra-nuclear heteropolytungstate. The poor resolution of the former clearly shows that the XRD is not the most adequate technique to identify the obtained species.

The vibrational spectroscopy seems to be more useful to differentiate the bond strength and bond length in condensed systems. Fig. 4 gives the comparative IR spectra (between 1500 and 400 cm^{-1}) of the precursor (a), the mixture of the copper phases (b) and the cobalt tetranuclear heteropolytungstate (c). The precursor, a lacunary Keggin phase, presents a very available and distorted PO_4 tetrahedral group, with P–O length bonds of different magnitude (P–OH and P–O)

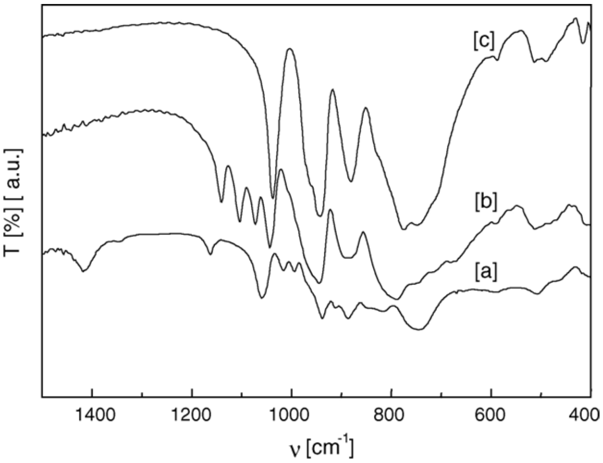

Fig. 4. FT-IR spectra of: (a) precursor $Na_8H[\Delta PW_9O_{34}]\cdot 19\ H_2O$, (b) mixture of Cu(II) phases and (c) Co_4-phase.

according to IR bands at 1015, 1058 and 1160 cm^{-1}. The tetrahedral symmetry is restored from the condensation of $[PW_9O_{34}]^{9-}$ units during the generation of the sandwich heteropolyanion. So, a unique IR band at 1038 cm^{-1} (ν_3 asymmetric mode) is observed in the Co_4-phase spectrum. On the contrary, the copper sample shows a series of bands between 1000 and 1200 cm^{-1}. The splitting can be associated, at least, to the mixture of phases and to the lowering of tetrahedral symmetry by the condensation of different type of polyhedral. The band at 1038 cm^{-1} can be related to the ν_3 mode of the PO_4 group of M_4-phase (which are located between 1029 and 1038 cm^{-1} for M = Mn, Zn and Co) whereas the weak bands at 1139, 1104 and 1071 cm^{-1} can be associated to the lowering of PO_4 T_d symmetry in the Cu_2-(a) and (b) isomeric forms (Fig. 2). The polarizing effect of Cu(II) lower than the corresponding to the W(VI), produces a distortion (by shifting of the P atoms from the tetrahedral centre or by electron density displacement of O atoms) with the reinforcement of some P–O–Cu bonds. The IR spectrum below 1000 cm^{-1} resembles that observed for the cobalt tetranuclear cluster as well as for the precursor. According to the presence of a mixture of copper heteropolyoxotungstates, there are different kinds of W–O bonds in the structures: W–O terminal and W–O–W and W–O–Cu bridge ones. The bands in the 900–1000 cm^{-1} region are assigned to the strongest bonds (stretching of the W=O terminal bonds) while the bands in the 600–900 cm^{-1} are attributed to the remaining W–O stretching bonds. The bands at 886, 790, 745, 715 and 675 cm^{-1} can be correlated to those at 886, 818 and 746 cm^{-1} for the precursor and to those at 881, 829 and 775 cm^{-1} for the Co_4-phase [16–17]. The assignment below 600 cm^{-1} is difficult because the W–O deformation modes are overlapped with the metal–O stretching vibration and the O–P–O bending modes of distorted tetrahedral.

Raman spectrum of Fig. 5 shows a strong line at 963 and a shoulder at 982 cm^{-1}. This can be associated to the presence of several W=O terminal bonds, which result in the most intense and sharpest Raman lines in heteropolyanions [18]. So, the comparison between Cu(II)-phase Raman and Raman spectra of the precursor and the Co_4-phase (966 and 974 cm^{-1}, respectively) in this region was not entirely possible [17]. The observed splitting is due to the mixture of copper heteropolyanions and to the Cu-Jahn-Teller distortion on the most vulnerable bonds.

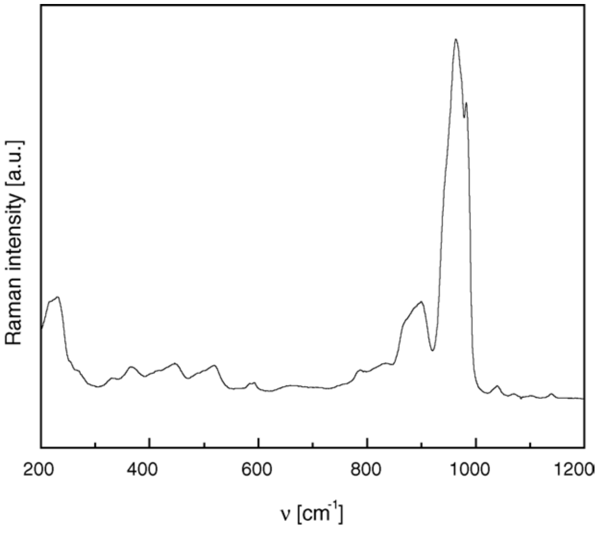

Fig. 5. Raman spectrum of mixture of Cu(II)-phases.

Table 1
Raman spectrum of (a) $[\Delta PW_9O_{34}]^{8-}$, (b) Co_4-phase and (c) mixture of Cu(II)-phases (cm^{-1})

(a) Raman frequency[a]	(b) Raman frequency[a]	(c) Raman frequency	Assignment
1161 vw			ν P–OH
		1139 vw	ν P–O
		1103 vw	
1017sh	1052 m	1074 vw	
		1040 vw	
966 vs	974 vs	982 vs	ν_s W–Ot
		963 vs	
928 sh	949 sh		ν_{as} W–Ot
898 m	889 m	898 m	ν W–O–W
851 w	808 w	833 w	From corner and edge-shared octahedral
655 vw			
599 vw	594 w	593 w	δ WOt
571 vw	523 w	520 w	W–O–W and P–O–P bendings
495 w	492 w	498 sh	M–O ··· W stretching modes

sh: shoulder, m: medium, s: strong, w: weak, vw: very weak and vs: very strong.

[a] Ref. [17].

On the other hand, the weak Raman line at 1040 cm^{-1} as well as the other three very weak signals between 1050 and 1150 cm^{-1} (1074, 1103 and 1139) can be assigned to the P–O symmetrical modes of different PO_4 groups or to the activation of asymmetrical vibrations by distortion effects [17].

Table 1 summarizes the principal Raman regions of the copper phases, including the corresponding values for the precursor and the Co_4-phase for comparison.

From the number and position of the vibrational spectrum it is clearly observed that the metal environments for the copper system are geometrically more distorted than those of the other phases.

3.2. Catalytic behavior

In Table 2, it is shown the results of the catalytic evaluation in the limonene oxidation with H_2O_2 under

Table 2
Products for the limonene oxidation

Catalyst	Selectivity (TON)				
	Epoxide	Carvone	Carveol	Diepoxide	Glycol
Precursor	89% (596)	0	1% (4)	3% (22)	7% (45)
Cu-phase	96% (774)	1% (6)	1% (6)	1% (11)	1% (10)
Co_4-phase	100% (3)	0	0	0	0

Ratio: L/H_2O_2/catalyst (1000/2000/1) at 2 °C and 40 h of reaction.

Table 3
Comparison of different substrate/oxidant/catalyst relations using the Cu-phase at 2 °C and 40 h of reaction

Relation L/H_2O_2/catalyst	Selectivity (TON)				
	Epoxide	Carvone	Carveol	Diepoxide	Glycol
1000/2000/1	96% (774)	1% (6)	1% (6)	1% (11)	1% (10)
2500/5000/1	97% (817)	0	2% (21)	0	1% (8)
5000/10000/1	94% (940)	0	2% (16)	1% (11)	4% (37)

biphasic conditions by using two different complex heteropolyoxometalates and their precursor. The catalyst with sandwich-type structure with a tetra-nuclear of Co(II) (Co_4-phase) showed a low turnover number (TON), while for Cu-mixed heteropolytungstate, was the phase of greatest activity with high selectivity towards epoxilimonene. Similarly, the $[PW_9O_{34}]^{9-}$ precursor, presumably due to its lacunary-type structure of low symmetry, as it was mentioned in the characterization, showed a good activity.

For the most active catalyst, the relation substrate/oxidant/catalyst was varied (Table 3), observing at higher ratios, an increment in the performance of epoxide given by the increase of turnover number with similar selectivities.

With a ratio 2500/5000/1, the TON to epoxide was higher (1884 at 18 h) at higher temperature (25 °C); therefore, with the increase of temperature, a good performance was reached at shorter time. Despite that the selectivity to epoxide was minor (83% at 18 h) by the oxirane ring opening (selectivity to glycols 12%), the yield to epoxide was approximately twice.

According to these results, it would be convenient to continue these studies with other substrate/oxidant/catalyst ratio at temperatures higher than 2 °C.

4. Conclusions

From the synthesized and characterised heteropolyoxometalate complexes, the phase containing Cu(II) has shown to be the most effective catalyst for the selective oxidation of limonene in biphasic conditions. It is suggested that this good activity is due to the existence of a mixed phase constituted by a Cu_4-phase and two Cu_2-isomers of low structural symmetry produced by the Jahn-Teller effect of Cu(II) ions. This feature is in agreement with the entatic state concept and would conform the base of a greater catalytic activity.

While increasing the substrate/oxidant/catalyst ratio, the turnover number of epoxilimonene increases.

When the reaction temperature was modified at 25 °C, the reaction speed was increased, doubling the epoxide TON after 18 h.

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