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Short Communication

Advance in the study of limonene epoxidation with H_2O_2 catalyzed by Cu(II) complex heteropolytungstates

María G. Egusquiza [a,*], Carmen I. Cabello [a,1], Irma L. Botto [c], Horacio J. Thomas [d], Sandra Casuscelli [b], Eduardo Herrero [b], Delia Gazzoli [e]

[a] "Centro de Investigación y Desarrollo en Ciencias Aplicadas Dr. J. J. Ronco", CINDECA, CCT CONICET La Plata — Universidad Nacional de La Plata, Calle 47 N° 257, 1900-La Plata, Argentina
[b] "Centro de Investigación y Tecnología Química", CITeQ, Facultad Regional Córdoba, Universidad Tecnológica Nacional, Cruz Roja Argentina esq. Maestro Lopez, 5016-Córdoba, Argentina
[c] "Centro de Química Inorgánica", CEQUINOR, CCT CONICET La Plata — Universidad Nacional de La Plata, Calle 47 esq. 115, 1900-La Plata, Argentina
[d] "Planta Piloto Multipropósito" PLAPIMU, CIC-PBA — Universidad Nacional de La Plata. Cam. Centenario y 508, 1897-Gonnet, Argentina
[e] Dipartimento di Chímica, Università di Roma "La Sapienza", Pzzale. Aldo Moro 5, Roma 00185, Italy

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ABSTRACT

The complex heteropolyoxotungstates of formula $K_{10}[M_4(H_2O)_2(PW_9O_{34})_2]\cdot 20H_2O$ (PWM) with M = Co(II), Zn(II), Cu(II) and Mn(II), and their precursor, Δ-$Na_8HPW_9O_{34}\cdot 19H_2O$ (Δ-PW_9), were evaluated as bulk in limonene epoxidation using H_2O_2 as oxidant, 1,2 dicloroethane as solvent and metiltricaprilamonium chloride (Aliquat 336) as a phase transfer agent at 2 °C. In these biphasic conditions PWCu was the most active phase. Subsequently this phase was supported on γ-Al_2O_3, the metal load was determined by AAS, ICP and X-ray fluorescence and the preservation of PWCu structure was confirmed by XPS and Raman microprobe. PWCu/γ-Al_2O_3 was evaluated at 70 °C with acetonitrile as solvent. The pure PWCu showed a higher conversion to epoxide but lower selectivity due to the formation of secondary products.

1. Introduction

The attainment of high added value products in conventional industrial processes requires strong oxidants, which are difficult to handle and store; besides they produce a large number of by-products, generally nitrogenous or sulfurate compounds or Cr^{3+} salts, which are very difficult to eliminate and highly polluting. Hydrogen peroxide is considered as an ideal "oxidant" for these types of processes since 47% of its weight is oxidant, it produces water as the only byproduct and consequently the generations of inorganic salts are avoided. Therefore, design and synthesis of adequate catalysts for oxidation processes allowing the use of this "ideal" oxidant are needed.

It is well known that heteropolyoxometalates present a number of chemical and structural properties that make them attractive as oxidation catalysts. They are structurally versatile in their ability to be substituted with different metal ions and controlling the number of these. On the other hand, an additional attribute of heteropolyoxometalates is their inherent stability against oxygen-donor species such as O_2 and H_2O_2 [1–3].

A great number of catalysts have been recently reported for the selective oxidation of organic substrates under benign environmental conditions.

The epoxidation reaction of olefins has attracted particular interest in recent years due to versatility of epoxides as intermediate agents in organic synthesis. Particularly, production of oxygenated terpenic derivatives and natural terpenoids is important for producing fragrances and food additives [4]. Among the latter, the limonene deserves special attention due to its relatively low cost, feasibility of becoming different oxygenated products of high added value, and its easy attainment from a renewable natural source [5–7].

Several catalytic oxidation processes of limonene have been studied [8–10]; however, none of them has shown the necessary characteristics for industrial scale application yet [11–14].

In previous studies the catalytic activity of a series of heteropolyoxotungstates of general formula, $K_{10}[M_4(H_2O)_2(PW_9O_{34})_2]\cdot 20H_2O$ (PWM) with M = Co(II), Zn(II), Cu(II) and Mn(II), and their precursor, Δ-$Na_8HPW_9O_{34}\cdot 19H_2O$ (Δ-PW_9), was analyzed in limonene oxidation [15]. As the PWCu phase showed good activity and selectivity in the limonene oxidation, kinetic studies were carried out changing the limonene/H_2O_2/catalyst ratio. Moreover the PWCu phase supported on alumina was evaluated as a heterogeneous catalyst.

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[*] Corresponding author. Fax: +54 221 421 1353/421 0711/422 0288/425 4277x125.
E-mail address: megus@quimica.unlp.edu.ar (M.G. Egusquiza).
[1] Member of the research staff of CICPBA Argentina and Facultad de Ingeniería U.N.L.P.

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2. Experimental

2.1. Synthesis and characterization of catalysts

The synthesis of complex heteropolytungstates (PWM) was carried out in aqueous solution, by condensation of lacunary derivatives of the phosphotungstic acid Δ-PW_9 thermally treated [16,17].

$$2[\Delta-PW_9O_{34}]^{9-}+4M^{2+}+2H_2O\rightarrow[PW_9M_2(H_2O)O_{34}]_2{}^{10-}$$

Precipitation of potassium salt of these complexes was due to the addition of KCl excess. The products were purified by recrystallization. The synthesized polyoxometalates were characterized using different physicochemical techniques previously reported [15,18].

The synthesis of the Cu(II) product, PWCu, is different compared with the species containing other metallic ions such as Co(II), Mn(II) or Zn(II) due to its thermal instability in solution. This phase undergoes a thermolysis, which produces a mixture of the expected phase and two structural isomers of the Keggin type of formula $K_{5,5}Na_{1,5}[PW_{10}Cu_2(H_2O)_2O_{38}]\cdot 13H_2O$, whose proportion depends on the temperature and time conditions. Thus, the synthesis was conducted at low temperature (60 °C) to obtain the best isomer–phase ratio; as a consequence, it was not purified by crystallization.

The supported catalyst was prepared by an equilibrium impregnation method, from an aqueous solution of PWCu, in contact with 300 mg of γ-Al_2O_3 by shaking for 24 h. The support presented the following textural parameters: specific area of 226 m^2/g, 0.65 cm^3/g volume of pore and particle size of 200 μm. After impregnation, the solution and the solid were separated by centrifugation and the solid was dried in oven for 24 h.

Both the pure and the supported phases were characterized by comparison through Raman microprobe by an Infinity (Jobin-Yvon) with a photodiode detector and integrated to an optic microscope excitation line Laser YAG Nd 532 nm and 2 cm^{-1} resolution and XPS spectroscopy by a Spectrometer Leybold Heraeus LHS10, in FAT mode with Al radiation (1486.6 eV). Also, the W and Cu charge was determined by different methods of chemical and physical analysis such as AAS, ICP and the X ray fluorescence. The atomic absorption analysis was carried out using a Varian AA 240 equipment, and determination of heavy metals by X ray fluorescence was conducted using an Innov-X Systems Alpha 4000 software LEAP (Light Element Analysis Program).

2.2. Catalytic evaluation

The reaction catalyzed by bulk PWM, with metiltricaprilamonium chloride (Aliquat 336) as phase transfer agent, was carried out at atmospheric pressure, at 2 °C and using dichloroethane as solvent [15]. Aliquots of organic phase were taken at different times of the reaction and analyzed by gaseous chromatography and GC mass. The relative uncertainties of the measurements were tested with repeated determinations. The percent relative uncertainty (CV (%)) of the result was calculated dividing the corresponding absolute uncertainty by the average of the measurements.

The reaction catalyzed by supported catalyst in the absence of PTA (phase transfer agent) was carried out like a typical reaction, limonene (L, 3.3 mmol) was dissolved in acetonitrile (2.04 g) and H_2O_2 35 wt.% in water (0.84 mmol) was added. The reaction started by adding the supported catalyst (76.3 mg) to the reactor thermostated at 70 °C. The non-converted hydrogen peroxide was determined by iodometric titration.

Aliquots were taken at different times of the reaction, filtered and then analyzed by gaseous chromatography and GC mass analysis as in the biphasic system.

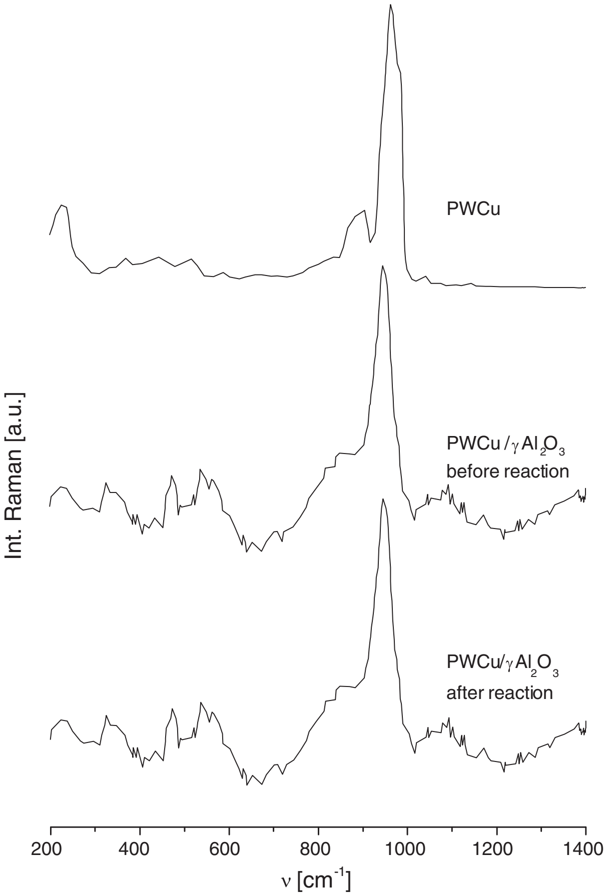

Fig. 1. Raman spectra for the phase PWCu, PWCu/γ-Al_2O_3 and PWCu/γ-Al_2O_3 post-reaction.

Conversion for both reactions was calculated according to the following expression:

$$\text{Conversion }(\%)=[\textstyle\sum\text{products }(\text{mol}\%)]\cdot 100/[\textstyle\sum\text{products }(\text{mol}\%)+\text{limonene(L) }(\text{mol}\%)].$$

Selectivity was calculated according to the following expression:

$$\text{Selectivity }(\%)=[\text{product}_i\ (\text{mol}\%)\cdot 100]/[\textstyle\sum\text{products }(\text{mol}\%)]$$

where i represents a certain product.

3. Results and discussion

3.1. Structural and spectroscopic behavior of the PWCu phase

The heteropolytungstates of formula $[PW_9M_2(H_2O)_2O_{34}]^{10-}$ are described as a "sandwich-type" structure where two polymeric fragments

Table 1
Atomic rates by XPS among the elements present in the PWCu.

PWCu	Value	
	Theoretical	Experimental
K/Cu	1.75	5.05
K/P	3.50	7.10
K/W	0.39	1.30
K/Na	2.33	7.47
Na/Cu	0.75	0.77
Cu/W	0.22	0.22
O^{2-}/W	3.78	3.92

Table 2
Atomic rates by XPS among the elements present in the PWCu/γ-Al_2O_3.

PWCu/ Al_2O_3	Value	
	Theoretical	Experimental
Na/W	0.15	0.56
Cu/W	0.22	0.54
K/Cu	2.75	1.48
Na/Cu	0.75	1.04
W/Al	–	0.03
K/Al	–	0.02
Na/Al	–	0.01
Cu/Al	–	0.01

Table 3
Conversion and selectivity to epoxide limonene with a L/H_2O_2/catalyst rate = 1000/2000/1 for Δ-PW_9 and PWM phases.

Phase	Conv. %[a]	Select, epox. %[b]
Δ-PW_9	68.2	89.3
PWCo	0.3	–
PWZn	0.6	100.0
PWMn	16.9	100.0
PWCu	96.1	89.0

[a] CV < 7%.
[b] CV < 5%.

of the precursor PW_9 are condensed by means of the intercalation of a tetranuclear cluster of divalent metal coordinated octahedrically to the oxygen [18].

Previous studies have demonstrated that the Cu derivative PWCu is mixed with two isomers with Keggin structure. The Jahn Teller effect leads to a clear availability of P–O bonds of lacunary precursor facilitating the instability of the Cu phase in aqueous medium unlike the behavior observed in the Zn and Co phases [15–18]. Cracking and further reordering of the structure result in the formation of two structures.

Fig. 1 shows the Raman microprobe spectra corresponding to the pure and the supported PWCu phases (the latter being plotted after and before the reaction). In these spectra, a shift of the main lines corresponding to the vibrational modes of W=O (960 cm^{-1}) bonds was observed, indicating a weakening of the modes due to PWCu-supported surface interaction, which involved a complex process of adsorption that led to certain distortion of the structure.

The line assigned to symmetric stretching for the P–O bond of PO_4 group (around 1100 cm^{-1}) showed a weak intensity in the pure phase; however it showed that this group preserved its typical tetrahedral symmetry in the supported species.

Tables 1 and 2 show the atomic rates among the elements present in the pure phase and in PWCu phase supported on alumina determined by XPS. By this method, regions Na1s, K2p, Cu2p, O1s, C1s, P2p, Al2s, Al2p and W4f were recorded. Na1s and K2p bands were clearly observed, while P2p was difficult to detect. The copper was detected as Cu(II) and W as W(VI), in both phases.

The surface XPS atomic ratios among the various elements, calculated from the peak areas and atomic sensitivity factors [19], are compared with the respective theoretical bulk ratios in Table 1 for pure PWCu and in Table 2 for the PWCu phase supported on alumina.

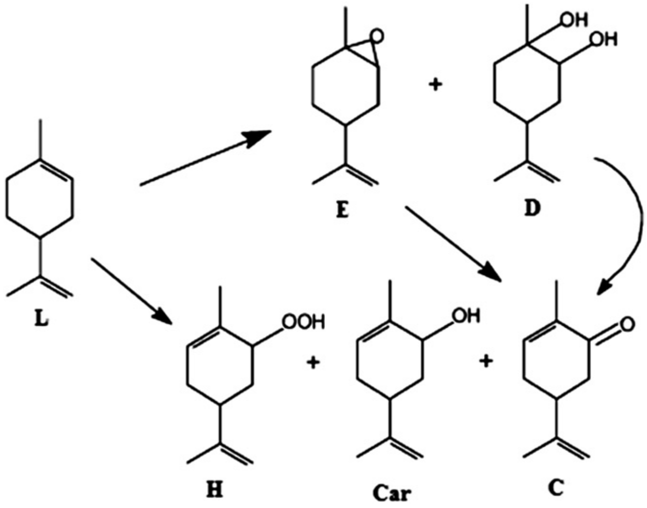

Fig. 2. Diagram of the reaction of the epoxidation of limonene, where (L) limonene; (E) 1,2-epoxilimonene; (D) diol; (H) hydroperoxide; (Car) carveol; (C) carvone.

The XPS Cu/W ratio of the original PCuW phase was close to the stoichiometric one (Table 1), whereas a much higher Cu/W ratio was obtained for the PWCu supported phase (Table 2).

These findings indicate that the interaction between the PWCu phase and the support caused destruction and/or a preferential orientation of the units and that Cu was concentrated on the support surface.

However, the bulk composition of the supported PCuW material, determined by X-ray fluorescence elemental analysis, quite agreed (0.68) with surface composition (0.54 by XPS), revealing that some structural changes had occurred during the adsorption process.

The analysis by AAS for the supported sample accounted for 14% of adsorbed W in γ-Al_2O_3. This value was obtained by simple balance of masses from the values of metal adsorbed before and after impregnation. Due to interferences among the elements it was impossible to determine Cu by this method. Also, analysis of PWCu supported on alumina by X ray fluorescence indicated an adsorption of (g of metal/100 g support) W = 16.5% and Cu = 3.88% showing a Cu/W ratio = 0.23. Values of 14 g of W/100 g of solid were obtained by the ICP method.

3.2. Epoxidation of limonene

The catalytic activity was evaluated for the phases, including Δ-PW_9, in a molar ratio L/H_2O_2/catalyst ratio = 1000/2000/1 according to the experience of previous works [20] (Fig. 2). Table 3 shows the conversion and selectivity observed for each phase for 40 h of reaction time. Fig. 3 shows the activity for all phases used as catalysts.

PWCu and Δ-PW_9 were the most active phases, showing high selectivity to epoxide. PWCo, PWZn and PWMn phases showed low catalytic activity. The PWMn system showed good selectivity with no other reaction product observed. The results showed a high conversion of limonene for the PWCu complex, much higher than that of the remaining phases, with a high selectivity to epoxide in short periods. However, as reaction advanced, selectivity to epoxide decreased slightly by increasing the production of secondary compounds.

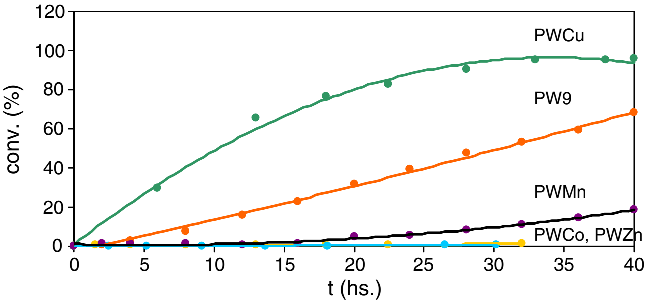

Fig. 3. Limonene conversion as a function of the reaction time for Δ-PW_9 and PWM with M = Co(II), Zn(II), Cu(II) and Mn(II).

Table 4
Conversion and selectivity to epoxide according to $L/H_2O_2/PWCu$ ratio.

$L/H_2O_2/PWCu$	Conv.[a] (% in 40 h)	Conv. (%)∗(dilution)	Selec. E[b] (% in 40 h)
1000/2000/1	96.1	96.08∗(1)[c] = 96.1	95.6
2500/5000/1	36.2	36.16∗(2.5)[c] = 90.4	96.6
5000/10,000/1	21.6	21.59∗(5)[c] = 107.9	94.1

[a] CV < 7%.
[b] CV < 5%.
[c] Dilution factor.

Table 5
Conversion and selectivity of the PWCu and PWCu/γ-Al_2O_3 phase at 7 h of reaction time.

Catalysts	Conversion of limonene (%)	Conversion of H_2O_2	Selectivity to epoxide (%)	Efficiency of H_2O_2
PWCu with PTA[a]	12.24	–	97.71	–
PWCu–γ-Al_2O_3 without PTA[b]	17.63	91.6	59.84 60.8	68.4

[a] Molar ratio: L/H_2O_2/catalyst (1000/2000/1) at 2 °C.
[b] Molar ratio: L/H_2O_2 (4/1), 76 mg of catalyst at 70 °C.

In response to increased activity and selectivity towards epoxilimonene obtained with PWCu, we selected this catalyst to study the influence of the molar ratio of L/H_2O_2/catalyst on the course of oxidation reaction while the other parameters were unchanged. These results are presented in Table 4.

Fig. 4 shows the conversion as a function of time for each of the L/H_2O_2/catalyst under study.

As it can be seen, the limonene conversion decreased by increasing the molar ratio L/H_2O_2/catalyst achieving a value close to 20 mol%. However, when the conversion values were calculated considering the dilution factor of the catalyst corresponding to the limonene concentration, equivalent conversions were obtained. These results indicated the existence of a linear relationship between activity and catalyst concentration. This fact demonstrated a “molecular reaction” which is typical of a homogeneous conventional catalyst in which the association of its molecular or ionic units in organic phase could not take place. Regarding the product selectivity, the epoxilimonene was obtained as major product in all the cases. Therefore, a molar ratio $L/H_2O_2/cat = 1000/2000/1$ appeared as the optimum value.

On the other hand, the catalytic activity of the phase PWCu supported on alumina was evaluated taking into account the importance of using a heterogeneous catalyst for the environment. In addition, another important point is the desirable replacement of the chlorate solvents with an environmentally friendly solvent such as acetonitrile. Table 5 and Fig. 5 show comparative conversions of the catalytic evaluation in the limonene epoxidation for the two systems under study after a reaction time of 7 h. The results indicated that the selectivity to epoxilimonene for the bulk catalyst using PTA was much higher due to the fact that the biphasic system prevented the hydrolysis of the oxirane ring. However, in the heterogeneous system (supported catalyst) a higher conversion of limonene was obtained. Then, the selectivity to epoxilimonene decreased with the occurrence of by-products, such as carvone (C), carveol (Car), diepoxide (not in the scheme) and glycol (D).

In all cases the mass balance was close to values which fell within the error of the method.

Finally, although work must continue to improve selectivity in the heterogeneous system, the results obtained are encouraging from the environmental point of view since a non toxic solvent, replacing the chlorinated solvents, was used in this system.

4. Conclusions

Among the heteropolytungstates, PWM with M(II) = Mn, Co, Cu and Zn, only the phase with Cu(II) and its precursor phase Δ-PW_9 showed catalytic activity in the epoxidation to limonene using H_2O_2 under biphasic conditions. The PWCu phase has proved to be the most active catalyst for the oxidation of limonene. Thus, these results give evidence about its chemical properties and different structural characteristics related to the presence of Cu(II). Among these features the following can be mentioned: a) the Jahn–Teller effect of Cu(II) which allows a higher exposition of the P–O group; and b) the high redox capacity of Cu(II) in an oxidative process.

The redox process induces the electronic transference which contributes to the oxygen addition on the C=C, leading to the formation of the limonene epoxide.

The different physico-chemical analyses conducted both on the pure phase and on the alumina supported phase indicate that the Cu/W ratio remains similar to the theoretical ratio according to the chemical composition of the pure phase. Also, the Raman and XPS spectroscopic techniques show the preservation of the structure on the surface.

The best catalytic activity using PWCu phase as catalyst was observed by the molar ratio $L/H_2O_2/cat = 1000/2000/1$.

The catalytic evaluation of the ã-Al_2O_3 supported PWCu system indicated that the reaction conducted in the absence of PTA showed a higher conversion than the reaction under biphasic conditions. However, the selectivity to epoxilimonene obtained with PWCu/Al_2O_3 was lower than PWCu under biphasic system due to the hydrolysis reaction of the oxirane ring. Although selectivity to epoxilimonene obtained with the supported catalyst has been low, the results are encouraging since the heterogeneous system avoids the use of chlorinated solvents and the previous steps to the synthesis are easier. Therefore, considering the high conversion of limonene achieved, further research should be conducted to reduce the by-products.

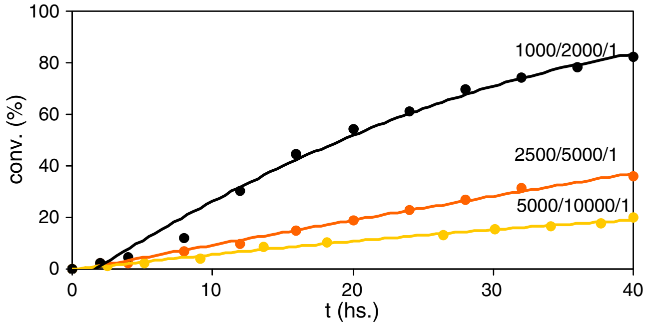

Fig. 4. Oxidation of limonene as a function of time for the different molar ratio $L/H_2O_2/PWCu$.

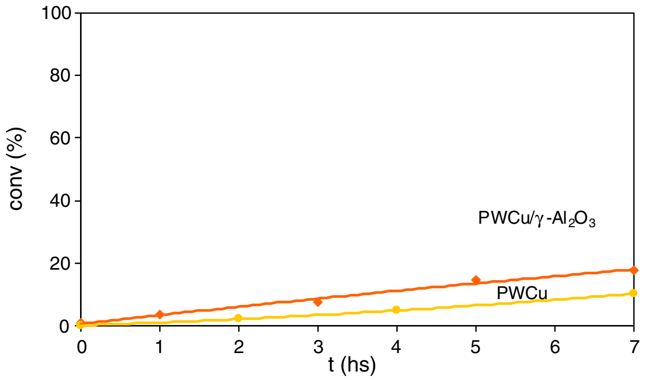

Fig. 5. Limonene conversion as a function of time catalyzed by PWCu and PWCu/γ-Al_2O_3.

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References

[1] R. Neumann, M. Gara, Journal of the American Chemical Society 116 (1994) 5509.
[2] R. Neumann, M. Gara, Journal of the American Chemical Society 117 (1995) 5066.
[3] M.T. Pope, A. Müller, Polyoxometalate Chemistry from Topology via Self-assembly to Applications, Kluwer Academic Publishers, The Netherlands, 2001.
[4] R.A. Sheldon, New Developments in Selective Oxidation, Elsevier, Amsterdam, 1990, p. 1.
[5] K. Bauer, D. Garbe, H. Surburg, Common Fragrance and Flavor Materials: Preparation, Properties and Uses, 2nd ed. VCH Publishers, NY, 1990.
[6] C. Blanco, E.E. Stashenko, M. Combariza, J.R. Martínez, Journal of Chromatography. A 697 (1995) 5011.
[7] A.M. Santa, J.C. Vergara, L.A. Palacio, A. Echavarría, Catalysis Today 80 (2008) 133.
[8] M.A. Armendia, V. Borau, C. Jiménez, J.M. Luque, J.M. Marinas, J.R. Ruiz, F.J. Urbano, Applied Catalysis A: General 216 (2001) 256.
[9] A. Corma, M.E. Dómine, F. Rey, M.T. Navarro, S. Valencia, S. Casuscelli, E. Herrero, Proceedings of XVII Simposio Ibero-americano de Catálise, Porto, Portugal, 2000, p. 581.
[10] M.E. Crivello, C.F. Pérez, J.D. Fernández, S.G. Casuscelli, E.R. Herrero, Proceedings of XVII Simposio Ibero-americano de Catálise, Porto, Portugal, 2000, p. 501.
[11] A.D. Silva, M.L. Patitucci, H.R. Bizzo, E. D'Elia, O.A.C. Antunes, Catalysis Communications 3 (2002) 435.
[12] P.A.L. Villa, A.F. Taborda, C. Monte de Correa, Journal of Molecular Catalysis A: Chemical 185 (2002) 269.
[13] C. Venturello, E. Alneri, M. Ricci, Journal of Organic Chemistry 48 (1983) 3831.
[14] C. Venturello, R.D. Aloisio, Journal of Organic Chemistry 53 (1988) 1553.
[15] S. Casuscelli, E. Herrero, M. Crivello, C. Pérez, M.G. Egusquiza, C.I. Cabello, I.L. Botto, Catalysis Today 107–108 (2005) 230.
[16] R. Massart, R. Contatn, J.M. Fruchart, J.P. Ciabrini, M. Fournier, Inorganic Chemistry 16 (1977) 2916.
[17] R.G. Finke, M.W. Droege, P.J. Domaille, Inorganic Chemistry 26 (1987) 3886.
[18] C.I. Cabello, M.G. Egusquiza, I.L. Botto, G. Minelli, Materials Chemistry and Physics 87 (2004) 264.
[19] C.D. Wagner, L.E. Davis, M.V. Zeller, J.A. Taylor, R.M. Raymond, L.H. Gale, Surface and Interface Analysis 3 (1981) 211.
[20] M. Bösing, A. Nöh, I. Loose, B. Kerbs, Journal of the American Chemical Society 120 (1998) 7252.