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Phosphotungstates as catalysts for monoterpenes oxidation: Homo- and heterogeneous performance

Salete S. Balula[a,*], Isabel C.M.S. Santos[b], Luís Cunha-Silva[a], Ana P. Carvalho[c], João Pires[c], Cristina Freire[a], José A.S. Cavaleiro[b], Baltazar de Castro[a], Ana M.V. Cavaleiro[d]

[a] REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, 4169-007 Porto, Portugal
[b] Departamento de Química, QOPNA, Universidade de Aveiro, 3810-193 Aveiro, Portugal
[c] Departamento de Química e Bioquímica, CQB, Faculdade de Ciências da Universidade de Lisboa, Campo Grande C8, 1749-016 Lisboa, Portugal
[d] Departamento de Química, CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal

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ABSTRACT

Lacunary (PW_{11}), mono-substituted ($PW_{11}M$) and sandwich type $M_4(PW_9)_2$ phosphotungstates ($M = Co^{II}$, Fe^{III}) exhibits high catalytic activity for geraniol and R-(+)-limonene oxidation under mild conditions, using hydrogen peroxide as oxidant and acetonitrile as solvent. The best homogeneous performance was found for the PW_{11} and for the $Co_4(PW_9)_2$. Complete conversion of geraniol and R-(+)-limonene was achieved after 1.5 h and 3 h of reaction, respectively, when catalyzed by PW_{11}. The yield of 2,3-epoxygeraniol was 100% in the presence of lacunary PW_{11} and mono-substituted compounds. PW_{11} and $Co_4(PW_9)_2$ were immobilized on an amine-functionalized SBA-15 (aptesSBA-15) and the composites materials were characterized by FT-IR, FT-Raman, UV–vis/DRS, ^{31}P MAS NMR, elemental analysis and SEM-EDS. Their heterogeneous catalytic activity was investigated for the same substrates and compared with that in homogeneous conditions. The PW_{11}@aptesSBA-15 and $Co_4(PW_9)_2$@aptesSBA-15 showed to be active heterogeneous catalysts for geraniol epoxidation with 100% of selectivity for 2,3-epoxide. R-(+)-limonene was also oxidized by PW_{11}@aptesSBA-15 achieving 90% of conversion after 24 h of reaction. Both composites could be separated after the reaction and reused for at least three cycles without loss of activity. The stability of the heterogeneous catalysts after catalytic reactions was investigated by different techniques of characterization.

1. Introduction

The development of catalysts for selective and environmentally friendly oxidation of organic compounds is nowadays a remarkable research goal. The development of eco-sustainable catalytic systems to transform cheap natural compounds into valuable intermediates for organic synthesis is an area of interest for both in the laboratory and in industry. The oxygenated products derived from terpene are of great interest due to their utilization in the production of fragrances and perfumes [1]. Generally important prerequisites for clean and efficient technologies are stable catalysts with high product selectivities and high activity at ambient temperatures without waste of the applied oxidant. A successful possibility is to use inorganic and therefore robust transition metal complexes as catalysts in combination with hydrogen peroxide as an oxygen donor. Transition metal substituted polyoxometalates (POMs) are attractive catalysts for oxidative reactions because they can be seen as having reactive low valent transition metal centers complexed by inorganic oxometalate ligands, that have high capacity as oxygen transfer agents [2–4]. These compounds were shown to be economically and environmentally attractive oxidation catalysts in both academic and industrial processes [5]. The hydrogen peroxide is the second most attractive oxidant after dioxygen because it is inexpensive, environmentally clean and easily handled [6]. During the last decade we have shown that Keggin-type polyoxotungstates can be effective homogeneous catalysts in the oxidation of several alkenes and alkanes with hydrogen peroxide [7–18]. These compounds include mono-substituted $[PW_{11}M(H_2O)O_{39}]^{m-}$ ($PW_{11}M$) and sandwich-type $[M_4(H_2O)_2(PW_9O_{34})_2]^{n-}$ ($M_4(PW_9)_2$), where M represents several transition metals such as Co^{II}, Fe^{II}, Mn^{III}, Cu^{II}, Ni^{II} and others. In this paper we report the oxidation of geraniol and R-(+)-limonene with H_2O_2 in acetonitrile, using the lacunary $[PW_{11}O_{37}]^{7-}$ (PW_{11}), the Fe^{III} and Co^{II} mono-substituted and sandwich-type polyoxotungstates as catalysts (Fig. 1). The outcome of the reactions depended strongly on the catalyst. To our knowledge, catalytic studies of R-(+)-limonene oxidation using mono-substituted or sandwich-type phosphotungstates have not been reported before.

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[*] Corresponding author. Tel.: +351 220402576; fax: +351 220402659.
E-mail address: sbalula@fc.up.pt (S.S. Balula).

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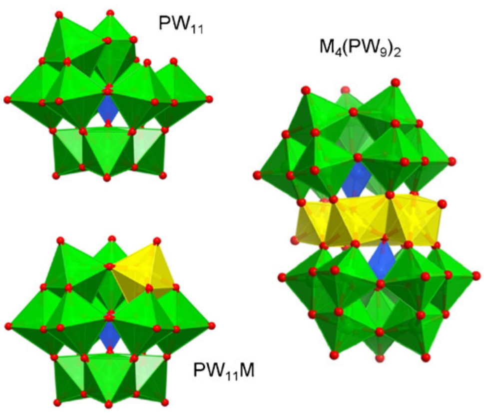


Fig. 1. Schematic representation of the structures of the selected POMs: lacunar PW_{11} (top left), mono-substituted $PW_{11}M$ (bottom left) and sandwich $M_4(PW_9)_2$ (right side).

Few papers can be found reporting the oxidation of this substrate catalyzed by POMs and these are homogeneous and biphasic systems also using other less green oxidants [19–21]. Also, a small number of reports on the oxidation of geraniol catalyzed by POMs have appeared in the literature [8,15,22].

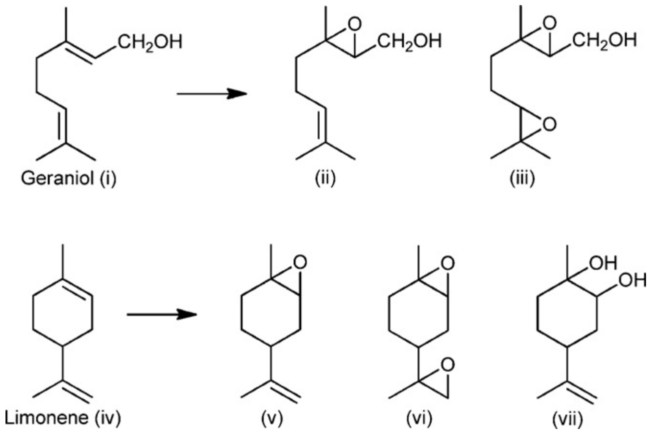
The high catalytic performance found for the homogeneous studied phosphotungstates required the need of catalyst recyclability. Thus, new heterogeneous catalysts based in phosphotungstates were prepared by immobilization of PW_{11} and $Co_4(PW_9)_2$ onto amine functionalized SBA-15 silica material. A few studies are reporting the immobilization of polyoxotungstates on SBA-15 for oxidative catalysis application [23–29]. To our knowledge, the present work reports for the first time the oxidation of geraniol and R-(+)-limonene catalyzed by heterogeneous phosphotungstates immobilized on functionalized SBA-15 support.

2. Experimental

2.1. Materials and methods

Geraniol (Aldrich), R-(+)-limonene (Aldrich), acetonitrile (Panreac), H_2O_2 30% (Riedel de-Häen, Aldrich) were used as received without further purification.

GC–MS analysis were performed using a Hewlett Packard 5890 chromatograph equipped with a Mass Selective Detector MSD series II using helium as the carrier gas (35 cm/s); GC-FID was carried out in a Varian Star 3400CX chromatograph to monitories catalytic reactions and a Varian CP-3380 to follow the heterogeneous reactions. In both experiments, the helium was the carrier gas (55 cm/s) and fused silica Supelco capillary columns SPB-5 (30 m × 0.25 mm i.d.; 25 μm film thickness) were used. Elemental analysis for W, Fe and Co were performed by ICP spectrometry (University of Aveiro, Central Laboratory of Analysis) and C, H, N elemental analysis was performed on a Leco CHNS-932. Hydration water contents were estimated by thermogravimetric analysis on a TGA-50 Shimadzu thermobalance. Infrared absorption spectra were obtained on a Mattson 7000 FT-IR spectrometer, using KBr pellets. FT-Raman spectra were recorded on a RFS-100 Bruker FT-spectrometer, equipped with a Nd:YAG laser with excitation wavelength of 1064 nm, with laser power set to 200 mW. Diffuse reflectance spectra (UV–vis/DRS) were registered on JascoV-560 spectrophotometer, using MgO as reference. Solid-state ^{31}P MAS NMR spectra were recorded on a 9.4 T Bruker Avance 400 spectrometer. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) studies were performed at “Centro de Materiais da Universidade do Porto” (CEMUP, Porto, Portugal), using a high resolution environmental scanning electron microscope (FEI Quanta 400 FEG ESEM) equipped with an energy-dispersive X-ray spectrometer (EDAX Genesis X4M). The samples were analyzed as powders coated with a thin gold film.



Scheme 1.

2.2. Synthesis of phosphotungstates

The tetrabutylammonium ($[(C_4H_9)_4N]$, TBA) salts of the following compounds were prepared by known procedures: $(TBA)_4H_3[PW_{11}O_{39}]$ (PW_{11}) [18], $(TBA)_4H[PW_{11}Co(H_2O)O_{39}]$ ($PW_{11}Co$) [18,30], $(TBA)_4[PW_{11}Fe(H_2O)O_{39}]$ ($PW_{11}Fe$) [18], $(TBA)_7H_3[Co_4(H_2O)_2(PW_9O_{34})_2]$ ($Co_4(PW_9)_2$) [31], $(TBA)_6[Fe_4(H_2O)_2(PW_9O_{34})_2]$ ($Fe_4(PW_9)_2$) [32,33]. All phosphotungstates were characterized by elemental and thermal analysis, infrared absorption spectroscopy and electronic absorption spectroscopy. Characterization of these compounds has been compared and confirmed with published results [18,31,33].

2.3. Supported phosphotungstates

Some of phosphotungstates anions prepared previously were immobilized in large porous SBA-15. This support material was obtained following a procedure adapted from the literature, [34] and surface of SBA-15 was modified by a grafting methodology adapted from a previous work [35]. The dried SBA-15 support was refluxed for 24 h in dry toluene with (3-aminopropyl)triethoxysilane (aptes) under argon. The resulting aptes-functionalized SBA-15 (aptesSBA-15) contained 1.2 mmol of NH_2 per 1 g of support material (4.6% of C, 1.6% of N and 1.6% of H). Immobilization of selected phosphotungstates was performed by stirring the mixture of 0.3 g aptesSBA-15 in 10 mL of acetonitrile with 0.1 mmol of TBA salt of PW_{11}, and $Co_4(PW_9)_2$, for 24 h at room temperature. The supported POM material (PW_{11}@aptesSBA-15 and $Co_4(PW_9)_2$@aptesSBA-15, respectively) were filtered and washed with acetonitrile until the filtrate did not reveal any POM (existence of POM in filtrate was followed by UV–vis spectroscopic experiments), and were dried under vacuum for several hours at 80 °C. These composites materials were characterized by elemental analysis (W, Co), UV–vis/DRS, FT-IR and FT-Raman spectroscopy. The loading of phosphotungstates achieved was 0.034 mmol for PW_{11}@aptesSBA-15 (6.9 wt.% of W) and 0.020 mmol for $Co_4(PW_9)_2$@aptesSBA-15 (4.9 wt.% of W).

2.4. Oxidation reactions

The oxidation reactions of geraniol (**i**, Scheme 1) and R-(+)-limonene (**iv**, Scheme 1) were carried out in acetonitrile, under air (atmospheric pressure) in a closed borosilicate 10 mL reaction vessel equipped with a magnetic stirrer and immersed in a thermostated oil bath. The oxidant used was H_2O_2 (30 wt.%) and the lacunary PW_{11}, the mono-substituted $PW_{11}M$ (M = Fe^{III}, Co^{II}), and the sandwich type $M_4(PW_9)_2$ (M = Fe^{III}, Co^{II}) were tested as homogeneous catalysts. In the oxidation of **i** the reaction was done at room temperature and protected from light, and the oxidative reactions of **iv** were performed at 80 °C. In a typical experiment, the substrate (1 mmol) and the catalyst (3 μmol), placed in the vessel, were dissolved in acetonitrile (1.5 ml), stirred, and the hydrogen peroxide was added to the reaction mixture, 500 μl (4.5 mmol). The reactions were followed by GC analysis and stopped when a completed conversion of the substrate was observed or when the product yields remained constant after two successive GC analyses. An aliquot was taken directly from the reaction mixture with a microsyringe at regular intervals, diluted in acetonitrile and injected into the GC or GC–MS equipment for analysis of starting materials and products. The reaction products reported here were identified as described elsewhere [36,37]. The same procedure was performed for the heterogeneous reactions using the supported phosphotungstates (PW_{11}@aptesSBA-15 and $Co_4(PW_9)_2$@aptesSBA-15). In this case, the heterogeneous catalysts were filtered off at the end of reactions, washed with acetonitrile several times, dried in air at room temperature overnight and then reused using the same reaction conditions.

2.5. Titration of hydrogen peroxide

The total concentration of unused hydrogen peroxide was determined by titration using the ceric sulphate method [38]. At regular intervals, an aliquot was accurately weighted, dissolved in diluted sulphuric acid and the peroxides titrated against 0.1 N ceric sulphate solution, using ferroin as indicador.

3. Results

3.1. Catalysts preparation and characterization

In spite of their different structures PW_{11} and $Co_4(PW_9)$ anions were immobilized onto the functionalized silica large porous support aptesSBA-15. SBA-15 was chosen as support material because the large surface area, easy surface modification with functional groups, high stability and low toxicity. This support was firstly functionalized with the organosilane (3-aminopropyl)triethoxysilane (to yield aptesSBA-15) by reaction of the hydroxyls groups of their surface, in a post-synthesis step [35]. Then, phosphotungstate PW_{11} and $Co_4(PW_9)_2$ were immobilized on aptesSBA-15 surface. The lacunary anions such as PW_{11} are highly nucleophilic and react easily with electrophilic groups [39]. The silicon atoms from the silanol (Si—OH) groups presented on the surface of silica materials present electrophilic properties. It was described in the literature that lacunary anions can be immobilized on silica supports by covalent bond established between the silanol groups and the POM via W—O—Si bonds [28]. The immobilization of the sandwich $Co_4(PW_9)_2$ may occur by an electrostatic or covalent interaction between the cobalt transition metal and the amine group of the support material. [39,40] The coordinating interaction between the water ligand and Co in $Co_4(PW_9)_2$ is weak, consequently this coordinate site can easily be displaced by some ligands such as amine groups. The POM easily bonds to the amine groups on surface of the support. The amount of amine groups and phosphotungstates on the surface of the material was established by elemental analysis (1.2 mmol of NH_2, 0.034 mmol of PW_{11} and 0.020 mmol of $Co_4(PW_9)_2$ in 1 g of material).

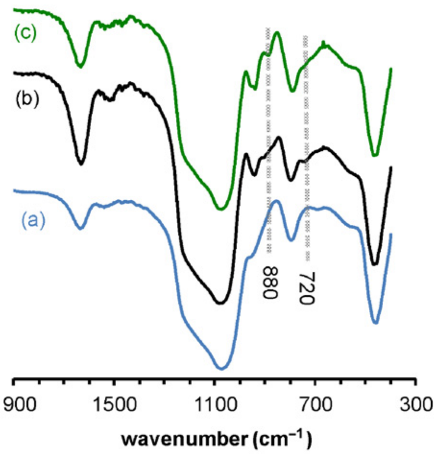


Fig. 2. FT-IR spectra of (a) aptesSBA-15, (b) PW_{11}@aptesSBA-15, (c) P_2Co_4@aptesSBA-15, in the wavenumber region between 300 and 1900 cm^{-1}.

Spectroscopic methods including UV–vis/DRS, FT-IR, FT-Raman and ^{31}P MAS NMR were performed to characterize the composite materials, in particular to verify the presence of phosphotungstate and also the stability of these compounds after their immobilization. Fig. 2 presents the FT-IR spectra of the supported phosphotungstates and the support aptesSBA-15, in the wavenumber region between 300 and 1900 cm^{-1}. The support aptesSBA-15 shows the main string bands from silica framework in the region of 400–1100 cm^{-1}: ν_{as}(Si—O—Si), ν_s(Si—O—Si) and δ(O—Si—O) [41]. These bands are very intense and obscure partially the characteristic bands of the POMs that appear also in the same region: ν_{as}(W—O—W), ν_{as}(W—O) and ν_{as}(P—O) [31,42–44]. Thus, comparing the spectrum of the support aptesSBA-15 with spectra of PW_{11}@aptesSBA-15 and $Co_4(PW_9)_2$@aptesSBA-15 it is possible to find two extra small bands near 880 cm^{-1} and 720 cm^{-1}, which may be attributed to the ν_{as}(W—O—W) indicating the presence of phosphotungstates. In the region of 1500–1550 cm^{-1} can be observed two weak bands corresponding to $\nu_s(NH_2)$ and $\delta(NH_2)$, that confirms the incorporation of amine groups on the material [45].

The FT-Raman spectra of the supported phosphotungstates are more elucidative than the FT-IR data because this technique is extremely sensitive to the Keggin POMs and the silica support does not show any band on the Raman region of these compounds (Fig. 3). The FT-Raman spectra of phosphotungstates compounds are very similar to the materials PW_{11}@aptesSBA-15 and $Co_4(PW_9)2$@aptesSBA-15. The spectra of TBA salts of PW_{11} and $Co_4(PW_9)_2$ and their corresponding composites show a strong band near 990–950 cm^{-1} attributed to ν_s(W—O) with terminal oxygen [15,16,43]. Furthermore, it can be seen a slightly shift of this band to lower wavenumbers when PW_{11} and $Co_4(PW_9)_2$ are immobilized on aptesSBA-15. The Raman spectrum of PW_{11} presents other band at 995 cm^{-1} due to ν_{as}(P—O). The same is not clearly identified for the sandwich $Co_4(PW_9)_2$ and also for the phosphotungstate composites. It is well known that the introduction of metal cations into the lacunary structure PW_{11} may decrease the splitting of the last two bands [46].

Reflectance diffuse is also a helpful technique because the support aptesSBA-15 does not show any prominent band in the range of 200–800 nm. The UV–vis/DRS spectra of lacunary PW_{11} and the sandwich $Co_4(PW_9)_2$ and their respective composites materials PW_{11}@aptesSBA-15 and $Co_4(PW_9)_2$@aptesSBA-15 are drawn in Fig. 4. All samples exhibit UV absorption maxima at ca. 250 and 300 nm which are attributed to oxygen-to-tungsten charge transfer at terminal W═O and W—O—W bonds of phosphotungstate, respectively [47]. The spectra of $Co_4(PW_9)_2$ (Fig. 4d) and the material $Co_4(PW_9)_2$@aptesSBA-15 (Fig. 4e) can be compared to

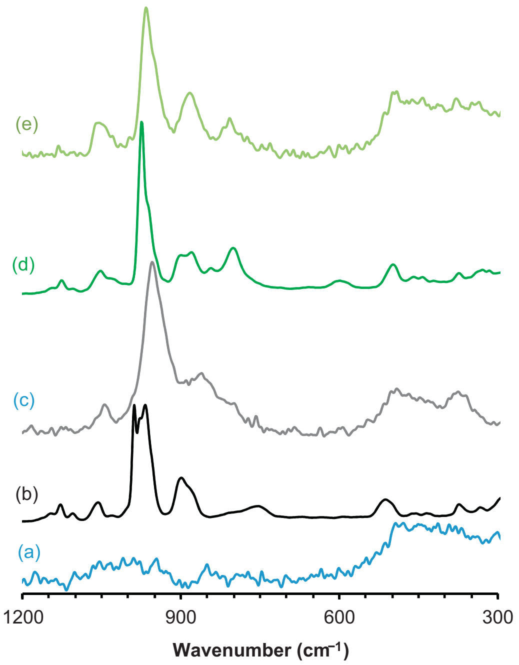


Fig. 3. FT-Raman spectra of (a) aptesSBA-15, (b) PW_{11}, (c) PW_{11}@aptesSBA-15, (d) $Co_4(PW_9)_2$ and (e) $Co_4(PW_9)_2$@aptesSBA-15, in the wavenumber region between 300 and 1900 cm^{-1}.

evaluate possible alterations of Co^{II} coordination environment of the sandwich compound after the immobilization on silica. This Co sandwich compound shows one *d*–*d* electronic transition band with a maximum at ca. 580 nm with a shoulder at about 520 nm and both are also observed when the compound is immobilized (Fig. 4e).

The integrity of lacunary PW_{11} compound was investigated before and after their immobilization on aptesSBA-15 by ^{31}P MAS NMR (Fig. 5) and in both spectra a single peak was observed. For TBA salt of PW_{11} the peak appears at −10.8 ppm and for the composite PW_{11}@aptesSBA-15 this is shifted to −11.3 ppm. This difference may be caused by the extreme sensitivity of ^{31}P nucleus to its local environment and by the interaction of PW_{11} with the support surface. In conclusion, the comparison performed between the isolated phosphotungstate and their composites using different techniques indicates that the immobilization of PW_{11} and $Co_4(PW_9)_2$ on the aptesSBA-15 support was effective, and no degradation of the phosphotungstate structures occurred.

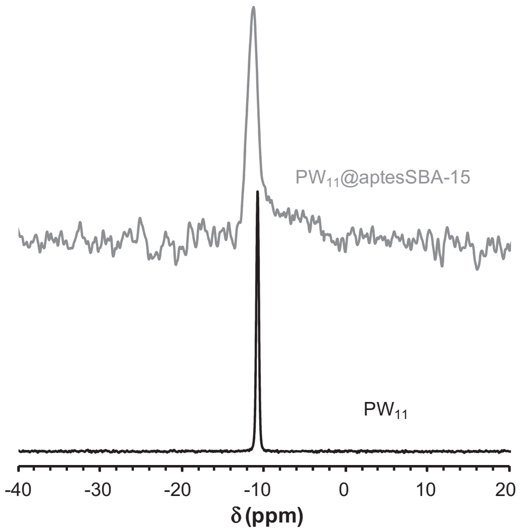


Fig. 5. ^{31}P MAS NMR spectra of TBA salt PW_{11} (bottom) and PW_{11}@aptesSBA-15 (top).

3.2. Homogeneous catalysis

The oxidation of geraniol and R-(+)-limonene were carried out in homogeneous phase using hydrogen peroxide, acetonitrile, and catalytic amounts of TBA salts of the lacunary PW_{11}, the mono-substituted $PW_{11}M$ and the sandwich-type $M_4(PW_9)_2$ (M = Co^{II} and Fe^{III}). The TBA salts are essential to ensure their adequate solubility in acetonitrile.

Geraniol (i) is an allylic alcohol that offer several possible places of oxidative attach, namely at the two double bonds, at the allylic carbon centers and at the carbon of the CH_2OH group. The oxidation of this substrate with H_2O_2 at room temperature produces as main product the 2,3-epoxygeraniol (ii) in the presence of all catalysts, indicating the high chemo-selectivity nature of the reactions. A small amount of diepoxide (iii) was found for all studied catalysts after 1 h of reaction. However, the selectivity for the main product was always higher than 70% (Scheme 1).

Table 1 shows the catalytic results for the different homogeneous catalysts tested for geraniol oxidation after 1.5 h of reaction. The best catalytic performance was observed for the lacunary PW_{11}

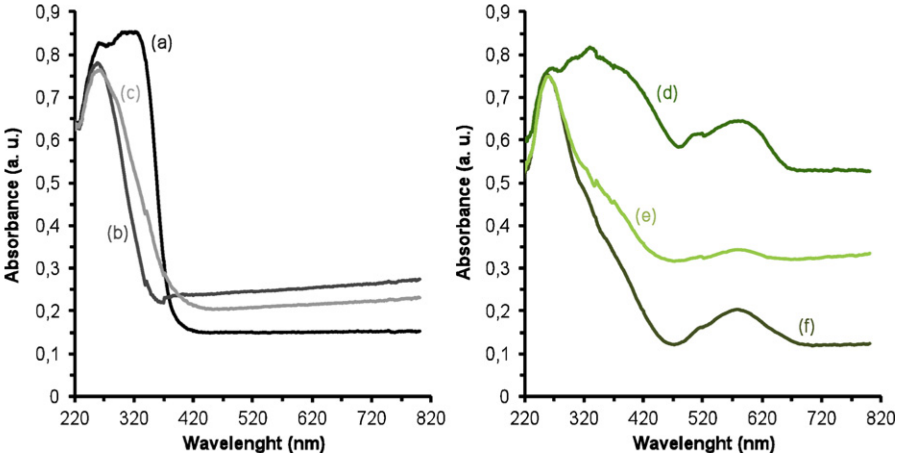


Fig. 4. Reflectance electronic spectra: (a) PW_{11}, (b) PW_{11}@aptesSBA-15, (c) PW_{11}@aptesSBA-15-ac, (d) $Co_4(PW_9)_2$, (e) $Co_4(PW_9)_2$@aptesSBA-15 and (f) $Co_4(PW_9)_2$@aptesSBA-15-ac, where ac stands for after catalytic uses.

Table 1
Data from the oxidation of geraniol using different catalysts after 1.5 h of reaction.[a]

Catalyst	Conversion (%)	TOF[c] (mol mol_{cat}^{-1} h^{-1})	Selectivity[b] (%)	H_2O_2[d] efficiency (%)
No catalyst	≈0	–	–	–
PW_{11}	96	550	100	73
$PW_{11}Co$	72	510	100	–
$PW_{11}Fe$	35 (89)[e]	136	100	48
$Fe_4(PW_9)_2$	30 (100)[e]	49	91	36
$Co_4(PW_9)_2$	100	341	74	49

[a] Reaction conditions: 1 mmol of geraniol, 4.5 mmol H_2O_2, 3 μmol phosphotungstate, 1.5 mL CH_3CN, room temperature and light protection.
[b] Based on the amount of consumed substrate; corresponding to 2,3-epoxigeraniol.
[c] TOF = (moles of geraniol consumed)/[(moles of phosphotungstate) × 0.16 h].
[d] H_2O_2 efficiency = [(moles of substrate oxidized/moles of H_2O_2 consumed) × 100].
[e] Conversion data obtained after 3 h of reaction.

and for the sandwich $Co_4(PW_9)_2$. In fact, the catalysts of iron showed much lower conversion data than the cobalt catalysts at least for short reaction times. Fig. 6 shows the kinetic profile of the best catalysts and it is possible to conclude that the PW_{11} and the $Co_4(PW_9)_2$ have similar kinetic profile. Both catalysts achieve almost complete conversion after 1 h of reaction and at this stage the selectivity remains 100% for 2,3-epoxide. The mono-substituted $PW_{11}Co$ also achieve a complete conversion of geraniol oxidation and 100% of selectivity for the 2,3-epoxide after 3 h of reaction. The efficiency of H_2O_2 usage was calculated for the oxidation of geraniol catalyzed by the different homogeneous catalysts (Table 1). The highest H_2O_2 efficiency is observed in the presence of the lacunary PW_{11} what means that the presence of Co^{II} and Fe^{III} into the phosphotungstate structure promote the decomposition of the oxidant. The amount of no productive decomposition of H_2O_2 is similar for both transition metals and also no prominent difference was observed for mono-substituted and sandwich compounds. In the presence of all catalyst, some amount of the added H_2O_2 is still present after 3 h of reaction. This fact could indicate that the used amount of H_2O_2 does not contribute for the lower performance of some of the studied phosphotungstates.

Few works has been published for the oxidation of geraniol catalyzed by Keggin type polyoxometalate and most of them have been executed using homogeneous systems [8,15,22]. Some of these work was performed using metal mono-substituted borotungstates as catalysts to oxidize selectively geraniol to 2,3-epoxygeraniol under similar experimental conditions used in this work [8,15,22]. However, an improvement of the catalytic results was attained in the presence of PW_{11} and $Co_4(PW_9)_2$.

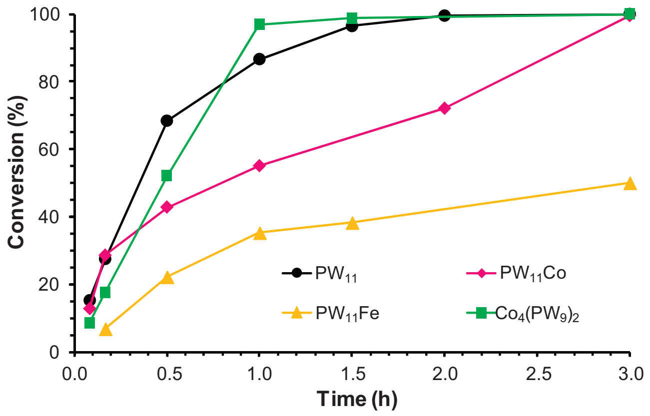


Fig. 6. Kinetic profiles for the homogeneous oxidation of geraniol with H_2O_2 in the presence of phosphotungstate catalysts. Reaction condition: 3 μmol catalyst, 1 mmol geraniol, 4.5 mmol H_2O_2, 1.5 mL CH_3CN, room temperature and light protection.

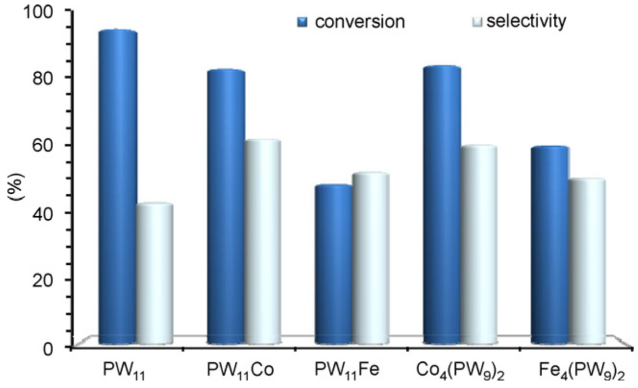


Fig. 7. Conversion and selectivity for the oxidation of R-(+)-limonene catalyzed by several phosphotungstates (after 3 h of reaction). The reaction conditions were: 3 μmol catalyst, 1 mmol R-(+)-limonene, 4.5 mmol H_2O_2, 1.5 mL CH_3CN and temperature 80 °C.

In the oxidation of R-(+)-limonene (iv, Scheme 1) the conversion achieved for the same reaction time was lower than that obtained for geraniol, in spite of the increase in temperature. Fig. 7 depicts the catalytic performance for the studied phosphotungstates after 3 h of oxidation of R-(+)-limonene with H_2O_2. The best catalysts are also the PW_{11} and the $Co_4(PW_9)_4$. Their time courses are presented in Fig. 8 and it can be noticed that the cobalt catalysts showed similar kinetic profile. In the presence of PW_{11} catalyst the conversion attains almost 100% after 3 h of reaction, and the reaction catalyzed by this phosphotungstate achieves higher conversion for less reaction time. The turnover frequency calculated after 10 min of reaction for PW_{11} is much higher (869 mol mol_{cat}^{-1} h^{-1}) than for the cobalt catalysts (around 70 mol mol_{cat}^{-1} h^{-1}). The selectivity for the different products of the R-(+)-limonene oxidation is between 40% and 50% depending of the catalysts. Three products:

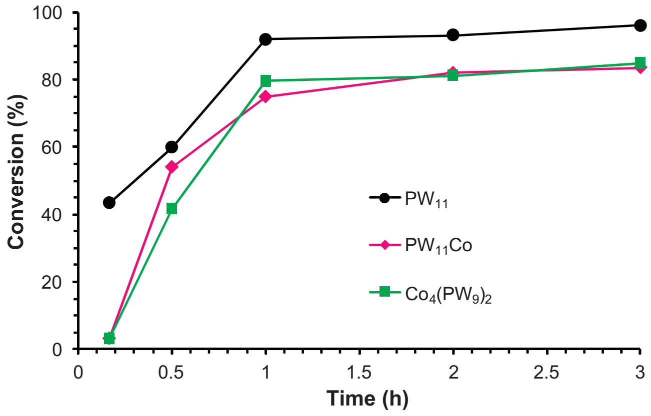


Fig. 8. Kinetic profiles for the oxidation of R-(+)-limonene with H_2O_2 in the presence of homogeneous lacunar and cobalt phosphotungstates catalysts.

Table 2
Performance of heterogeneous phosphotungstates catalysts for the oxidation of geraniol and R-(+) limonene with H_2O_2.

Catalyst	Time (h)	Geraniol[a]		R-(+)-limonene[b]	
		Conversion (%)	Selectivity (%)[c]	Conversion (%)	Selectivity (%)
aptesSBA-15	24	0	0	0	0
PW_{11}@aptesSBA-15	4	50	100	57	42[d]
	24	96	100	90	54[d]
$Co_4(PW_9)_2$@aptesSBA-15	4	33	100	8	100[e]
	24	77	100	15	95[e]

[a] Reaction conditions: 1 mmol of geraniol, 4.5 mmol of H_2O_2, 1.5 mL CH_3CN, 87 mg of PW_{11}@aptesSBA-15 or 150 mg of $Co_4(PW_9)_2$@aptesSBA-15 (containing 3 μmol of POM), room temperature, light protection.

[b] Reaction conditions: 1 mmol of R-(+)-limonene, 4.5 mmol of H_2O_2, 1.5 mL CH_3CN, 87 mg of PW_{11}@aptesSBA-15 or 150 mg of $Co_4(PW_9)_2$@aptesSBA-15 (containing 3 μmol of POM), 80 °C.

[c] Based on the amount of consumed substrate; corresponding to 2,3-epoxigeraniol.

[d] Based on the amount of consumed substrate; corresponding to limonene-1,2-diol.

[e] Selectivity for limonene-1,2-epoxide.

1,2-epoxide (v), diepoxide (vi) and 1,2-diol (vii) were found. Initially 1,2-epoxide is formed but after the first 30 min of reaction the diol is already the main product in the presence of all catalysts. The oxidation of this substrate with H_2O_2 had been studied before in a biphasic system (water-dichloroethane medium) catalyzed by sandwich polyoxometalates [20,21]. These studies were performed at low temperature but reasonable catalytic results were reached only for long reaction times.

The present study suggests that the lacunary PW_{11} is more efficient homogeneous catalyst than the compounds with the insertion of transition metal such as Co^{II} and Fe^{III} in its framework. This fact could be related with the most efficient interaction between the lacunary PW_{11} and H_2O_2 than the mono-substituted and the sandwich POMs, probably due to the presence of the five oxygen atoms in the lacunary region which are free to interact with other species. The higher catalytic performance of the lacunary compound is an advantage because this is the precursor of mono-substituted compounds, what indicate that the pos-insertion of transition metals in its structure is unnecessary to enhance high yields for the oxidation of geraniol and R-(+)-limonene with H_2O_2.

3.3. *Heterogeneous catalysis*

The most active homogeneous catalysts for the oxidation of geraniol and R-(+)-limonene with H_2O_2, PW_{11} and $Co_4(PW_9)_2$, were immobilized onto a functionalized silica support aptesSBA-15. Their performance as heterogeneous catalysts was then investigated using the same experimental conditions than in the homogeneous reactions. The catalytic performance for PW_{11}@aptesSBA-15 and $Co_4(PW_9)_2$@SBA-15 is showed in Table 2.

As depict in Table 2, the oxidation reactions does not occurred and no conversion was observed in the presence of the functionalized support material (aptesSBA-15). The two heterogeneous catalysts were active for the oxidation of geraniol and only the 2,3-epoxigeraniol (ii) was formed. The PW_{11}@aptesSBA-15 is slightly more active catalysts than $Co_4(PW_9)_2$@aptesSBA-15 since it was attained higher conversion after 4 h of reaction. Furthermore, after 24 h of reaction near complete conversion was achieved using PW_{11}@aptesSBA-15, however the same conversion was not realized in the presence of $Co_4(PW_9)2$@aptesSBA-15. The difference of activity found between these phosphotungstates when immobilized was not observed during their performance in homogeneous systems. This difference of activity is still more pronounced for the oxidation of R-(+)-limonene, where the $Co_4(PW_9)_2$@aptesSBA-15 showed almost absence of activity, even after 24 h of reaction. The active center of the sandwich $Co_4(PW_9)_2$ may be centered on the two cobalt metals with the terminal water ligand. On the other hand, the active center(s) of the lacunary PW_{11} should be some or all the five oxygen atoms from the lacuna region that are free to coordinate or interact with solvents and other species. These compounds are probably differently immobilized on the surface of aptesSBA-15. The lacunary PW_{11} may be immobilized via W—O—Si bonds as previously suggested in the literature [28] or by simple electrostatic interaction with the surface. In opposite, the immobilization of the sandwich $Co_4(PW_9)_2$ may occur by the interaction of the cobalt center and the amine groups on the surface of the material. The difference of catalytic activity observed for these heterogeneous catalysts may be caused by different ways of immobilization or different interaction between active centers and the support surface.

Fig. 9 compares the kinetic profiles between the homogeneous and heterogeneous catalysts for oxidation of R-(+)-limonene with H_2O_2. The selectivity obtained for the oxidation of this substrate in the presence of heterogeneous catalysts is still low because identical amounts of limonene-1,2-diol (vii) and limonene-1,2-epoxide (v) were found. In the presence of the heterogeneous catalysts the formation of the diepoxide was practically insignificant. The literature reports only an example of heterogeneous catalytic oxidation of limonene by a silicotungstate immobilized onto surface-modified SiO_2 and in this case, 78% of yield to limonene-8,9-epoxide was obtained after 24 h of reaction [48]. The selectivity and the nature of the main product must be strongly influenced by active center of the catalyst, as well as by the methodology of immobilization and the support.

The solid catalysts can be easily separated by simple filtration followed by washing (with acetonitrile and *n*-hexane) and

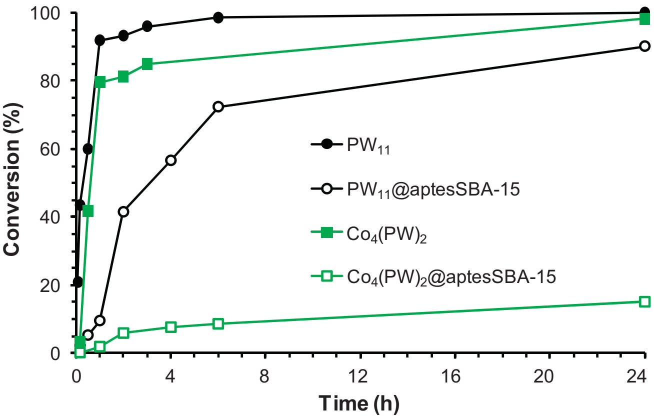


Fig. 9. Kinetic profiles for the oxidation of R-(+)-limonene with H_2O_2 in the presence of homogeneous and heterogeneous catalysts.

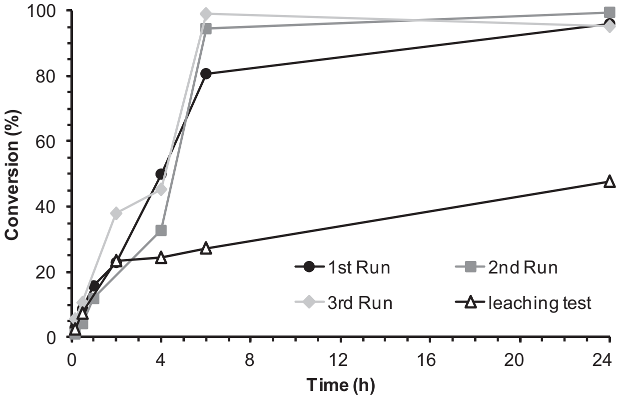


Fig. 10. Kinetic profiles of PW_{11}@aptesSBA-15 for different recycling cycles (first, second and third run) and for leaching analysis of geraniol oxidation reaction using H_2O_2 as oxidant (leaching test).

dried at room temperature to be used in a fresh reaction under identical experimental conditions. The catalysts were recycled in order to test their stability and activity in consecutive reaction cycles. Fig. 10 shows the reusability of the heterogeneous system PW_{11}@aptesSBA-15 for oxidation of geraniol during 24 h of reaction. It can be seen that the activity of this catalyst is maintained during the consecutive cycles and the complete conversion is achieved after 24 h of reaction. The same behavior was observed for $Co_4(PW_9)_2$@aptesSBA-15 where the conversion obtained after 24 h is still higher for the second (98%) and third cycles (95%) than for the first cycle (77%). The selectivity for all the consecutives cycles of both catalysts was always 100% for 2,3-epoxide of geraniol. To further investigate the activity of the heterogeneous catalyst versus the possible homogeneous reaction with the leached of active species from the support surface, the solid catalysts were separated from the reaction mixture by carefully filtration after 2 h of reaction when the conversion was higher than 20% and the reaction was continued with the remaining filtrate. This experiment was performed for the oxidation of geraniol, and Fig. 10 also compares the kinetic profiles with and without filtration of solid PW_{11}@aptesSBA-15 after 2 h. It can be observed that after this reaction time without solid catalyst the conversion decreases and after 24 h the conversion was only 47% (leaching test) instead of 96% obtained in the presence of solid PW_{11}@aptesSBA-15. Similar experiment was performed for the same reaction catalyzed by $Co_4(PW_9)$2@aptesSBA-15. In this case, the loss of activity by the solid catalysts filtration was only 15% what means that the homogeneous contribution for the increases of conversion was higher for $Co_4(PW_9)_2$@aptesSBA-15 than for PW_{11}@aptesSBA-15 system. These results may suggest that a partial leaching of the active centers from the heterogeneous catalysts were lost for the solution. The ICP analysis was performed to quantify the possible leaching of POM after three consecutive reaction cycles. Thus, tungsten analysis was carried out for the PW_{11}@aptesSBA-15 and $Co_4(PW_9)_2$@aptesSBA-15 recovered after three consecutive reaction cycles, and no significant loss of tungsten content was found for PW_{11}@aptesSBA-15 (6.9 wt% of W before and 6.1 wt% after catalysis). However, for $Co_4(PW_9)_2$@aptesSBA-15 a loss of 27% of the initial $Co_4(PW_9)_2$ was observed after the reaction cycles (4.9 wt% of W before and 3.5 wt% after catalysis). To investigate the presence of cobalt complex in solution after 24 h of heterogeneous catalytic reaction, the solution from the reaction was collected and analyzed by UV–vis spectroscopy, however the characteristic *d*–*d* band of Co^{II} was not observed.

The heterogeneous catalysts PW_{11}@aptesSBA-15 and $Co_4(PW_9)_2$@aptesSBA-15 recovered after the reaction were characterized by different techniques, in order to check the catalysts stability after reaction cycles. The analysis of UV-vis/DRS spectrum for PW_{11}@aptesSBA-15 (Fig. 4c) presents the same oxygen-to-tungsten charge transfer band as observed before catalytic run. Also identical UV-vis/DRS spectrum was found for $Co_4(PW_9)_2$@aptesSBA-15 after its use in the catalysis reaction (Fig. 4f), showing the *d*–*d* transition band with a shoulder characteristic of Co^{II} from sandwich compound. These results suggest that the structure of PW_{11} and $Co_4(PW_9)_2$ remain intact after three heterogeneous catalytic cycles. This stability was also confirmed by FT-IR and by FT-Raman, where the characteristic bands of these phosphotungstates [ν_{as}(W—O—W) observed in FT-IR and ν_s(W—O) observed in FT-Raman] were also found after catalytic reaction. The integrity of the support material was analyzed by scanning electronic microscopy (SEM), and as observed in Fig. 11 the morphology of the material is similar before and after catalysis. Furthermore, the EDS analysis was performed to determine the qualitative composition of the materials before and after catalytic reaction. Tungsten was identified in the two heterogeneous catalysts before and after catalytic uses. In the case of $Co_4(PW_9)_2$@aptesSBA-15 cobalt was also identified, and the ratio Co/W was compared before and after catalytic reaction revealing similar values (wt% ratio W/Co = 19.7/1.12 before catalytic uses and 20.0/1.26 after catalytic uses), what indicates no decomposition of $Co_4(PW_9)_2$ structure. In conclusion, the results obtained from these different techniques indicate that the support material is robust and stable after oxidative reactions and also no decomposition of active phosphotungstates occurred.

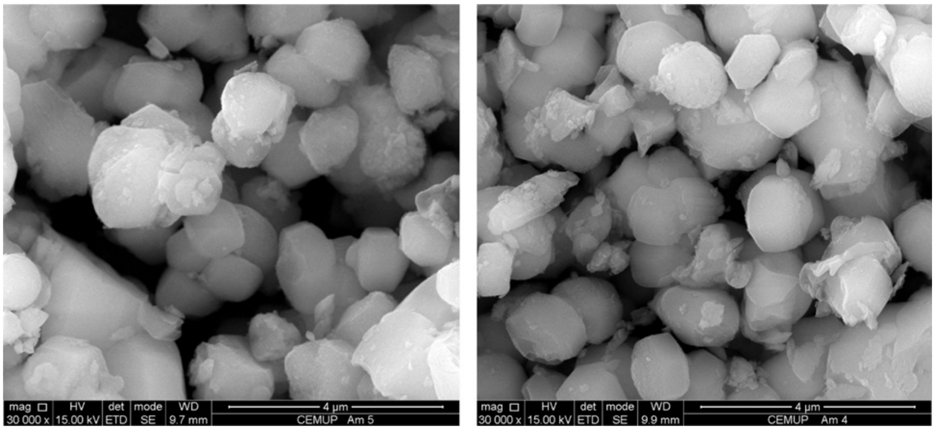


Fig. 11. Scanning electronic microscopy images of $Co_4(PW_9)_2$@aptesSBA-15 before (left) and after (right) to be used as catalyst in the oxidation of geraniol with H_2O_2.

4. Conclusions

The reported work demonstrates that the phosphotungstates ions, lacunary PW_{11}, mono-substituted $PW_{11}M$ and sandwich $M_4(PW_9)$ (M is Co^{II} or Fe^{III}) are active homogeneous catalysts for the oxidation of geraniol and R-(+)-limonene with H_2O_2. In particular, the lacunary and the cobalt catalysts demonstrated to be more active than the iron compounds for the oxidation of both substrates. Also, the lacunary and the mono-substituted $PW_{11}M$ ($M = Co^{II}$ and Fe^{III}) showed to be more selective catalysts than the sandwich. The 2,3-epoxide was the only product obtained from geraniol oxidation catalyzed by PW_{11} and the mono-substituted $PW_{11}M$. A complete conversion of this substrate was achieved after 1.5 h of reaction when catalyzed by PW_{11} and $Co_4(PW_9)_2$. In the presence of the last catalyst also the diepoxide was formed. The complete conversion of R-(+)-limonene oxidation was also achieved after 3 h of reaction when the lacunary PW_{11} was the catalyst. The selectivity for limonene-1,2-diol was between 40% and 50% in the presence of all catalysts and other two products were detected: limonene-1,2-epoxide and diepoxide. The lacunary PW_{11} and the sandwich $Co_4(PW_9)_2$ showed the best homogeneous catalytic performance and, consequently, were immobilized to prepared novel heterogeneous catalysts: PW_{11}@aptesSBA-15 and $Co_4(PW_9)_2$@aptesSBA-15 These phosphotungstates were immobilized for the first time and their catalytic performance was analyzed. PW_{11}@aptesSBA-15 showed high catalytic activity for geraniol and R-(+)-limonene. Both substrates were practically complete oxidized after 24 h of reaction. For geraniol oxidation only the 2,3-epoxigeraniol was produced. However for R-(+)-limonene the 1,2-diol (yield 54%) was the main product but 1,2-epoxide and diepoxide were also obtained. The two heterogeneous catalysts were used in consecutive reaction cycles without loss of activity, and their structural stability was also investigated by their recovery after consecutive cycles and characterization analysis by several spectroscopy and microscopy techniques that indicate absence of major catalyst decomposition. However, some homogeneous contribution in the heterogeneous catalytic systems were detected by the leaching analysis what indicate that the covalent attach of the phosphotungstate to the support via amine group may not be stable and further study to improve the covalent bond of polyoxometalates to silica materials need to be performed.

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