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Monolacunary $K_8SiW_{11}O_{39}$-Catalyzed Terpenic Alcohols Oxidation with Hydrogen Peroxide

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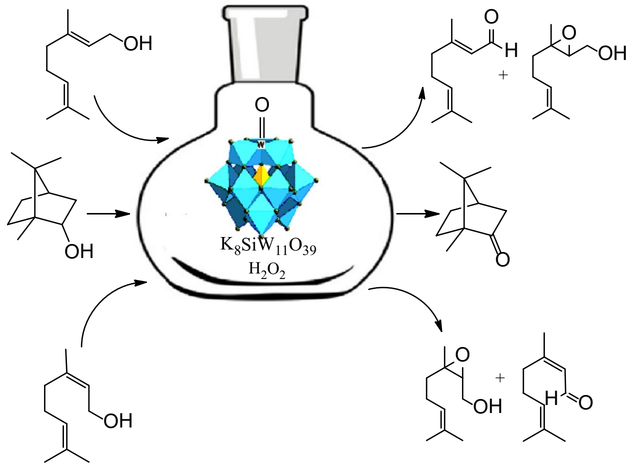
Abstract

Lacunar potassium undecasilicotungstate salt catalyst was highly efficient in oxidation reactions of terpenic alcohols with hydrogen peroxide. Carbonylic products were selectively obtained from alcohols such as borneol, nerol, geraniol and β-citronellol. The $K_8SiW_{11}O_{39}$ catalyst was synthesized in one pot reaction starting from precursor salts (KCl, Na_2WO_4, and Na_2SiO_3). The catalyst salt was characterized by FT-IR, TG/DSC, BET, XRD analyses and potentiometric titration. The main reaction parameters were assessed. Based on experimental data, a reaction pathway was proposed. In borneol oxidation, TON of 2720 was achieved, indicating the high catalytic activity. As far we know, it is the first time where the monolacunar catalyst is used without an additional introduction of metal transition into Keggin anion. A comparison of the catalytic performance of different lacunar silicotungstic acid salts exchanged with different cations was performed. The $K_8SiW_{11}O_{39}$ catalyst was used without loss activity.

Graphical Abstract



Keywords Lacunar silicotungstic acid potassium salt · Hydrogen peroxide · Catalytic oxidation · Terpenic alcohols

1 Introduction

Terpenic alcohols are an abundant, renewable and attractive raw material for synthesis of fine chemicals, drugs and agrochemicals [1–3]. Especially, its carbonylic derivatives always have organoleptic properties that make them ingredient of flavours, fragrances and perfumes [4, 5].

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Industrially, the production of carbonyl products has been until today carried out with toxic stoichiometric oxidants, which generate residues that should be disposal into environment. Green oxidants such as hydrogen peroxide are a benign environmentally alternative, nonetheless, it requires the presence of metal catalyst to be activate [6, 7].

Polyoxometalates are a class highly versatile of catalysts with acidic and redox properties that are used in homogeneous and heterogeneous processes [8, 9]. Several heteropolyacids are efficient catalysts in oxidation reactions with oxygen or hydrogen peroxide [10]. Among the polyoxometalates, the Keggin heteropolyacids (HPAs) are most used in catalysis. The most common Keggin HPAs are clusters of metal oxygen with anions of general formulae $X^{n+}M_{12}O_{40}{}^{n-m}(X^{n+}=P^{5+}, Si^{4+}; M=Mo, W; m=8)$.

Keggin HPAs are strong Bronsted acids but have also redox properties, being thus catalysts used either in acidic or oxidative processes [11]. However, they have low surface area and are soluble solids in polar solvents, a drawback that hamper its use in certain reactions. To overcome these late disadvantages, the HPA catalysts have been supported on solid matrixes that have high surface area [12]. This way, solid supported HPA catalysts have shown active in acid-catalyzed reactions such esterification, transesterification isomerization, as well as oxidation reactions [13–17].

Organic reactions as esterification and oxidation generate water as by-product; moreover, some reactants are used in aqueous solutions (i.e., aqueous hydrogen peroxide). These features may contribute for the solid-supported catalyst leaching. An alternative approach to circumvent this problem is convert the Keggin heteropolyacids to solid salts. To do it, the protons should be replaced by large radius cations (ca. > 1.30 Å), a characteristic that can give them high surface area and insolubility in polar solvents.

Although ammonium alkyl derivative organic cations have being used, a procedure very common is the total or partial replacement of the protons by the cesium [18]. The partial exchange of protons by those cations make insoluble the HPAs, increase its surface area and even retain its acidity properties. Nonetheless, the level of substitution of protons by cations such as Cs^+ or K^+ plays a pivotal rule on catalytic activity of HPA salts [19]. In some cases, the Cs^+ HPA salts present difficulty to be removed from reaction medium. Thus, they have been supported on silica or mesoporous materials [19–21].

Another structural modification that allows improve the activity of HPA catalysts in oxidation reactions is the removal of a MO unity from the Keggin heteropolyanion (i.e. M = Mo or W). In general, these lacunar catalysts have a vacancy that can be filled by metal transition cation, which potentially may enhance its catalytic activity. Recently, several works in literature have explored the activity of transition metal substituted lacunar HPA salt catalysts in oxidation reactions of alcohols and olefins [22].

Lacunar Keggin type POMs can be easily synthesized by removal of one W-O or M-O units from octahedral of the Keggin heteropolyanion (i.e., $XM_{12}O_{40}{}^{n-}$; n = 3 when $X=P^{5+}$; n = 4 when $X=Si^{4+}$), giving mono lacunary heteropolyanions ($XM_{11}O_{39}{}^{m-}$; m = 7 when $X=P^{5+}$; m = 8 when $X=Si^{4+}$) [23]. Depends on the pH of synthesis, di or tri lacunary species can be formed. A common synthesis route is to promote an increase of pH value of a solution containing the Keggin heteropolyacid, resulting in the protons exchange by the metal cations present in the alkaline medium. The extension of hydrolysis of the Keggin anion is governed by the pH control [24]. Another process is to start from precursors salts (i.e., tungstate or molybdate, silicate or phosphate) and perform the synthesis in one-pot reaction [25].

Lacunar heteropolyacid salts can contain highly charged counterions such as small-sized metal cations or cations of large radium. The firsts are compounds that are soluble in water and polar organic solvents. Contrariwise, when larger cations are used in the synthesis, the solid heteropoly salts are insoluble. Indeed, charge, size, shape, and hydrophobicity are some important features that offer strong interactions between the ionic components [25, 26].

Song et al Keggin HPA salts synthesized α-$K_5PW_{11}O_{39}(MOH_2)$ ($M=Mn^{2+}$, Co^{2+}, Ni^{2+}, and Zn^{2+}) and assessed its catalytic activity in liquid phase oxidation of 2-propanol with hydrogen peroxide [27]. They have found that the conversions followed the trends: $K_5PWMn_{11}O_{39} > K_5PWCo_{11}O_{39} > K_5PWNi_{11}O_{39} > K_5PWZn_{11}O_{3,}$ which was consequence of that reduction potential and absorption edge energy of these catalysts.

Patel et al. described the that Keggin-type Cs^+ salt of a mono Mn^{+2}-substituted phosphotungstate ($Cs_5PMnW_{11}O_{39}$) on styrene oxidation with tertbutyl hydroperoxide [28]. Conversions of 61 and 99% selectivity of benzaldehyde were achieved. This same research group synthesized $Cs_5PNiMo_{11}O_{39}$ catalyst and assessed its activity on Suzuki–Miyaura cross coupling reactions [29]. Although it is not oxidative process, we highlight that those cesium catalysts were soluble under reaction conditions (water: ethyl alcohol mixture). However, those authors developed a process to recovery the catalyst. They cooled reaction solution to room temperature, and then extracted the organic products with ethyl ether; consequently, the catalyst migrated to the aqueous solutions. Afterwards, the dryness of the solution provided the solid catalyst, which was repeatedly reused without loss activity [29].

Lacunary heteropolyanions can also underwent dimerization or trimerization generating di or tri-lacunar species. Mizuno et al. studied the epoxidation of 1-octene with H_2O_2 catalyzed by a series of tetrabutylammonium silicotungstate salts in CH_3CN at 305 K [30, 31]. They have found that whereas the dilacunary salt, which was the most active catalyst, other mono- and tri-vacant lacunary compounds had moderate activity. The saturated specie (i.e., $SiW_{12}O_{40}^{4-}$) was almost inactive.

Ding et al. investigated the activity of dilacunary silicotungstate (i.e., $K_8(\gamma\text{-}SiW_{10}O_{36})\cdot 13H_2O$) in oxidation reactions of alcohols with 30% aqueous hydrogen peroxide [32]. The reaction was carried out in an aqueous/oil biphasic system, which allowed easy recovery of a catalyst under reaction mild conditions. High yields of ketones were obtained at room temperature the dilacunary silicotungstate was five times recycled without decrease of catalytic activity.

In this work, we carried out the reaction of terpenic alcohols in the presence of monolacunar silicotungstate catalyst. The adequate choice of solvent (dimethylacetamide, DMA), allowed that this catalyst achieve high conversions and selectivity for carbonylic products. Borneol, a secondary bicyclic terpenic alcohol important to synthesis of fine chemicals was selected as model molecule. The main reaction variables (catalyst load, temperature, reactants stoichiometry) were assessed. The reaction scope was extended to the other terpenic alcohols. The catalyst was recovered and reused without loss activity.

2 Experimental Section

2.1 Chemicals

All chemicals were purchased from commercial sources. Sodium tungstate, sodium metasilicate were acquired from Sigma–Aldrich (99 wt%). Potassium chloride and sodium hydrogen carbonate were Vetec (99 wt%). Borneol (99 wt%, racemic mixture Sigma Aldrich), β-citronellol (racemic mixture 90–95 wt%, Sigma Aldrich), linalool (Sigma Aldrich, 99 wt%), nerol (Sigma Aldrich, 97 wt%) and geraniol (Sigma Aldrich, 98 wt%) were used as received. Dimethylacetamide (DMA) was acquired from Sigma–Aldrich. Hydrocloric acid (36.5 wt%) was Quimica Moderna. The 34 wt% aqueous H_2O_2 (Sigma) was the oxidant in all reactions.

2.2 Synthesis of Monolacunar Potassium Silicotungstate Salt

The catalyst was synthesized as described in literature [32]. Na_2SiO_3 (1.1 g, 50 mmol) and Na_2WO_4 (182 g, 0.55 mol) were separately dissolved in 100 mL of water. Under magnetic stir, the Na_2SiO_3 solution was poured into Na_2WO_4 solution, and the slow addition of HCl (165 mL, 4 $molL^{-1}$) resulted in the $H_4SiW_{12}O_{40}$ acid. The dropwise addition of $NaHCO_3$ solution converted $H_4SiW_{12}O_{40}$ to lacunar salt (i.e., $Na_8SiW_{11}O_{39}$) adjusted the pH to 5.5 and this value was maintained constant for 100 min.

Thus, obtain potassium silicotungstate salt, solid KCl (*ca.* 90 g) was added to the solution with gentle stirring. After 15 min, the precipitate was filtered through a sintered glass filter. The catalyst was recrystallized in hot water. If necessary, the insoluble material was quickly removed by filtration, and the salt was precipitated again by new addition of solid KCI (*ca.* 80 g). Finally, the precipitate was filtered, two times washed (*ca.* 50 mL portions) with 2 $molL^{-1}$ KCl aqueous solution, and air dried. The $K_8SiW_{11}O_{39}$ catalyst was heated to 473 K for 3 h in air prior the characterization steps and catalytic tests.

2.3 Characterization of Catalyst

The textural properties of lacunar potassium salt catalyst were studied by H_2 desorption/adsorption using NOVA 1200e High Speed, Automated Surface Area and Pore Size Analyzer Quantachrome Instruments. Previously, the sample was degassed by 1 h. The specific surface area was calculated by Brunauer-Emmett-Teller equation applied to the desorption/ adsorption isotherms.

Powder X-rays diffraction pattern of catalyst was recorded with a X-ray Diffraction System model D8-Discover Bruker using Ni filtered Cu-kα radiation ($\lambda = 1.5418$ Å), working at 40 kV and 40 mA. The measurements were done in intervals of 0.05° with a counting time of 1.0 s in the 2θ range of 5–80 degrees.

FT-IR/ ATR spectrum of the lacunar salt was recorded on an FT-IR Varian 660 spectrometer with reflectance accessory utilizing KBr plates under ambient conditions.

The potentiometric titration (Bel pH meter, model W3B) measured the amount and the strength of the acid sites as described by Pizzio et al. [33]. A suspension of catalyst in CH_3CN was stirred by 3 h and then titrated with n-butylamine (*ca.* 0.05 N, toluene). The acidity of the catalyst measured by this technique allows us to evaluate the total number of acid sites as well as their acidic strength.

2.4 Catalytic Runs

Typically, a 25 mL three-necked glass flask, equipped with a sampling system and a reflux condenser was charged with DMA (*ca.* 10 mL), terpenic alcohol (*ca.* 2.0 mmol), and an adequate amount of $K_8SiW_{11}O_{39}$ catalyst. The reaction was carried out using magnetic stirring and heating to 353 K temperature. After added hydrogen peroxide at adequate molar ratio, the reaction was carried out for over 3 h.

To follow the reaction progress, aliquots were periodically collected and analyzed in a gas chromatograph (Shimadzu, GC 2010, capillary column, FID). The main products were identified through GC-MS analyses (Shimadzu

MS-QP 2010 ultra, mass spectrometer, electronic impact mode at 70 eV, coupled to a Shimadzu 2010 plus, GC). Additionally, reaction products were co-injected in GC with authentic samples.

The influence of main reaction variables (i.e. reactants stoichiometry, temperature, catalyst load) was investigated. Blank-reactions were performed for each molar ratio. Borneol was selected as a model molecule. The reaction scope was extended to the other terpenic alcohols (geraniol, nerol, β-citronellol, α-terpineol, linalool).

2.5 Recovery and Reuse of the Catalyst

After the end of the reaction, the solid catalyst was three times washed with dichloromethane to extract the remaining products. After it has been Then it was heating in plate to near dryness, it was dried at room conditions. The solid catalyst was weighed and reused in another catalytic run.

3 Results and Discussion

3.1 Catalysts Characterization

3.1.1 FT-IR Spectroscopy Analyses

The literature attributes the main typical absorption bands of monolacunary salt as follows: 994 cm^{-1} (Si-O_a), 945 cm^{-1} (W-O_d), 875 cm^{-1} (W-O_b-W), 805 and 730 cm^{-1} (W-O_c-W) [28]. On the other hand, Pizzio and Blanco have found that FT-IR spectrum of $H_4SiW_{12}O_{40}$ displayed the absorption bands at 1020, 982, 926, 884 and 778 cm^{-1} [33]. The Fig. 1 shows that all these bands are present in FT-IR spectrum of salt synthesized.

The absorption bands of lacunary salt are shifted to higher wavenumber if compared to those of precursor heteropolyacid. The same phenomenon was observed by Romanelli et all, when synthesized sodium lacunar salts [34]. The main absorption bands of lacunar salt and silicotungstic acid are placed at 991 e 1014 cm^{-1} (ν_{as} W=O), 943 e 978 cm^{-1} (ν_{as} Si-O_a), 852 e 910 cm^{-1} (ν_{as} W-O_b-W) e, 787 e 762 (ν_{as} W-O_c-W), respectively.

Nonetheless, Pizzio et al concluded that alone FT-IR it is not enough to confirm the transformation of the $SiW_{12}O_{40}{}^{4-}$ to $SiW_{11}O_{39}{}^{8-}$ lacunar phase during the salt synthesis. They have found that the main bands of the latter are placed at 1008, 959, 946, 882, 869, 794 and 720 cm^{-1} [33]. Those bands are close of them present in FT-IR of lacunar potassium salt.

3.1.2 Analyses of Powder X-Rays Diffraction Patterns

It is important highlight that water molecules number per unitary cell strongly affects the XRD patterns of HPAs or its salts. On this sense, Derrick et al recorded data from hydrates silicotungstic acid and showed the existence of stable phases of composition $H_4SiW_{12}O_{40}·nH_2O$ where n = 24, 14, 6 and 0 [35]. They have prepared $H_4SiW_{12}O_{40}·6H_2O$ heteropolyacid to 150 °C and through direct comparison of XRD spectrum we conclude that their data fits well with those recorded by us.

The X-rays diffractograms of precursors (tungstate and metasilicate), parent silicotungstic acid and the lacunar potassium silicotungstic salt are presented in Fig. 2. The main diffraction lines are placed in the region $5 < 2\theta < 35$ degrees. Tungstate has monoclinic symmetry $C_{2/m}$ (Z = 4).

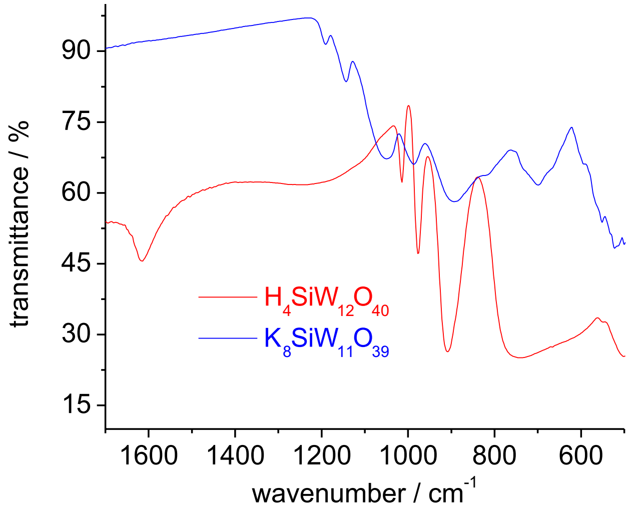


Fig. 1 FT-IR spectra of silicotungstic acid and lacunar potassium silicotungstate salt

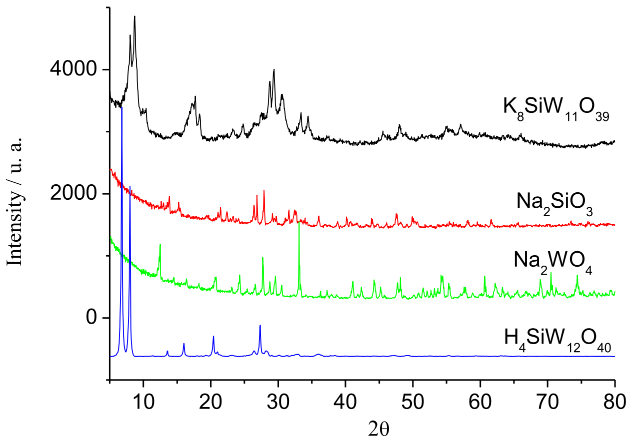


Fig. 2 Powder XRD patterns of $K_8SiW_{11}O_{39}$ lacunar salt compared to the precursors tungstate, silicate and the parent $H_4SiW_{12}O_{40}$

Comparing diffraction patterns of synthesized salt $K_8SiW_{11}O_{39}$ with literature data (JCPD file no. 34-0205) we have found that they perfectly correspond to the cubic phase [22]. The increasing of width of peaks is evidence of greater size of crystallites. All the three samples were crystalline in nature.

The powder X-ray diffraction patterns of $H_4SiW_{12}O_{40}$ and $K_8SiW_{11}O_{39}$ were compared (Fig. 2). It was found that the synthesized salt has similar diffraction lines pattern to the parent $H_4SiW_{12}O_{40}$, which has main XRD peaks in the region of $5° < 2θ < 30°$. It is suggestive that the Keggin anion is present in their framework of lacunar salt. These lines were shifted to higher 2θ angles in X-rays diffraction spectrum of lacunar salt. An increasing of values of 2θ angles means that interplanar distance was decreased and consequently the unitary cell was also decreased. In addition, the introduction of potassium cations into heteropolyanion structure increased the amount of diffraction lines.

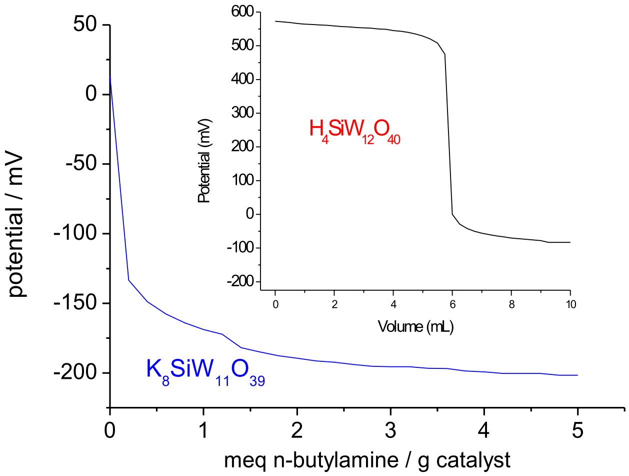


Fig. 3 Potentiometric titration curves with n-butylamine of $H_4SiW_{12}O_{40}$ and $K_8SiW_{11}O_{39}$ catalysts

3.1.3 Measurement of Acidity Strength of HPA Catalysts

The plots of the electrode potential as a function of mEq. N-butylamine per g of the catalyst is shown in Fig. 3. The acidic strength of surface sites is assigned as follow: very strong sites ($Ei > 100$ mV); strong sites ($0 < Ei < 100$ mV); weak sites ($100 < Ei < 0$ mV) and very weak sites ($Ei < 100$ mV) [33].

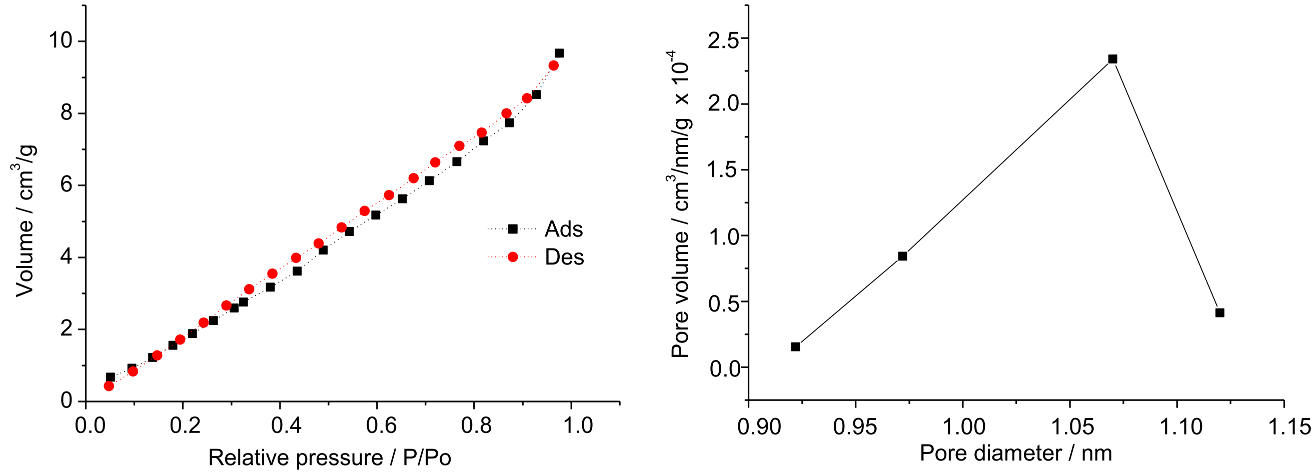
It is observed that while the silicotungstic acid has very strong acid sites, the lacunary potassium salt has very weak acid sites (Fig. 3). Moreover, the profile of titration curve of lacunar salt quickly drops, indicating the almost protons were removed during the synthesis.

3.1.4 Analyses of Porosimetry of the Lacunar Potassium Silicotungstate Salt

The porosity properties of lacunar potassium salt were investigated. Isotherms of adsorption/ desorption as well as the distribution, volume and diameter of porous are shown in Fig. 4.

In general, the surface area of heteropolyacid increases when the protons are exchanged by potassium cations. Indeed, while the surface area of $H_4SiW_{12}O_{40}$ was <3.0 m^2/g, the surface area of lacunar salt was 10.2 $m^{2/}g$ [27].

The isotherms reflect Type II characteristics, which are typical of not porous solids, suggesting that there was physic adsorption in multilayers. It was observed the total reversibility, indicated by the absence of hysteresis cycle in the



(a) **(b)**

Fig. 4 Isotherms of adsorption and desorption (**a**) and volume and diameters porous (**b**) of $K_8SiW_{11}O_{39}$ catalyst adsorption–desorption isotherms of the lacunary catalyst [27, 36].

The pore volume (< 0.02 $cm^3 g^{-1}$) as well as the pore sizes showing values in the region between 0.90 and 1.15 nm confirm that the lacunary potassium silicotungstate catalyst is microporous. These porosity and isothermal adsorption/desorption characteristics are supported by the literature data [33, 36].

3.1.5 Thermal Analyses of Lacunary Potassium Silicotungstate Salt

Thermogravimetric analysis of lacunary potassium silicotungstate salt shows two regions of loss weight; the first one before 200 °C assigned to loss of all water molecules (i.e., 7 mols of water molecules per mol of catalyst). The second one, attributed to decomposition of Si–O–W framework followed by the noticeable peak in DSC curves around 610 °C. The final products are an oxides mixture (Fig. 5).

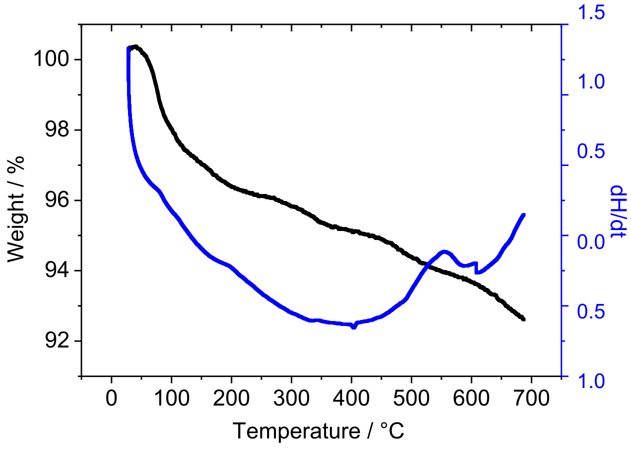


Fig. 5 TG-DSC Curves of samples of lacunary catalysts. Black line is the TG curve and blue line the DSC curve

The introduction of potassium cation as well as the removal of an WO unit from Keggin anion resulted in a decreasing of the decomposition temperature in relation to the parent heteropolyacid, probably as consequence of loss symmetry [27].

3.2 Catalytic Tests

3.2.1 Effect of Stirring Speed

The effect of stirring speed of the reaction solution was previously checked aiming to avoid the possible issue of mass transfer limitations. We carried out the reactions with stirring speed of 350, 700 and 1050 rpm. No significant change was found when the catalyst load was 10 mol% (i.e., the maximum load used). Therefore, all the runs were carried with stirring rate of 350 rpm.

3.2.2 Effect of Catalyst Load

Recently, we have found that Na_2WO_4 catalyst was highly efficient in oxidation reactions of alcohols with hydrogen peroxide in DMA solutions [37]. Hida and Nogusa assigned this efficiency the ability of solvent in stabilize a tetraperoxotungstate intermediate, that is the specie catalytically active in this reaction [38]. For this reason, the DMA was the solvent on this present work. The effect of catalyst load was assessed the kinetic curves are displayed in Fig. 6.

In general, the camphor was always the main product formed in $K_8SiW_{11}O_{39}$-catalyzed oxidation reactions of

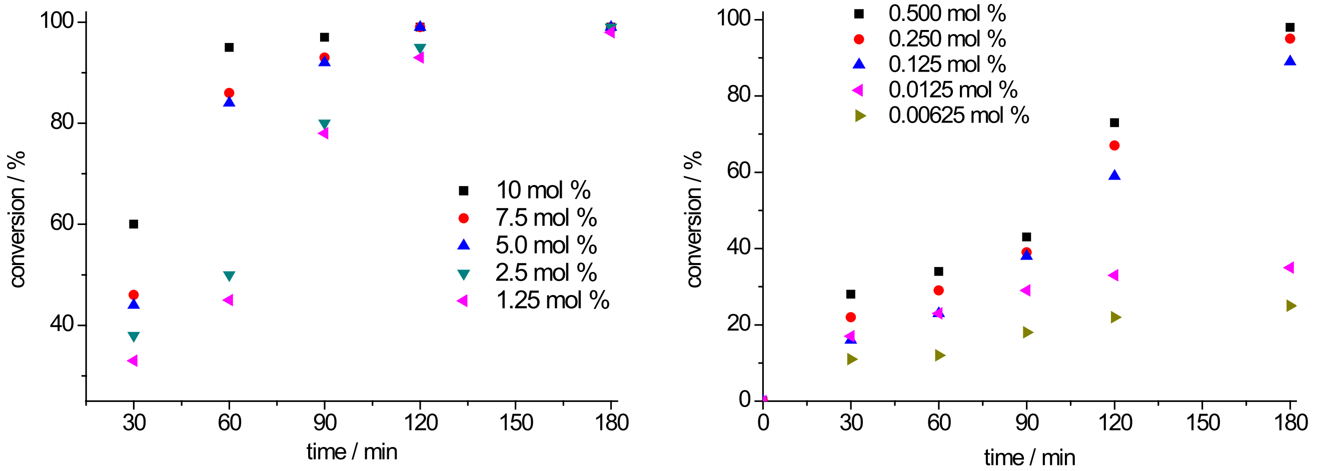


Fig. 6 Effect of catalyst load on kinetic curves of $K_8SiW_{11}O_{39}$-catalyzed oxidation reactions of borneol with H_2O_2. Reaction conditions: borneol (1.34 mmol); H_2O_2 (4.02 mmol); temperature (333 K); reaction time (3 h); DMA (10 mL)

borneol with H_2O_2 (ca. selectivity equal or higher than 90%) (Scheme 1).

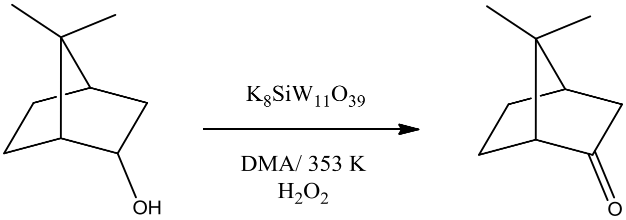
We have found that the catalyst was highly active, consequently, a great number of catalytic runs were performed to assess the effect of concentration. All the runs performed are listed in Table 1, including the TON achieved.

The lacunar catalyst was highly active; when a drastic reduction of catalyst concentration of 10–0.125 mol% was performed, only a little decreasing of conversion was achieved. Consequently, the TON obtained was very significant. When the catalyst concentration was 0.0125 mol%, a conversion was 34%, however, the TON was 2720, indicating the high activity of catalyst.

3.3 Insights on Reaction Pathway

Previously, when we investigated the mechanism of the Na_2WO_4-catalyzed borneol oxidation by hydrogen peroxide, we have found that the addition of H_2O_2 to the sodium tungstate/ DMA solution resulted in the disappearance of strong band at 931.5 cm^{-1} wavenumber, which was present in the FT-IR spectrum of Na_2WO_4 [37]. It was an evidence that W=O double bonds that are typical of tungstate anion were absent in the Na_2WO_4-catalyzed borneol oxidation by hydrogen peroxide.

Another evidence of this peroxidation step was the absorption bands at frequencies lower than 597 cm^{-1}, which are assigned to the vibrations of tungsten- oxygen single bonds, typical of peroxotungstate complexes [39–41]. Based on these findings and in the work of Hida and Nogusa, we proposed that a specie tetraperoxotungstate is a key-intermediate on that reaction [38, 39].



Scheme 1 Oxidation of borneol by H_2O_2 in the presence of $K_8SiW_{11}O_{39}$ catalyst in DMA solutions

In the present work, after the synthesis of lacunar salt as depicted in the Scheme 2, we suppose that only a tungsten atom per mol of catalyst can be peroxidized. Therefore, we can conclude that a peroxotungstate complex is the catalytically active specie on this oxidation reaction.

Thus, we propose a reaction pathway were a peroxided intermediate (1) has a highly electron-deficient tungsten atom that may undergo nucleophilic attack of borneol hydroxyl group (Scheme 2).

This attack then results in an opening of highly unstable three-center ring, where a hydrogen atom of hydroxyl group of borneol will be transferred to the oxygen atom that is bonded to the tungsten, giving OOH group and bornyl-alkoxide (omitted by simplification). It is possible that in this step both groups remain coordinated to the tungsten atom. It is very common the formation of species like these (i.e., intermediates with peroxide and or alkoxide groups bonded to tungsten atom) in tungsten-catalyzed oxidations [40–42]. Nonetheless, as we haven't any experimental evidence corroborating that this step has really occurred into tungsten coordination sphere, it was not included it in the Scheme 2.

In the last step, the simultaneous elimination of water and oxidized substrate (i.e., camphor) generate the lacunar heteropolyanion that can once more react with one mol of H_2O_2 and then participate of more one catalytic cycle (Scheme 2).

3.4 Assessment Other Variables of $K_8SiW_{11}O_{39}$-Catalyzed Borneol Oxidation Reaction With Hydrogen Peroxide

In oxidation reactions, the proportion substrate: oxidant is always a key aspect; since the hydrogen peroxide is used in aqueous solutions, an increase on its load may trigger concurrent reactions or even affect the catalyst activity.

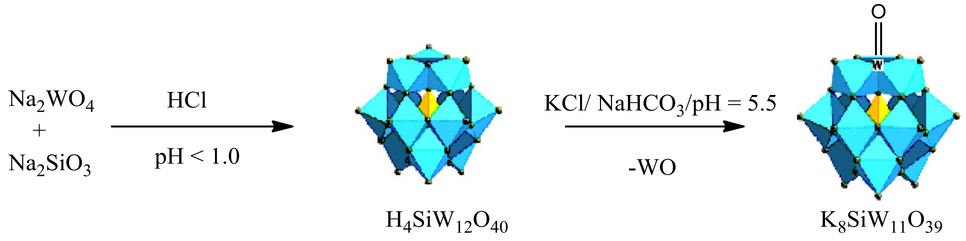
To assess this effect, we carried out reactions with the proportion of reactants varying of 1:1 to 1:5. The kinetic curves are displayed in Fig. 7. As demonstrate in Fig. 7b, with exception of reaction carried out with a stoichiometric proportion (*ca.* 1:1), the reaction selectivity was not affected by increasing on oxidant load. In all other proportions the

Table 1 Effect of catalyst load on conversion and TON of $K_8SiW_{11}O_{39}$-catalyzed oxidation reactions of borneol with H_2O_2

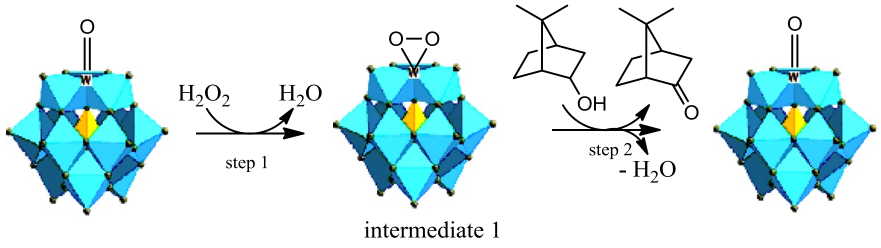
Run	Conc. (mol%)	Conv. (%)	TON	Run	Conc. (mol%)	Conv. (%)	TON
1	10.0	99	9.9	7	0.500	97	194
2	7.50	99	13.3	8	0.250	97	760
3	5.00	98	19.8	9	0.125	89	712
4	2.50	98	39.6	10	0.0625	42	672
5	1.25	97	77.8	11	0.0125	34	2720

Reaction conditions: borneol (1.34 mmol); H_2O_2 (4.02 mmol); temperature (353 K); reaction time (3 h); DMA (10 mL)

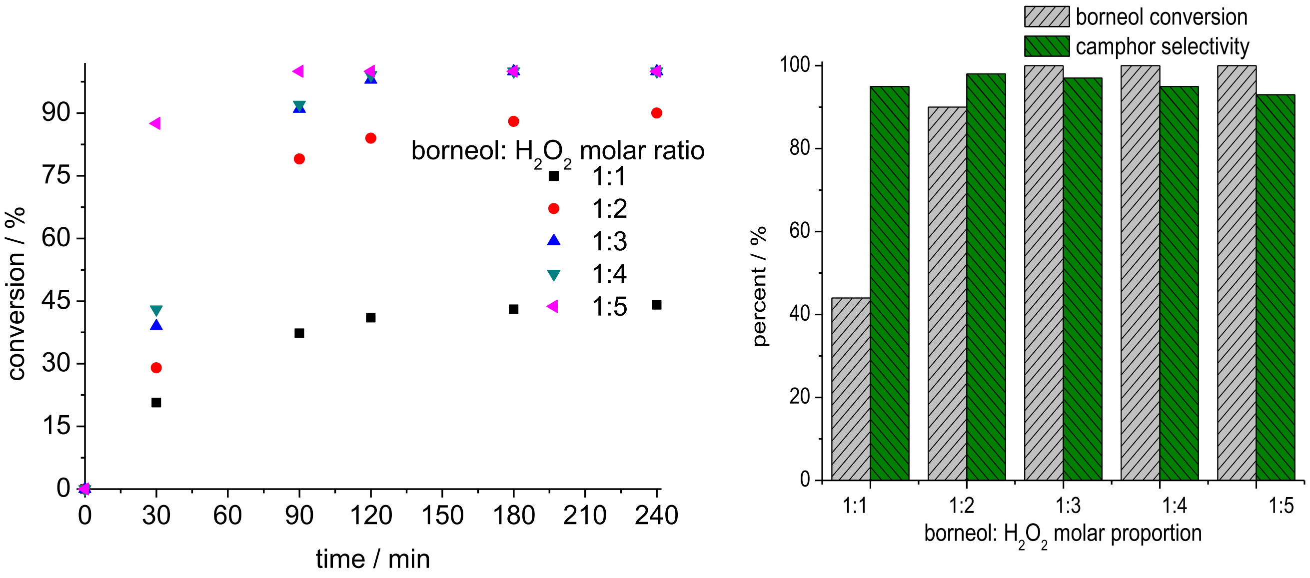
Scheme 2 Synthesis of lacunar salt (**a**) and probably reaction pathway (**b**) of $K_8SiW_{11}O_{39}$-catalyzed oxidation of borneol by H_2O_2



(a) synthesis of the lacunar catalyst



(b) reaction pathway



(a) **(b)**

Fig. 7 Effect of oxidant load on kinetic curves (**a**) and conversion and camphor selectivity (**b**) of $K_8SiW_{11}O_{39}$-catalyzed oxidation reactions of borneol with H_2O_2. Reaction conditions: borneol (1.34 mmol); reaction time (3 h); $K_8SiW_{11}O_{39}$ (1.25 mol%); temperature (353 K); DMA (10 mL)

conversions were equal or higher than 93%. The effects of temperature on kinetic curves of $K_8SiW_{11}O_{39}$-catalyzed oxidation reactions of borneol with H_2O_2 are shown in Fig. 8. An increase of temperature resulted in a higher initial rate of reaction as well as a higher final conversion.

On the other hand, whereas to observed when we varied the stoichiometry of reactants, the reaction camphor selectivity was strongly affected by changes on temperature. Indeed, conversion and camphor selectivity have an almost equal behavior (Fig. 8a).

We have found that in reactions at temperatures lower than 343 K, species alkylperoxides were also formed, compromising the camphor selectivity (Fig. 8b). These compounds were not detectable by GC analysis, but had its

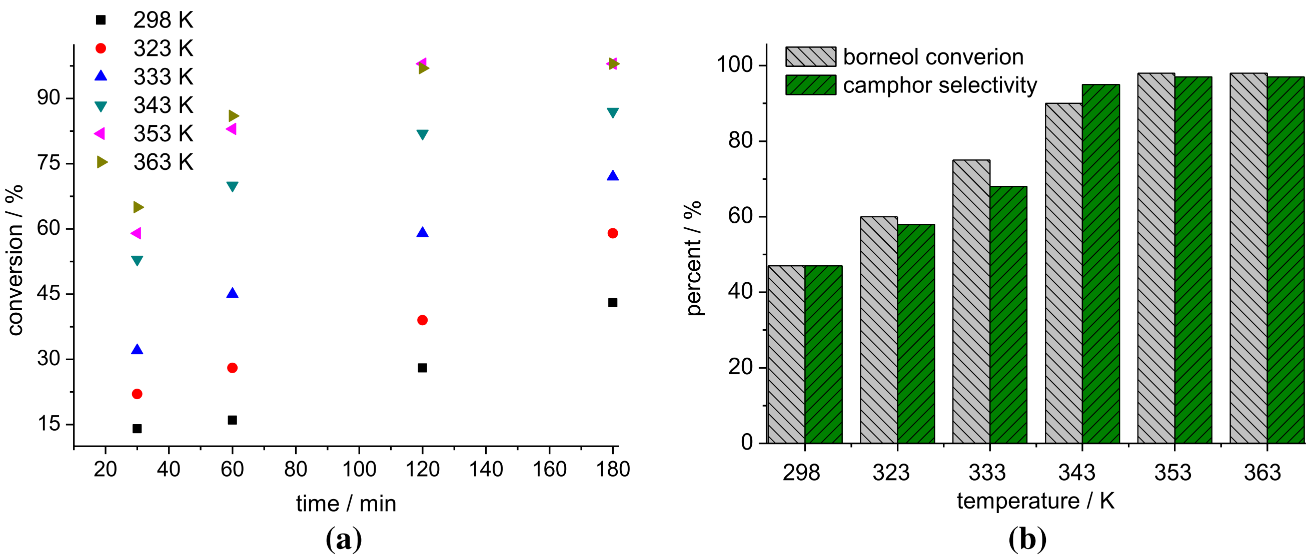


Fig. 8 Effect of temperature on kinetic curves (**a**) and conversion and camphor selectivity (**b**) of $K_8SiW_{11}O_{39}$-catalyzed oxidation reactions of borneol with H_2O_2. Reaction conditions: borneol (2.00 mmol); H_2O_2 (6.00 mmol); reaction time (3 h); $K_8SiW_{11}O_{39}$ (1.25 mol%); DMA (10 mL)

formation confirmed through triphenylphosphine tests, as proposed by Shulpin et al [43]. These results agree with literature [35].

We can conclude that optimized conditions for the $K_8SiW_{11}O_{39}$-catalyzed borneol oxidation with hydrogen peroxide to achieve *ca*. 90% of conversion and selectivity were as follows; borneol: hydrogen peroxide molar ratio (2:1); temperature (343 K), catalyst load and reaction time (5 mol% and 90 min respectively), or if a longer time of reaction will be acceptable (0.5 mol%, 180 min, respectively).

3.5 Catalyst Reuse

The $K_8SiW_{11}O_{39}$ is a solid catalyst and was insoluble in the reaction medium (i.e. DMA). To recover it, we employed the same procedure used to purify the reaction products (see experimental, Sect. 2.5). We achieved a recovery rate varying from 88 to 92% along three cycles of reuse. This high recovery suggests that procedure used was efficient. Therefore, it was possible to reuse this solid catalyst in another reaction. The results of reuse and recovery rate of the catalyst are shown in Fig. 9.

The stability of catalyst was verified via FT-IR analyses (Fig. 10). The main absorption bands of $K_8SiW_{11}O_{39}$ catalyst remained intact after three cycles of reuse.

3.6 Effect of Substrate on $K_8SiW_{11}O_{39}$-Catalyzed Terpenic Alcohols Oxidation Reaction with Hydrogen Peroxide

The reaction scope was extended to the other terpenic alcohols (Fig. 11).

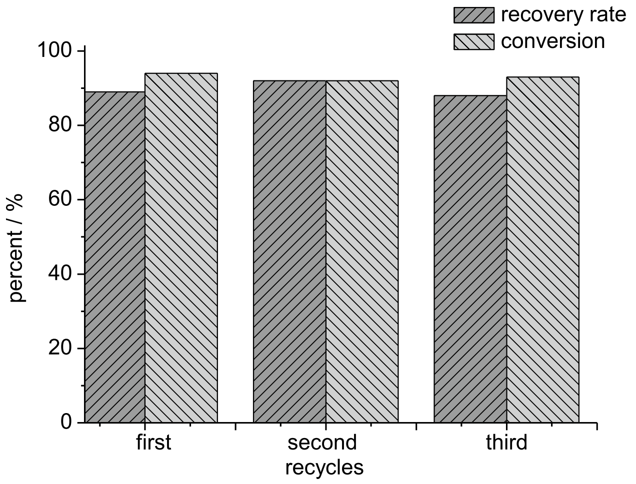


Fig. 9 Recovery rates of $K_8SiW_{11}O_{39}$ catalyst and conversion of the oxidation reactions of borneol with H_2O_2. Reaction conditions: borneol (2.00 mmol); H_2O_2 (6.00 mmol); reaction time (3 h); $K_8SiW_{11}O_{39}$ (5.0 mol%); temperature (353 K); DMA (10 mL)

The primary alcohols (β-citronellol) and allylic (geraniol, nerol), tertiary (linalool and α-terpineol) were the substrates selected. All these alcohols have double bonds, which can be potentially functionalized (i.e., through epoxidation or nucleophilic addition reactions).

The kinetic curves and selectivity and presented in Fig. 12a and b, respectively. Expectedly, the reactions with the tertiary alcohols (linalool and α-terpineol) achieved low conversions (ca. 50 and 47%, respectively). Although the hydroxyl group of these alcohols cannot be oxidized, they have double bonds that underwent nucleophilic addition

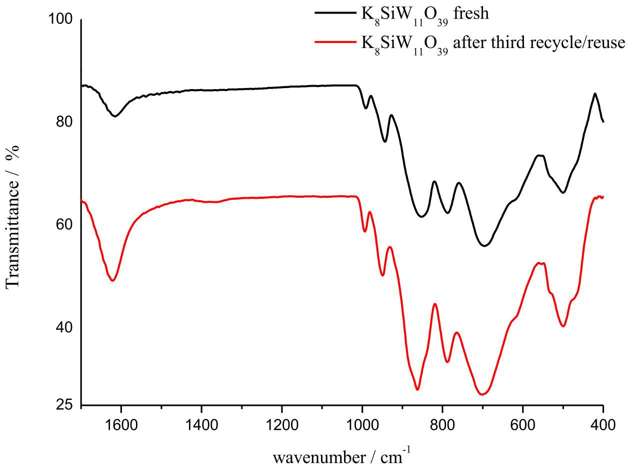


Fig. 10 FT-IR spectra of fresh and reused $K_8SiW_{11}O_{39}$ catalyst

reactions of water present in the oxidant. In addition, a mixture of epoxides was also detected (Fig. 12b).

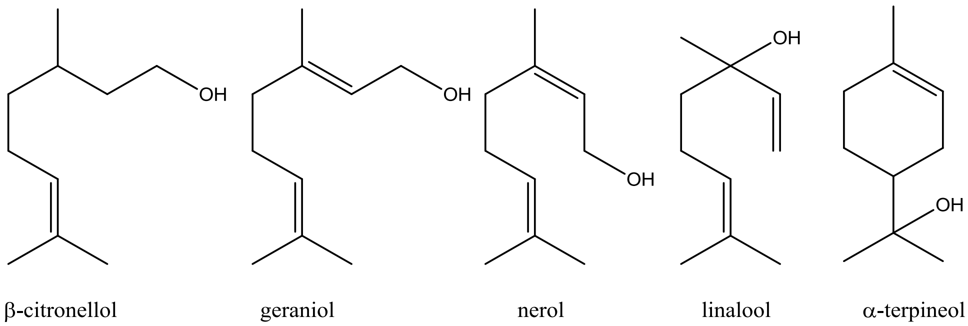
The allylic alcohols are more reactive than those inactivated, consequently, the selectivity for carbonylic products of β-citronellol (i.e. β-citronellal) was lower than those of geraniol and nerol (i.e., geranial and neral, respectively) (Fig. 12a).

This effect also affected the conversion; while geraniol and nerol (i.e. geometric isomers) achieved almost complete conversion within three reaction hours, the conversion of β-citronellol was only 72% (Fig. 12a).

Linalool and α-terpineol were converted to a complex mixture of minority products, formed through nucleophilic addition reactions of water to the double bonds, for these reasons we excluded of Fig. 12.

Conversely, geraniol and nerol were selectively converted to two products; epoxides and aldehydes (Fig. 12b). Equally to the β-citronellol, they have a tri-substituted double bond less reactive, probably due to a hindrance steric. This trisubstituted double bond, whereas to two trisubstituted double

Fig. 11 Structural formulae of the terpenic alcohols



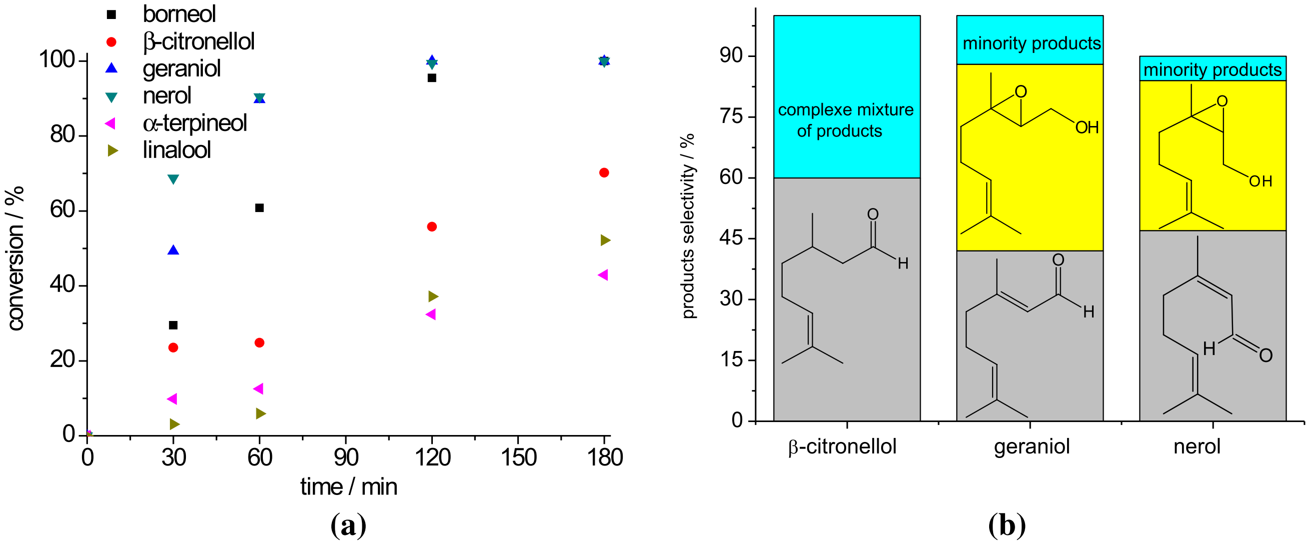


Fig. 12 Kinetic curves (**a**) and reaction selectivity (**b**) of $K_8SiW_{11}O_{39}$-catalyzed oxidation reactions of terpenic alcohols with H_2O_2. Reaction conditions: terpenic alcohol (2.0 mmol); H_2O_2 (6.0 mmol); $K_8SiW_{11}O_{39}$ catalyst (1.25 mol%); temperature (363 K); DMA (10 mL)

Table 2 Effect of heteropolyanion in the catalytic activity of lacunar potassium salts in the borneol oxidation reactions with hydrogen peroxide

Run	Catalyst	Conversion (%)	Camphor selectivity (%)
1	$K_8SiW_{11}O_{39}$	98	98
2	$K_7PW_{11}O_{39}$	95	93
3	$K_7PMo_{11}O_{39}$	34	93

Reaction conditions: borneol to H_2O_2 (1:3); lacunar salt catalyst (5 mol%); temperature (333 K); DMA (10 mL)

bonds of geraniol and nerol that were epoxidized, has two methyl groups and remained intact after the oxidation reactions.

3.7 Effect of Catalyst Nature: Assessments on the Impact of Heteropolyanion and Countercation on Activity of Catalyst in Borneol Oxidation Reaction with Hydrogen Peroxide

Due to high efficiency of the lacunar silicotungstic potassium salt, we have decided to investigate the effect of others heteropolyanions. We synthesized the potassium salts of phosphotungstic and phosphomolybdic acids and assessed their catalytic activity in borneol oxidation with hydrogen peroxide. The main results are displayed in Table 2.

The literature has described the success of lacunar Keggin heteropolyacid salts (i.e., containing tungsten and molybdenum as addenda atoms) in oxidations with hydrogen peroxide [44]. However, the type of substrate and the reaction conditions (i.e., homogeneous or biphasic, pH, additives) sometimes difficult to understand why the tungsten or molybdenum salt was the most active catalyst [45]. Herein, in addition to this effect, the heteroatom present in the Keggin anion seems to have also played a vital role for the efficiency of catalyst.

The tungsten HPAs were more active than molybdenum (Table 2). This result agrees with the literature, which described that the W-based polyoxometalate catalysts are more active than the Mo catalysts [46]. Nonetheless, this point is still controversial; the literature has described works where the activity of molybdenum or tungsten heteropolyacids has been assessed even for heteropolyacids simultaneously containing the two metals [47]. Therefore, there are examples where molybdenum catalysts are also effective [48].

In according with the Scheme 2, the addenda atom of the catalyst (i.e., Mo or W) should be peroxidized and then promote the transferring of oxygen of peroxide to the substrate [45]. Therefore, the nucleophilic attack of hydrogen peroxide on Mo or W(VI) atoms of the heteropolyanions give the active species. Certainly, a higher electronic density on these addenda atoms should to improve this step.

The activity of silicotungstic acid salts generated by the total exchange of the protons by different cations was assessed and the kinetic curves are displayed in Fig. 13.

Among the catalysts assessed, only those salts containing TBA (i.e., tert-butyl ammonium) and Na^+ cations were almost soluble. The cesium and ammonium salts were insoluble. Therefore, it is reasonable suppose that the solubility was a positive characteristic that favored the activity of heteropoly salt catalysts. The literature describes that a higher acid strength is also important in these reactions. Indeed, the TBA was also a highly active catalyst [49, 50].

4 Conclusion

One of the most significant reactions in organic chemistry is oxidation reaction of alcohols, which provide a variety of products such as carbonyl compounds and epoxides. Especially, when the substrate are renewable raw material and the oxidant is environmentally benign, these reactions assume greater importance. In this work, we investigate the oxidation of terpenic alcohols with hydrogen peroxide over lacunar catalyst (i.e., $K_8SiW_{11}O_{39}$). This catalyst was efficiently synthesized in one pot reaction using the adequate precursors (Na_2WO_4, Na_2SiO_3 and KCl salts) at pH 5.5. The catalyst was characterized by FT-IR, BET, XRD and potentiometric titration. In oxidation reactions of borneol, the catalyst achieved high TON (ca. 2720) and high camphor selectivity (ca. 90%). Based on experimental data, a reaction pathway was proposed, involving a tungstoperoxide intermediate. Geraniol and nerol were almost completely

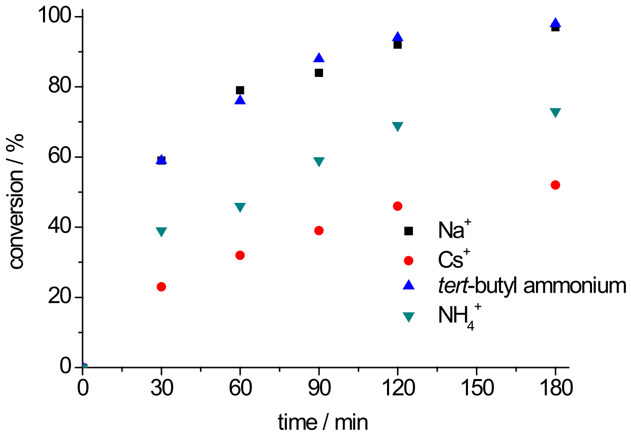


Fig. 13 Effect of countercation in kinetic curves of lacunar undecasilicotungstate salt-catalyzed oxidation reactions of borneol with H_2O_2. Reaction conditions: borneol to H_2O_2 (1:3); lacunar salt catalyst (5 mol%); temperature (333 K); DMA (10 mL)

converted and selectively gave epoxides and aldehydes at equimolar proportions. A selectivity of ca. 60% β-citronellal was obtained. The trisubstituted bond double present in the geraniol, nerol and β-citronellol that contain two methyl groups remained intact. In addition to be highly active and selective, this solid catalyst was efficient recovered and reused without loss activity. The effects of the heteropolyanion and of the cation present in the lacunar salt were studied. Tungsten lacunar potassium salts were more active than one molybdenum. Soluble lacunar silicotungstic acid salts (i.e., Na^+ and TBA cations) were more active than insoluble salts (i.e., Cs and NH_4^+).

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