Transition Metal-Substituted Potassium Silicotungstate Salts as Catalysts for Oxidation of Terpene Alcohols with Hydrogen Peroxide

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Abstract

In this work, the catalytic activity of the transition metal-substituted potassium silicotungstate salts (i.e. $K_{8-n}SiM^{n+}W_{11}O_{39}$ ($M^{n+}=Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}$ and Fe³⁺) was investigated on the oxidation reactions of the terpene alcohols with H_2O_2 aqueous solution. The metal-substituted silicotungstate salts were easily synthesized in one-pot reactions of the precursor metal solutions (i.e. Na_2WO_4 , Na_2SiO_3 and MCl_n) with KCl added in stoichiometric amount; after this precipitation step, the solid heteropoly salts were filtered and dried in an oven. This procedure of synthesis avoids multi-step processes that starts from the pristine heteropolyacid. The substituted metal heteropoly salts were characterized by infrared spectroscopy, measurements of the specific surface area (BET) and porosimetry by isotherms of adsorption/desorption of N_2 , X-rays diffraction, thermal analyses, dispersive X-rays spectroscopy, scanning electronic microscopy. The acidity strength was estimated by potentiometric titration with *n*-butylamine. All the salts were evaluated as catalysts in terpenic alcohols oxidation reactions with H_2O_2 . The $K_5SiFeW_{11}O_{39}$ was the most active and selective catalyst toward oxidation products. The impacts of the main reaction variables such as catalyst concentration, temperature, oxidant load, and nature of the terpene substrate were assessed. The highest activity of the $K_5SiFeW_{11}O_{39}$ catalyst was assigned to the highest Lewis acidity.

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Graphic Abstract



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1 Introduction

Monoterpenes are renewable and abundant raw material whose oxygenate derivatives are attractive feedstock for a wide gamma of synthetical applications, which are of interest for flavoring, food, pharmaceutical, and agrochemical industries [1, 2]. The oxidation products obtained from terpenic alcohols have still organoleptic properties that are highly valuable for the fragrance and perfume industries [3, 4]. Among the various oxidation reactions, those involving primary and secondary terpene alcohols remains a relevant synthetic methodology to afford either epoxides, aldehydes, or ketones [5–8].

The pharmaceutical industry faces challenges in relation to the development of oxidative processes due to environmental and sustainability reasons, such as the disposal of hazardous by-products and safety concerns associated with the use of flammable organic solvent [9, 10]. Green oxidant such as hydrogen peroxide is very desirable in such oxidation processes, because it is a nonflammable liquid, easily handling, commercially affordable, inexpensive, atom-efficient, and give water as the only by-product [11, 12]. This way, the oxidation processes may be according to principles of sustainable green chemistry. Nonetheless, oxidation with hydrogen peroxide requires the presence of a catalyst to be efficient [13]. Various metal compounds have been used as catalysts in oxidations with hydrogen peroxide; oxides, complexes, and salts are only some examples [14–16].

Heterogeneous catalysts have as a great advantage to be easily separated from the reaction mixture by filtration or centrifugation steps, and then can be reused in consecutive reactions. For this reason, several supported-solid metal catalysts have been used in oxidation processes [17]. However, the reusability of the solid catalysts depends on the stability of their acidic sites, which have not to be deactivated and leached during the reactions.

Keggin heteropolyacids (HPAs) are solid clusters of metal–oxygen with highly desirable properties that make them potential catalysts applicable in a plethora of chemical transformations [18, 19]. These polyoxometalates are compounds that are at the forefront of fundamental and applied catalysis [20]. The *type*-Keggin HPAs have a strong Brønsted acidity that makes them efficient catalysts in various acid-catalyzed reactions [21, 22].

Keggin HPAs have also interesting catalytic properties, such as the ability to promote oxidation reactions in the presence of hydrogen peroxide through the formation of active catalytically species [23–25]. Conversely, the solid HPAs have a low specific surface area, a disadvantage that may be overcome by supporting the HPAs on the porous solids that should have a high surface area. Notwithstanding, this strategy has a serious drawback; the reactions performed in polar solvents or that produce water as a by-product can compromise the activity and stability of solid-supported HPA catalysts.

A great advantage of HPA catalysts is that their chemical and physical properties can be improved through different structural modifications, an approach that will be explored in this work [26]. For instance, they can be converted to salts after the protons exchange by cations with charge, size, shape, and high hydrophobicity, a modification that reduces the solubility of these compounds in polar solvents [27–29]. In this regard, cesium heteropoly salt catalysts have been widely explored in the literature [30, 31]. Potassium heteropoly salts are also viable catalysts because their precursor is cheaper than cesium [32–34].

Another modification easily performed in Keggin HPAs is the removal of one MO unit, which creates a vacancy on the anion structure, and facilitate the coordination of an oxidant such as hydrogen peroxide, promoting then the oxygen atom transfer to organic substrates [35, 36]. These lacunar heteropoly salts have demonstrated to be efficient catalysts in oxidation reactions of olefin and alcohols [36–38]. For instance, lacunar sodium phosphotungstate salts were highly active catalysts in oxidation reactions of the terpenic alcohols [39]. Likewise, the lacunar silicotungstate salts of potassium and cesium were catalysts successfully used in the same oxidation reactions [40, 41].

Lacunar Keggin HPA salts are a class of molecular metal oxides with adjustable structural properties at the atomic level [42]. Their catalytic activity can be significantly enhanced by filling their vacancies with transition metal cations, a modification that improves their reversible multi-electron redox properties [43]. In general, these substituted metal heteropoly salts have been synthesized through a multi-step route, where firstly a vacancy is created in the anion of the pristine HPA by an adjust of pH, and afterward, the lacunar salt solution is reacted with a solution containing the transition metal cation, a strategy that has gained attention in the field of catalysis [44–46]. These catalysts have been widely used in oxidation reactions of various substrates, including olefins, methacrolein, and aromatic compounds [47–52].

Herein, we describe that transition metal-substituted potassium silicotungstate salts (i.e. $K_{8-n}SiM^{n+}W_{11}O_{39}$ ($M^{n+}=Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}$, and Fe³⁺) were successfully synthesized through a one-pot synthesis route, being then spectroscopically characterized, and evaluated as catalysts in terpenic alcohol oxidation reactions with hydrogen per-oxide. A positive aspect of this work is to avoid the use of solid-supported HPA catalysts, which commonly are

obtained from a laborious synthesis work up and are more susceptible to leaching problems and deactivation. Herein, alternatively, the solid catalysts were easily synthesized through stoichiometric precipitation reactions. The influences of the main reaction variables were investigated. The activity of the most active catalyst (i.e. $K_5SiFeW_{11}O_{39}$) was compared to their synthesis precursor. The highest activity of the $K_5SiFeW_{11}O_{39}$ catalyst was discussed in terms of the structural properties.

2 Materials and Methods

2.1 Chemicals

All the chemicals and solvents were purchased from commercial sources and utilized without prior handling as received. For the synthesis of $K_{8-n}SiM^{n+}W_{11}O_{39}$ ($M^{n+} = Cu^{2+}$, Co^{2+} , Ni^{2+} , Zn^{2+} and Fe^{3+}), the precursors were CoCl₂ (Vetec, 98 wt. %), CuCl₂ (Vetec, 97 wt. %), FeCl₃ (Vetec, 97 wt. %), NiCl₂ (Vetec, 99 wt. %), ZnCl₂ (Vetec, 99 wt. %) and DMA grade Sigma-Aldrich.

2.2 Catalysts Synthesis

All the catalysts were synthesized adapting a procedure described in the literature [41, 53]. Stoichiometric amounts of Na_2SiO_3 and Na_2WO_4 were separately dissolved in water (ca. 100 mL), and gently mixed. The addition of HCl acidified the medium, giving the soluble $H_4SiW_{12}O_{40}$ acid. The dropwise addition of NaHCO₃ solution until pH 5.5 converted the $H_4SiW_{12}O_{40}$ to soluble lacunar salt (i.e. $Na_8SiW_{11}O_{39}$), being constantly stirring by 1 h. After the slow addition of the metal chloride solution, the mixture was stirred by 3 h at 333 K; the substituted metal potassium silicotungstate salt was precipitated with an addition of solid KCl. Afterward, the precipitate was filtered through a sintered glass filter. After recrystallization in hot holder, the salt was once more precipitated, filtered, and washed two times (ca. 50 mL portions) with KCl aqueous solution, and air dried. The K_{8-n}SiMⁿ⁺W₁₁O₃₉ catalyst was heated at 473 K for 3 h in an oven before the use to remove the remaining HCl.

All the catalytic runs were carried out in a 50 mL threenecked glass flask, equipped with sampling system, a reflux condenser, in a thermostatic bath with magnetic stirrer. Typically, terpene alcohol and the catalyst were stirred and heated (*ca.* 333 K) by 5 min; then, an addition of H_2O_2 started the reaction. Blank reactions were similarly performed.

2.3 Reaction Monitoring and Products Identification

The progress reaction was followed taking aliquots at regular intervals and analyzing them via gas chromatography (GC Varian 450, FID, fitted with Carbowax capillary column (0.25 μ m×0.25 mm×30 m)). The temperature program was as follows: 80 °C/ 1 min, 10 °C/min up to 220 °C, hold time of 5 min. Temperatures of the injector and detector were 250 and 280 °C, respectively. The conversion of substrates was calculated by matching the area of substrate GC peak into the corresponding calibration curves.

The man reaction products were identified by analyses carried out on a Shimadzu GC-2010 gas chromatograph coupled with a MS-QP 2010 mass spectrometer (Tokyo, Japan) with a DB5 capillary column (0.25 μ m × 0.25 mm × 30 m)

Table 1 Transition metal substituted heteropoly salts

| Catalyst | Color | |
|--|--------------|----|
| K ₆ SiCoW ₁₁ O ₃₉ | dark red | 87 |
| K ₆ SiCuW ₁₁ O ₃₉ | bluish green | 88 |
| K ₅ SiFeW ₁₁ O ₃₉ | Brown | 88 |
| K ₆ SiNiW ₁₁ O ₃₉ | light green | 91 |
| K ₆ SiZnW ₁₁ O ₃₉ | White | 96 |

^aExperimental yield considering the stoichiometric amount obtained



Fig. 1 FTIR /ATR spectra of lacunar and metal substituted silicotung-state salts

and He as the carrier gas at 2 mL/min. The GC injector and MS ion source temperatures were 250 and 260 °C, respectively. The MS detector operated in the EI mode at 70 eV, with a scanning range of m/z 50–400.

2.4 Catalysts Characterization

The elemental composition was determined during scanning electron microscopy (SEM) analyses, using a JEOL JSM-6010/LA microscope fitted with energy dispersive spectrometry equipment (EDS). All images and EDS spectra were recorded using 20KV acceleration potential and 10 mm working distance.

The hydration water content and thermal stability of heteropoly salts was estimated by thermogravimetric analysis on a TGA/DSC-6000 Perkin-Elmer thermobalance up to 973 K. FTIR/ ATR spectra of the HPAs and their potassium salts were obtained by using the KBr pellet and recorded on an FTIR Varian 660 spectrometer with reflectance accessory.

The powder X-rays diffraction patterns of the solid catalysts were obtained by using an X-ray Diffraction System model D8-Discover Bruker. The conditions were Ni filtered Cu-k α radiation (λ = 1.5418 Å), operating at 40 kV and 40 mA. Analyses were done in 0.05° steps, 1.0 s counting time, scanning 20 angle 5 to 80°.

The acidity strength of heteropoly catalysts was measured by potentiometric titration in a potentiometer Bel, model W3B, as reported by Pizzio et al. [32]. Typically, 50 mg of sample were suspended in CH₃CN solutions, which were stirred 3 h and titrated with *n*-butylamine solution in toluene (*ca.* 0.025 molL⁻¹).

Porosity analyses of heteropoly salts were performed in NOVA 1200e High Speed, Automated Surface Area equipment and Pore Size Analyzer Quantachrome Instrument. Before the analysis, the samples were previously degassed by 1 h. The specific surface area was estimated by Brunauer–Emmett–Teller equation applied to the nitrogen desorption/ adsorption isotherms.

3 Results and Discussion

3.1 Catalysts Characterization

In general, heteropoly salts have been synthesized in multisteps routes using pristine heteropolyacid as the starting material [35, 54]. Herein, in a one-pot procedure, we efficiently synthesized the metal substituted heteropoly salts, starting from the precursor metal solutions and precipitating them with solid KCl. Table 1 shows the yields achieved.

The information obtained via EDS analysis confirmed the elemental composition of all the synthesized catalysts. Table 3SM shows a comparison of theoretical and experimental tungsten contents. We found only a slight difference between theoretical and experimental values, regardless of the transition metal doped on the heteropolyanion of the potassium silicotungstate salt. Infrared spectroscopy is an essential tool to verify the integrity of Keggin anion, which is the primary structure of heteropoly salts. The typical absorption bands are placed at the wavenumbers of 550 to 1700 cm^{-1} , the fingerprint region of these compounds. Table 1SM summarizes the main absorption bands present in the infrared spectra of the lacunar salt before and after the doping of the transition metal (Fig. 1).

The FTIR spectrum of $K_8SiW_{11}O_{39}$ showed bands at 943, 991, 852, and 787 cm⁻¹, corresponding to the symmetric stretching of Si–O, W–O¹, W–O²–W, and W–O³–W bonds, respectively. The superscript "1" in an oxygen atom indicates that it is in a terminal position, as well as the superscripts "2" and "3" refer to the oxygen atoms sharing edge or corner, respectively [55].

The main change observed in the infrared spectra of lacunar salts after the doping of transition metal was a shift toward the higher wavenumber of absorption band assigned to the W–O³–W bond (i.e. 852 cm^{-1} in the precursor, $870-890 \text{ cm}^{-1}$ in the metal substituted salts; Table 1SM). This effect was attributed to the complexation of transition metal to the oxygen atom of heteropolyanion and was previously reported [37]. This displacement was less pronounced in the infrared spectrum of $K_6SiZnW_{11}O_{39}$; Zn^{2+} ions have all their "d" orbitals filled and probably are less effective to coordinate with oxygen atoms. It was possible also to observe another band at lower wavenumber (ca. 440 cm^{-1}), which was assigned to the transition metal-oxygen bond [54–56]. Therefore, FTIR spectra clearly show that no drastic change happened when a transition metal was included in the framework of Keggin anion [57-59].



Fig. 2 XRD patterns of lacunar silicotungstate salts before and after the doping of transition metal

The powder XRD patterns of silicotungstate salts provide information about the secondary structure of Keggin salts and are shown in Fig. 2. The diffractograms of lacunar salt and metal-doped salts presented the typical diffraction lines of Keggin anion at $2\theta < 10^{\circ}$, $2\theta \approx 15^{\circ}$, and $2\theta \approx 28^{\circ}$ [56]. The silicotungstate salts that were dopped with iron or zinc had a slight loss of crystallinity; conversely, nickel, cobalt, and copper salts presented diffraction peaks in a higher amount and with greater intensity if compared to unsubstituted lacunar salt (Fig. 2). The doping of transition metal on the Keggin anion resulted in new diffraction lines, mainly at values of 2θ greater than 25° . The same effect was described in previous works [51, 57–60]. A comparison with literature revealed that the characteristic peaks of metal oxides were absent in the diffractograms shown in Fig. 2 [61–65].

The TG/DTG analyses allowed to determine the hydration level of silicotungstate salts and investigate their thermal stability (Fig. 1SM). In addition, mass losses of all samples on TG curves gave an order of magnitude difference on the DTG profiles, as indicated by the DTG scale. The losses of crystallization water molecules of salts generated strong peaks noticed in the DTG curves between 328 and 410 K. Only for the salts $K_5SiFeW_{11}O_{39}$ and $K_6SiNiW_{11}O_{39}$ were noticed two well-defined peaks within this interval temperature; for the other salts, a broad peak was observed at this temperature range. Table 2SM shows that the hydration level varied from 7 to 10 mol H₂O/ mol catalyst. The salt samples were stable up to 673 K; at higher temperatures, they were decomposed to metal oxides due to the decomposition of the Keggin anion.

The N₂ adsorption–desorption isotherms and the pores size distribution of potassium silicotungstate salts are displayed in Figs. 2SM and 3SM. The profile of distribution curves of the pore's diameter of the potassium silicotungstate salts varied from 1.1-1.2 nm, a typical characteristic of microporous solids (Fig. 3SM). The size of pores diameter was 1.0-1.2 nm. According to the IUPAC recommendations, the BET isotherms of the salts were classified as type I, which are characteristic of microporous materials. No hysteresis loop was noticed on the isotherms of potassium salts.

 Table 2
 Surface area, volume, and pores size of potassium silicotungstate salts

| Catalyst | Surface area (m^2g^{-1}) | Pores volume (cm ³ g ⁻¹ × 10 ⁻²) | Pores size (nm) |
|--|----------------------------|---|-----------------------|
| K ₈ SiW ₁₁ O ₃₉ | 10.9 | 1.4 | 1.1 |
| K ₆ SiCoW ₁₁ O ₃₉ | 9.6 | 1.0 | 1.1 |
| K ₆ SiCuW ₁₁ O ₃₉ | 11.0 | 1.3 | 1.2 |
| K ₅ SiFeW ₁₁ O ₃₉ | 10.6 | 1.1 | 1.2 |
| K ₆ SiNiW ₁₁ O ₃₉ | 10.7 | 1.0 | 1.2 |
| K ₆ SiZnW ₁₁ O ₃₉ | 12.8 | 1.3 | 1.1 |



Fig. 3 Potentiometric titration curves of lacunar potassium silicotungstate salt and metal-doped potassium silicotungstate salts

The corresponding average values of the size and volume of pores, besides the surface area shown in Table 2.

The potentiometric curves of the metal substituted potassium silicotungstate salts are shown in Fig. 3. The initial electrode potential (Ei) indicates the maximum strength of the acidic sites present on the salt surface. The titration curves of the metal-substituted potassium silicotungstate salts had a similar profile and revealed that they presented strong acidic sites (0 < Ei < 100 mV). However, among the synthesized salts, iron-doped potassium silicotungstate (i.e., K₅SiFeW₁₁O₃₉) was the only that had very strong acidic sites (Ei > 100 mV) [32].



Scheme 1 Transition metal-doped potassium silicotungstate salt-catalyzed borneol oxidation reactions with hydrogen peroxide

The strength of acidity determined by potentiometric titration is a consequence of Lewis and Brønsted acid sites. Although the protons of silicotungstic acid have been exchanged by potassium cations, once that the transition metal cations are also Lewis acids, remains still a certain acidity. Moreover, it is possible these metal cations react with hydration water molecules giving then H_3O^+ ions. For this reason, the transition metal-substituted salts were stronger acids than precursor lacunar potassium salt. Remarkably, the iron-doped silicotungstate salt presented the strongest acid sites.

3.2 Influences of Reaction Parameters on the Terpenic Alcohol Oxidation by H₂O₂

3.2.1 Effect of Catalyst

Initial screening to select the most active catalyst was performed, and the main results are displayed in Fig. 4. In



Fig. 4 Effect of the silicotungstate catalyst on the kinetic curves, conversion (**a**), and selectivity (**b**) of borneol oxidation with hydrogen peroxide. Reaction conditions: borneol (1.34 mmol), catalyst (5 mol %), H_2O_2 (2.68 mmol), temperature (363 K), DMA (10.0 mL)

general, secondary alcohol oxidation reactions are harder than primary ones, for this reason, borneol selected as the model substrate. Camphor was the main product selectively formed in all the reactions (Scheme 1).

Previously, we have verified that the lacunar potassium salt was an efficient catalyst in oxidation reactions of terpenic alcohols with H_2O_2 [40]. Inspired by this founding, we decided to try improving the activity of this catalyst, including a transition metal cation into their Keggin heteropolyanion. After doing it, we realize that three catalysts achieved a total conversion of borneol: the lacunar salt (i.e. $K_8SiW_{11}O_{39}$), and the metal-substituted salts (i.e., $K_6SiNiW_{11}O_{39}$ and $K_5SiFeW_{11}O_{39}$) (Fig. 4).

The $K_6SiCuW_{11}O_{39}$ -catalyzed reaction reached the lowest conversion, while the reactions in the presence of $K_6SiCoW_{11}O_{39}$ or $K_6SiZnW_{11}O_{39}$ accomplished conversions of 73 and 92%, respectively. Nonetheless, among three catalysts that reached a complete conversion, only the iron-substituted salt (i.e., $K_5SiFeW_{11}O_{39}$) made it within the first-hour reaction.

In an early work, another nickel salt (i.e. $K_5PNiW_{11}O_{39}$) was the most active catalyst among several metal-substituted potassium HPA salts, however, in that case, benzaldehyde was the substrate oxidized by H_2O_2 in CH_3CN solutions [51]. Conversely, in benzyl alcohol oxidation reactions with H_2O_2 in toluene, the $K_6SiCoW_{11}O_{39}$ salt was the most efficient catalyst [52]. These different results are evidence that the activity of the catalyst depends on the various aspects; the sort of heteroatom present in the Keggin heteropolyanion (i.e. $SiW_{11}O_{39}^{8-}$ or $PW_{11}O_{39}^{7-}$), the kind of substrate (i.e., alcohol, aldehyde), the solvent (i.e. toluene, CH_3CN), and finally, the type of transition metal cation introduced in the heteropolyanion.

Choi et al. investigating the oxidation of 2-propyl alcohol and demonstrated that the measurements of reduction potential and absorption edge energy of HPA catalysts could be utilized as a correlating parameter to track the oxidation catalysis of these salts [55]. In that work, those authors verified that the acetone yield increased with an increase of reduction potential and with a decrease of absorption edge energy. The activity obeyed the order: $K_5PMnW_{11}O_{39}$ > $K_5PCoW_{11}O_{39} > K_5PNiW_{11}O_{39} > K_5PZnW_{11}O_{39}$, a distinct sequence than the one verified herein. Although the catalysts used in that work have been like those evaluated herein, there are significant differences in relation to the present work; firstly, in that case, molecular oxygen was the oxidant used. Moreover, those reactions were carried out without solvent, only in 2-propyl alcohol, and at a higher temperature (ca. 353 K).

When hydrogen peroxide is the oxidant in metal-catalyzed reactions, there are two mechanisms that are commonly accepted to explain the alcohol oxidations: peroxometal pathway and oxometal pathway [66, 67]. The first one involves oxo-intermediates (i.e. M=O), which are very common when the metal cation has a d⁰ electronic configuration; probably, it may be occurring when the catalyst is the K₈SiW₁₁O₃₉ lacunar salt, which contains a d⁰ cation (i.e. W⁺⁶) [68]. In this case, the oxidation state of metal varied in 2 units along the catalytic cycle (i.e. W⁴⁺/W⁶⁺).

According to the second mechanism, the metal cation is peroxidized giving a peroxide metal intermediate (i.e. MOOH). Metal cations of the first transition series may react through this pathway. No change in the oxidation state of the metal occurs during the catalytic cycle. We think that transition metal-substituted HPA salts-catalyzed reactions may proceed via this second way. It may explain the higher activity of substituted metal heteropoly salt if compared to the lacunar precursor salt (Fig. 4a and b).

Therefore, we suppose that the highest activity of irondoped potassium silicotungstate salt can be assigned to the higher oxophilic character of Fe³⁺ cation if compared to the other transition metal. This greater affinity by the oxygen atom present in the hydrogen peroxide facilitates the formation of an iron silicotungstate-peroxide intermediate. It is a consequence of high Lewis acidity of Fe³⁺ cations, higher than the acidity of the M²⁺ cations (see Fig. 3). On the other hand, that HASB theory may be also to explain the results. The Fe³⁺ is a hard acid while the all the other metal cations are soft acids if compared to the iron. Therefore, the higher oxophillic character is justified because the oxygen is also hard base and the interaction between oxidant-catalyst will be more favorable when the salt is the iron-doped potassium silicotungstate.



Fig. 5 Comparison of conversion of borneol and selectivity to camphor in borneol oxidation with hydrogen peroxide. Reaction conditions: borneol (1.34 mmol), catalyst (0.25 mol %), H_2O_2 (2.68 mmol), temperature (363 K), DMA (10.0 mL). 2 h reaction



Fig. 6 Effect of K_5 FeSi $W_{11}O_{39}$ catalyst load on the borneol oxidation with H_2O_2 . Reaction conditions: borneol (1.34 mmol), catalyst load (variable), H_2O_2 (2.68 mmol), temperature (363 K), DMA (10.0 mL)



Fig. 7 TON of K5SiFeW11O39-catalyzed borneol oxidation reactions with H2O2

The superior performance of iron-doped potassium silicotungstate salt in borneol oxidations is shown in Fig. 5. Although the reaction in the presence of sodium tungstate catalyst has achieved high conversion and selectivity, it is important to highlight that was totally soluble and used at a load ten times higher [69].

3.2.2 Effect of Catalyst Load

Once the $K_5SiFeW_{11}O_{39}$ was the most active catalyst it was selected to assess the effects of other reaction variables. The kinetic curves are displayed in Fig. 6. Due to the various levels assessed, a split in two figures was done. Initially, we can observe that the reaction rate is affected by the catalyst

load. A greater load of catalyst allows that the maximum conversion could be achieved in a shorter time interval. It suggests that the formation of probable reaction intermediates (i.e., peroxidized heteropolyanion), as described in the literature, is enhanced when the proportion catalyst: peroxide is increased [40] (Fig. 6a). On the other hand, when a lower catalyst load is used, the reaction becomes slower, and higher reaction time is required to achieve the maximum conversion (Fig. 6b).

In Fig. 6a, only the reactions carried out with load equal or lower than 0.63 mol % did not present a high initial rate, however, within 3 h of runs they achieved a complete conversion. In Fig. 6b, clearly, this effect can be noticed. Although not showed, in all the runs the camphor selectivity was higher than 90%. Figure 7 shows the TON (i.e. turnover number) obtained in all the reactions.

The molar ratio between mol of converted borneol/mol of $K_5SiFeW_{11}O_{39}$ catalyst provides the TON achieved by the catalyst in each reaction. The elevate TON reached is evidence of the high activity of this catalyst. The highest TON achieved herein (ca. 4050) was higher than that obtained in $K_8SiW_{11}O_{39}$ -catalyzed borneol oxidation reactions (ca. 2720) [40]. It means that the inclusion of Fe³⁺ cation into the Keggin anion structure significantly improved their catalytic activity.

3.2.3 The Impacts of Solvent

The effect of the solvent was addressed in the $K_5SiFeW_{11}O_{39}$ -catalyzed reactions (Fig. 8). The catalyst was not totally soluble, however, in stronger donor solvents such as N,N-dimethyl acetamide (DMA) and N,N-dimethylformamide (DMF), the oxidation of borneol achieved high conversions. The reactions in protic solvent (i.e. CH₃OH)



Fig. 8 Effect of solvent on the conversion of K_5 SiFe $W_{11}O_{39}$ -catalyzed oxidation of borneol with H_2O_2 (**a**) and selectivity to campbor (**b**). Reaction conditions: borneol (1.34 mmol), K_5 SiFe $W_{11}O_{39}$ (5 mol %), H_2O_2 (2.68 mmol), temperature (363 K), solvent (10.0 mL)



Fig. 9 Effect of temperature on the reaction rate of borneol oxidation with H_2O_2 (**a**) and impacts of temperature on conversion (**b**). Reaction conditions: borneol (1.34 mmol), $K_5SiFeW_{11}O_{39}$ (0.31 mol %), H_2O_2 (2.68 mmol), DMA (10.0 mL)

or CH_3CN were not efficient. Hida and Nogusa assigned to the beneficial effects of DMF and DMA solvents to their ability to stabilize metal-peroxide intermediates in alcohol oxidations [69].

Conversely, while the reaction conversions were sensible to the solvent, the selectivity was less affected. Camphor was always the main product, although its formation has been lowered in methyl alcohol if compared to other solvents. Although the pH of the solvent is also an important aspect of this sort of reaction, the insolubility of borneol in aqueous solution prevented that it could be investigated herein.

3.2.4 Effects of Temperature on the Reaction Rate of Borneol Oxidation

An increase in temperature reaction may improve either the initial rate of reactions as well as the selectivity. To assess this effect, we carried out catalytic runs with temperatures varying from 303 to 363 K (Fig. 9).

Regardless of the reaction temperature, the camphor selectivity was always greater than 85%. No significant changes in the distribution of products was observed. However, the conversions were strongly impacted: at temperatures below 353 K, the maximum conversion observed on the reactions were less than 40%. Nonetheless, if compared to the precursor $K_8SiW_{11}O_{39}$, the $K_5SiFeW_{11}O_{39}$ catalyst



Fig. 10 The influence of the amount of oxidant agent (H_2O_2) on the conversion of borneol and selectivity to camphor on $K_5SiFeW_{11}O_{39}$. Reaction conditions: borneol (1.34 mmol), $K_5SiFeW_{11}O_{39}$ (0.025 mol %), time (180 min), DMA (10.0 mL)

was much more active. In this work, the temperature effect was studied using 0.31 mol % of catalyst, whereas to the described for the $K_8SiW_{11}O_{39}$, where a load of 1.25 mol % was necessary [40].

3.2.5 Effect of Reactant Stoichiometry

As previously demonstrated (Sect. 3.2.2.), the reactions carried out with a low load (ca. 0.05 mol % of $K_5SiFeW_{11}O_{39}$ catalyst and a molar ratio of 1:2 (borneol: H_2O_2) achieved high conversion. For this reason, aiming to do cleaner the effect of oxidant, the catalyst was used at lower load (ca. 0.025 mol %). The main results of conversion and selectivity are displayed in Fig. 10.

An increase of oxidant load gave a consequent increase in the conversion, nonetheless, the camphor selectivity was almost unchanged. It demonstrates that oxidant load has a positive impact on the reaction conversion. Probably, even though a low catalyst load was present, an excess of peroxide promotes the formation of the catalytically active species.

3.2.6 Oxidation of the Unsaturated Terpene Alcohols

To assess the efficiency of $K_5SiFeW_{11}O_{39}$ catalyst, other terpenic alcohols were selected to be oxidized. The reason for this study was evaluating the conversion and selectivity of the substrates with other susceptible sites to oxidation, such as the double bonds, which can be also epoxidized. In these reactions, primary (i.e. β -citronellol), tertiary (i.e. linalool), and primary allylic (i.e. geraniol and nerol) alcohols were used. The main results of the conversion are presented in



Fig. 11 Conversion of terpene alcohols with H_2O_2 as an oxidation agent on $K_5SiFeW_{11}O_{39}$ catalyst. Reaction conditions: terpenic alcohol (1.34 mmol), $K_5SiFeW_{11}O_{39}$ (0.31 mol %), H_2O_2 (2.68 mmol), temperature (363 K), DMA (10.0 mL)

Fig. 11. Besides the carbonylic products, epoxides were also obtained in all the reactions.

In addition to the borneol, nerol, and geraniol were also highly reactive alcohols. These alcohols were completely converted to aldehydes and epoxy-alcohols (Schemes 2 and 3).

The epoxidation of the trisubstituted double bond of geraniol and nerol is a hydroxy group assisted reaction. This effect was previously demonstrated in epoxidation reactions catalyzed by titanium, niobium and tungsten oxides catalysts [70–72].

Linalool and β -citronellol (Fig. 12) were also tested as substrates in oxidation reactions. The poor reactivity of trisubstituted double bond trisubstituted in relation to the epoxidation reaction was confirmed when β -citronellol was oxidized. This primary alcohol gave β -citronellal as the only product; no epoxide was detected.

Previously we verified that epoxidation of double bonds of nerol and geraniol is a hydroxy group assisted reaction. Therefore, even though nerol, geraniol, and β -citronellol had another trisubstituted double bond, it is hardly epoxidized. Conversely, the terminal double bond of linalool was epoxidized, however, only a low conversion (ca. 40%) was achieved on this reaction.

Herein, the oxidation reaction of linalool by H_2O_2 catalyzed by $K_5SiFeW_{11}O_{39}$ achieved only 40% conversion, with the formation of epoxide alcohol. On the other hand, in a previous work, when linalool was reacted with peroxide in the presence of a lacunar sodium phosphotungstate salt (i.e. $Na_7PW_{11}O_{39}$), it was converted to cyclic derivatives (i.e. tetrahydrofuran and pyran) [73]. Notwithstanding, in addition to the different catalyst (i.e. soluble lacunar





Scheme 3 $K_5SiFeW_{11}O_3$ -nerol catalyzed oxidation with H_2O_2



Fig. 12 Linalool and β -citronellol structures

phosphotungstate sodium salt versus insoluble iron substituted potassium silicotungstate salt), the temperature and the solvent used in that work were different; while in that work, reactions were carried out at 298 K temperature and in acetonitrile, herein we have used 393 K and DMA solvent).

The superior performance of iron substituted potassium silicotungstate salt in oxidations of terpene alcohols (i.e., geraniol and nerol) is shown in the supplemental material (Figs. 4SM and 5SM).

4 Conclusion

In this research, transition metal substituted potassium silicotungstate salts (i.e. $K_{8-n}SiM^{n+}W_{11}O_{39}$ ($M^{n+}=Cu^{2+}$, Co^{2+} , Ni^{2+} , Zn^{2+} , and Fe^{3+}) were synthesized, characterized, and used to catalyze the oxidation of terpenic alcohols with hydrogen peroxide. Among the salts assessed, the $K_5SiFeW_{11}O_{39}$ was the most active and selective catalyst toward the oxidation products. The catalytic activity was discussed in terms of higher Lewis acidity of Fe³⁺ cation, a characteristic that distinguished it from the other salts. A high TON (4260) was achieved in K₅SiFeW₁₁O₃₉-catalyzed reactions of borneol oxidation, which was higher than that previously reported for their precursor (i.e. $K_8SiW_{11}O_{39}$; ca. 2720). Nerol and geraniol were also efficiently oxidized, giving their respective aldehydes and epoxides as the main reaction products. Experiments with β -citronellol and linalool showed that the epoxidation reaction of the trisubstituted double bond is a hydroxy group assisted reaction. The easy synthesis procedure, the high efficiency of the catalyst, and the use of an environmentally benign oxidant are positive aspects of this catalytic system.

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