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Monoterpenes etherification reactions with alkyl alcohols over cesium partially exchanged Keggin heteropoly salts: effects of catalyst composition

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Abstract

In this work, cesium partially exchanged Keggin heteropolyacid (HPA) salts were prepared, characterized, and evaluated as solid catalysts in monoterpenes etherification reactions with alkyl alcohols. A comparison of the activity of soluble HPAs and their insoluble cesium salts showed that among three different Keggin anions the phosphotungstate was the most efficient catalyst. Assessments on the effects of the level of the protons exchange by cesium cations demonstrated that $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ solid salt was the most active and selective phosphotungstate catalyst, converting β-pinene to α-terpinyl methyl ether. The influences of the main reaction parameters such as reaction temperature, time, catalyst load, substrate nature (i.e., alcohols and monoterpenes) were investigated. We have demonstrated that the simultaneous presence of the cesium ions and protons in the catalyst plays an essential role, being the 2.5–0.5 the optimum molar ratio. The $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ salt was efficiently recovered and reused without loss of catalytic activity.

Graphic abstract
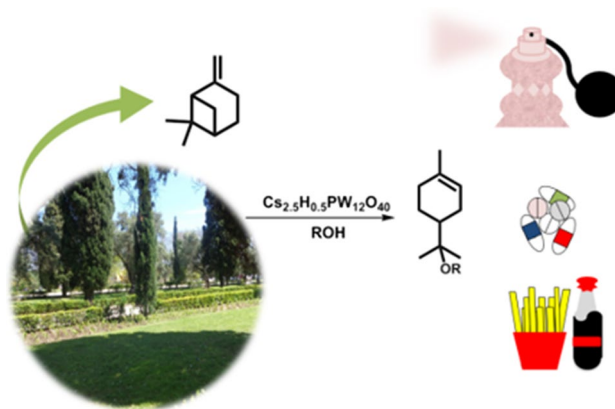
Keywords Cesium partially exchanged heteropoly salts · Monoterpenes · Etherification

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Introduction

Monoterpenes are inexpensive and renewable raw materials used to produce fine chemicals, which are attractive for fragrancies, food, and pharmaceutical industries (Besson et al. 2013). The development of sustainable catalytic processes following the green chemistry principles to add value

to these cheap feedstocks became relevant due to economic and environmental reasons.

The functionalization of limonene, α- and β-pinene produce building blocks for the synthesis of drugs, agrochemicals, and ingredients of perfumes (Silva et al. (2018); Oliveira et al. 2009). Esterification, oxidation, hydroxylation, and epoxidation reactions are some of the processes used to obtain the monoterpene derivatives that are useful for those fine chemical industries (Oliveira et al. 2009; Saladino et al. 2009; Castanheiro et al. 2005). In this regard, monoterpene ethers have singular olfactive properties, and their synthesis becomes still more interesting if carried out over solid acid catalysts (Catrinescu et al. 2013). In particular, the synthesis of α-alkyl terpinyl ethers deserves highlight, because these compounds have a pleasant grapefruit-like aroma and it is used as a flavor additive or fragrances (Silva et al. 2015).

In general, α-alkyl terpinyl ethers have been synthesized in acid-catalyzed etherification reactions of the limonene or mainly α-pinene. However, these processes when carried out in the presence of the homogeneous acid catalysts have serious drawbacks, such as a large generation of effluents, residues of neutralization, problems of reactors corrosion, and moreover, the impossibility to reuse the catalyst (Li and Liang 2017). Thus, solid acids such as zeolites, clays, mesoporous silica, or sulfonic resins have been the catalysts employed on these processes (Catrinescu et al. 2013,2015; Hensen et al. 1997a,b; Castanheiro et al. 2008; Pito et al. 2009). For instance, microporous and mesoporous carbon catalysts achieved 60% selectivity for terpinyl ether and complete conversion of α-pinene, the best result obtained in such processes (Matos et al. 2014).

Heteropoly acids (HPAs) are solid catalysts that have unique architecture and catalytic properties that can be easily adjusted by modifying their shape, charge, and chemical composition (Odyakov et al. 2015; Srilakshmi et al. 2005; Liu et al. 2015). For these reasons, they have emerged as environmentally benign acidic catalysts for several organic transformations (Han et al. 2014; Silva and Liberto 2016).

Keggin-type HPAs are metal–oxygen clusters with a discrete molecular structure, which contain anions with general formulae $[XM_{12}O_{40}]^{n-}$, where commonly the "X" is a heteroatom as P^{5+} or Si^{4+}, and M is an addenda atom as Mo^{6+} or W^{6+} (Kozhevnikov 1998; Kim et al. 2012; Han et al. 2017). While phosphomolybdic acid (i.e., $H_3PMo_{12}O_{40}$) is an efficient catalyst in oxidation reactions, phosphotungstic acid (i.e., $H_3PW_{12}O_{40}$) has the best catalytic performance in various organic reactions owing to their purely strong Brønsted acidity, which is higher than that presented by the mineral acids (Cavani 1998; Silva and Teixeira 2017; Kozhevnikov et al. 1996; Silva et al. 2010; Fernandes et al. 2012; Zheng et al. 2011).

Keggin HPAs are nonporous solid and has a low surface area; to circumvent this disadvantage, they have been supported on different solid materials (Silva and Liberto 2016; Caiado et al. 2013; Mattos et al. 2017). Nonetheless, solid-supported catalysts undergone serious downsides such as the lixiviation triggered by the high polarity of the reaction medium. To win this challenge, HPA catalysts can be easily converted to insoluble salts, which after an adequate adjust of substitution level of protons results in efficient solid acid catalysts (Coronel and Silva 2018). This substitution of the H^+ ions with Cs^+ leads to an increase of the surface area and the formation of pores, which depends on the degree of substitution (Kamiya et al. 2010; Okuhara et al. 2000). Moreover, the mesoporous structure of $Cs_{2.5}PW_{12}O_{40}$ salt is an advantage that allows a quick diffusion of the reagents into porous of the catalyst, an aspect that may explain their high activity on the liquid–solid reactions (Okuhara et al. 2000). Therefore, cesium salts have been the goal of extensive research. Deserves highlight the studies of Misono et al., which have established that phosphotungstic acid salts with a Cs molar ratio of 2.5–2.7 are highly active in many acid-catalyzed reactions (Okuhara et al. 2000; Misono et al. 2000; Mizuno and Misono 1997).

In this work, we report a study, where cesium partially exchanged Keggin HPA salts were evaluated as catalysts in etherification reactions of monoterpenes with alkyl alcohols. β-pinene was the selected monoterpene due to its uncommon reactivity. All the cesium salts of Keggin HPAs (i.e., $H_3PW_{12}O_{40}$, $H_3PMo_{12}O_{40}$, $H_4SiW_{12}O_{40}$) were characterized by FT-IR, DRX, BET, EDS/SEM, and TG/DSC analyses. The amount and the strength of the acidic sites were measured by potentiometric titration with *n*-butylamine. After choosing the more active Keggin HPA salt, our primary goal was to evaluate how the level of protons exchange by the cesium ions affected the catalytic activity and selectivity on the etherification reactions of the β-pinene. Afterward, we tried to understand the key factors of this process; the role of the acidity of the catalyst (i.e., nature and strength of acid sites), the influences of the physic properties of catalyst (i.e., surface area, porosity), as well as the effect of the reaction conditions (i.e., the catalyst load, temperature, and time). The reaction scope was extended to the other alkyl alcohols (i.e., ethyl, propyl, isopropyl, butyl) and monoterpenes (i.e., camphene, limonene, and α-pinene). The leaching and catalyst reusability were investigated.

Materials and methods

Chemicals

All the chemicals have analytical reagent grade and were used without purification, excepted the furfural that was previously distilled. Hydrated heteropolyacids (e.g., $H_3PW_{12}O_{40},$ $H_3PMo_{12}O_{40}$ $H_4SiW_{12}O_{40}$ 99 wt.%) were

acquired from Sigma-Aldrich. Cs_2CO_3 was purchased from Merck (99 wt.%). Alcohols (i.e., methyl, ethyl, propyl, isopropyl and butyl) having purity between 99.5 and 99.8 wt.%, were also purchased from Sigma-Aldrich. Monoterpenes (i.e., α- and β-pinene, limonene) were also acquired from Sigma-Aldrich (99 wt.%).

Preparation of cesium exchanged Keggin heteropolyacid catalysts

Cesium salt catalysts were prepared in accordance with the literature (Park et al. 2010; Dias et al. 2004). Typically, an aqueous solution of Cs_2CO_3 was added dropwise to a solution of the HPA. The stoichiometric ratio of Cs^+ to H^+ was controlled by variation of the volume of the Cs_2CO_3 solution. A minimum addition of $Cs_2CO_{3(aq)}$ triggered the precipitation of a white solid. The slurry was aged overnight at room conditions. Afterward, the solution was evaporated at vacuum at 353 K, and the catalyst was dried 12 h in an oven.

Catalysts characterization

XRD analysis of the powdered catalysts was recorded with a X-rays diffraction system model D8-Discover Bruker using Ni as the source of X-rays, which were filtered Cu-kα radiation ($\lambda = 1.5418$ Å), activated at 40 kV and 40 mA. The measurements were collected with a scanning rate of 0.05°/1 s in the 2θ range of 5°–80°.

Infrared spectra were recorded on a Varian 660-IR model Fourier transformed infrared coupled with the attenuated total reflectance technique (FT-IR/ATR). Thermogravimetric analyses were performed on a Perkin Elmer simultaneous thermal analyzer (STA) 6000. Typically, a sample was weighted (ca. 10 mg) and heated at a rate of 10 K/min under N_2 flow. The temperature range of TG curves was 303–973 K.

The textural properties of Cs HPA salts were measured by the BET (Brunauer–Emmett–Teller) method using N_2 as probe gas at 77 K; the desorption/adsorption isotherms were measured in a NOVA 1200e high speed, automated surface area and pore size analyzer Quantachrome Instrument. The samples were previously degassed under vacuum 4 h at 423 K. The specific surface area was calculated by BET equation applied to the desorption/adsorption isotherms.

The acidity strength of Cs heteropoly salts was measured by potentiometric titration, as described by Pizzio et al. (2003). A potentiometer Bel, model W3B, with glass electrode was used. The titration was done suspending an adequate mass of a Cs salt sample in CH_3CN, which was stirred by 24 h and then titrated with *n*-butylamine solution in toluene (ca. 0.025 mol L^{-1}).

The morphology of the Cs heteropoly salts was characterized by scanning electron microscopy (SEM) images

acquired in a JEOL JSM-6010/LA microscope. This equipment with an energy dispersive spectrometry system (EDS) was used to qualitatively analyze the chemical composition of catalysts. SEM images and EDS spectra were recorded using 10 mm working distance and 20 kV acceleration voltage. The composition elemental analysis for cesium salts was performed by ICP-MS spectrometry (ICP-MS (model Nexion 300D, Perkin Elmer). The solutions were prepared by digesting the salts in HF under microwave heating.

Catalytic runs and products identification

Catalytic tests were performed in a glass reactor (25 mL) fitted with a sampling septum and under magnetic stirring. In a typical run, β-pinene (ca. 3.74 mmol) was solved in the methyl alcohol (ca. 10 mL) and the reactor temperature was adjusted to 333 K. Then, the solid Cs heteropoly catalyst was added to the solution and the reaction was started. The reactions were monitored taking aliquots at regular time intervals and analyzing them by gas chromatography in a Shimadzu GC 2010, fitted with capillary column and FID. Dodecane was the internal stander. The main products were identified by GC/MS analyses (Shimadzu MS-QP 2014 ultra mass spectrometer instrument) operating at 70 eV, coupled with a Shimadzu 2014 GC.

Recovery and reuse of the catalyst

After the end of the reaction, the solid catalyst was centrifuged, filtered, washed three times with propyl alcohol and dried at 353 K in an oven. The solid $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ salt catalyst was weighted and reused in other catalytic tests.

The leaching tests were performed heating and stirring the catalyst with methyl alcohol during 30 min; after removing the catalyst, the β-pinene was added to the methyl alcohol and the reaction carried out 240 min. In addition, another leaching test was done; β-pinene was solved in methyl alcohol and the solid catalyst was added. The suspension was stirred and heated at reaction temperature 30 min; after this period, the reaction was stopped, the catalyst was centrifuged and removed. The solution remaining was stirred and heated at reaction temperature during 240 min. GC analyses allowed monitoring the reaction progress in all the experiments.

Results and discussion

Characterization of cesium salt catalysts

FT-IR spectroscopy analyses

FT-IR spectra of three cesium partially exchanged salts with different heteropolyanions, and their respective precursor acids were recorded to assess whether the primary structure (i.e., Keggin anion) of HPA was retained after the synthesis. Were selected the HPA salts containing 0.5 mol of H^+ ions/mol of Cs salt (Fig. 1SM).

The infrared spectrum of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was compared to their precursor acid (Fig. 1SM), and exhibited four characteristic peaks for phosphotungstic acid: ν_{as} (P–O) = 1080 cm^{-1}, ν (W=O) = 980 cm^{-1}, ν (W–O$_b$–W) = 890 cm^{-1}, and ν (W–O$_c$–W) = 795 cm^{-1} (Bajuk-Bogdanovic et al. 2008). Absorption bands at these wavenumbers were also seen when phosphomolybdate was the anion. These bands were assigned to the similar vibration modes involving Mo atoms. No significant shift was observed in the main absorption bands of Cs HPA salts. Since the absorption band of the P–O bond (ca. 1080 cm^{-1}) was noticed at the same wavenumber in the spectra of parent acids and their salts, it is possible to conclude that no lacunar species were formed, and that the Keggin anions preserved intact their structures. A comparison of the spectrum obtained from the silicotungstic salt with those of their precursor acid assure that silicotungstic anion had its structure preserved, after the partial exchange of the protons by Cs$^+$ ions (Pizzio and Blanco 2007).

Since the infrared spectra of HPA salts showed that the typical absorption bands of phosphotungstate anion were not shifted even varying the degree of substitution of protons (see Fig. 1), it is possible to infer that no significant change occurred in their structure.

Powered XRD and TG-DSC thermal analyses

The powder X-rays diffraction patterns of Cs heteropoly salts and their precursor acids indicated that the synthesized salts were crystalline in nature (Fig. 2SM). While the XRD patterns of three precursor acids showed the main XRD peaks in the region of $5° < 2\theta < 45°$, the Cs heteropoly salts presented well-defined diffraction peaks along the all 2θ angle range studied, indicating a higher crystallinity level.

Firstly, it is noteworthy that the amount of water molecules per unit cell affects the XRD patterns of HPAs or their salts. For instance, Derrick et al. studied this effect analyzing the XRD patterns of the silicotungstic acid containing a variable number of water molecules (i.e., $H_4SiW_{12}O_{40}·nH_2O$, where $n = 24$, 14, 6 and 0) and verified the existence of different stable phases depending on the hydration level (Berry et al. 2014). Thus, we performed TG/DTG analysis (curves are in the supplemental material; Fig. 2SM) of the HPAs and their cesium salts, which may be useful in the study of powder XRD patterns of these compounds. The hydration level was determined by TG/DTG analysis (Table 1SM). It was equal to 3 mol H_2O/mol of $Cs_3PW_{12}O_{40}$ or $Cs_3PMo_{12}O_{40}$, and 4 mol H_2O/mol of $Cs_4SiW_{12}O_{40}$. These values were smaller than those obtained for the parent acids, an aspect that, in addition to the presence of cesium, may also explain the differences in the XRD patterns shown in Fig. 2SM.

TG-DTG curves showed that the losses of mass occurred in two range of temperatures; the first related to the
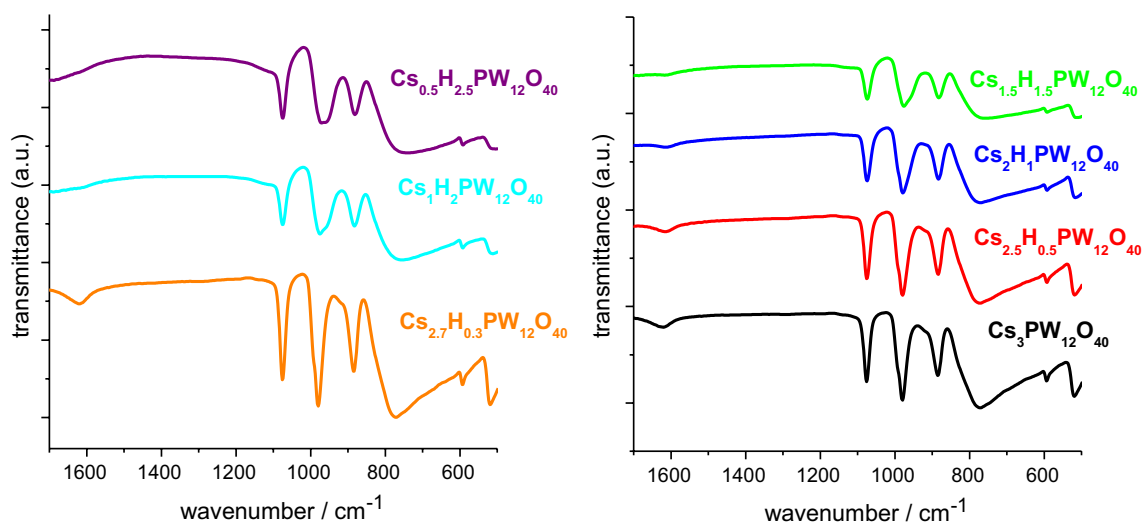

Fig. 1 Effect of level of protons exchange on the FT-IR spectra of Cs heteropoly salts of the phosphotungstic acid

elimination of the physisorbed water (ca. 303–415 K), and the other related to loss of water molecules strongly bonded to the multiple primary heteropolyanions, which crystallize them into a hydrate (ca. 403–673 K) (Fig. 3SM) (Yang et al. 2000). Apparently, the removal of water molecules from the precursors occurred during the synthesis of cesium salts. This result is in accordance with the literature (Yang et al. 2000).

The effect of the degree of cesium exchange on the crystallinity of the Keggin HPA salts was assessed only for the more active catalyst (i.e., cesium phosphotungstate). The powdered XRD patterns of the salts containing different loads of cesium were also recorded (Fig. 2). Although X-rays diffractograms of cesium salts have presented a high number of diffraction lines, which had a higher intensity and were more well-defined than precursor HPAs, apparently for this level of protons exchange, only a slight alteration on heteropolyanion structure was observed. Regardless of the degree of cesium exchange, the XRD patterns of salts showed diffraction peaks that satisfactorily agree with the JCPDS database of $H_3PW_{12}O_{40}$ (PDF #50-1857 and 75-2125). In addition, these diffractograms match also with XRD patterns of $H_3PW_{12}O_{40}$ presented in Fig. 2, which confirmed the bcc packing of Keggin heteropolyanions.

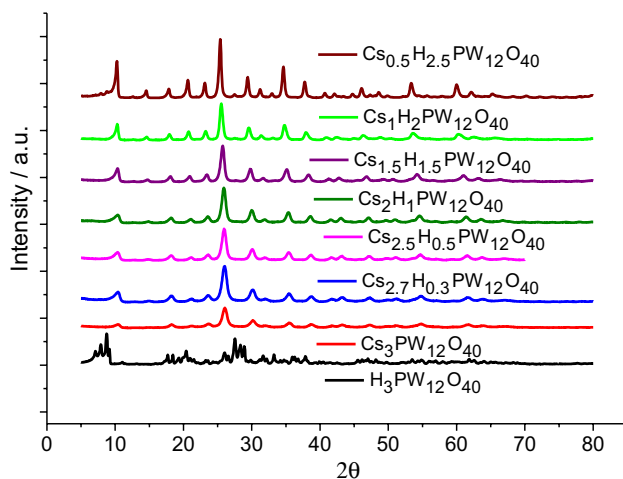**Fig. 2** Effect of protons exchange level on the XRD patterns of powdered phosphotungstic acid and their Cs heteropoly salts

We verified that when the water was present in a lower amount in the Keggin anions of the salts the width of the diffraction lines was increased. This correlation between hydration level and crystallinity agrees with the literature (Yang et al. 2000; Essayem et al. 1995). TG-DTG analyses of salts with a variable level of cesium showed that as higher the amount of Cs ions, lower the amount of water present (Table 2SM). Therefore, the weight loss decreased with increasing Cs content, which can be assigned to the lower level of hydration, as reported in the literature (Essayem et al. 1995).

Table 1 shows the crystallite size of Keggin HPAs and their cesium salts containing 0.5 mol H^+ ions/mol catalyst. These data were calculated by the Scherrer equation, which was applied to the more intense XRD peaks of these samples. It should be highlighted that the peaks selected for this calculation were at 2θ angles of 8° and 27°.

Narasimharao et al. described that regardless of the Keggin anion the crystallite size was being gradually reduced when the cesium amount was increased (Table 1) (Narasimharao et al. 2007). The crystallite sizes of the phosphotungstate salts containing a variable Cs load were equally obtained applying the Scherrer equation to the more intense diffraction peak of XRD spectra (Table 3SM).

Those authors verified that an increase of cesium load of 0.0–2.2 decreased the crystallite size; conversely, for cesium loads higher than 2.2. the crystallite size increased (Narasimharao et al. 2007). They assigned this effect to the formation of $Cs_3PW_{12}O_{40}$ aggregates on the cesium partially exchanged salts, which then give particles. Herein, it was observed a decrease until 1.5 mol of Cs, which had 10.5 nm crystallite size. For higher loads, the sizes oscillated between 12.1 and 9.1 nm (Table 3SM), suggesting that the same effect occurred, however, at different intensity.

Measurements of acidity

The strength and total amount of the acid sites present in the cesium salts were determined after the potentiometric titration of the samples with *n*-butylamine. Initially, we titrated the suspension of the precursor acids and their cesium salts containing 0.5 mol of H^+ ions/mol of catalyst (Fig. 4SM). For comparison, a solution containing the precursor acid with the same H^+ ions concentration was also titrated. The

Table 1 Effects of the Keggin anion on the crystallite size of cesium exchanged heteropolyacid salts containing 0.5 mmol of H^+ ions/mol catalyst

Entry	Catalyst	Crystallite size (nm)	Entry	Catalyst	Crystallite size (nm)
1	$H_3PW_{12}O_{40}$	30.3	4	$Cs_{0.5}H_{2.5}PW_{12}O_{40}$	9.2
2	$H_3PMo_{12}O_{40}$	12.2	4	$Cs_{0.5}H_{2.5}PMo_{12}O_{40}$	15.4
3	$H_4SiW_{12}O_{40}$	44.3	4	$Cs_{0.5}H_{3.5}SiW_{12}O_{40}$	21.4

acidity strength was classified according to the measured of initial electrode potential (E_i); $E_i > 100$ mV (very strong sites); $0 < E_i < 100$ mV (strong sites); $-100 < E_i < 0$ mV (weak sites); and $E_i < -100$ mV (very weak sites) (Pizzio and Blanco 2003).

The three HPAs exhibit very strong acid sites, with an electrode potential of 700 mV. Nonetheless, even after the partial removal of the acidic protons, the precursor acids were converted to cesium salts, which presented very strong acidic sites, as demonstrated by the high E_i value (ca. 550 mV; Fig. 4SM).

The acid sites number was calculated from the equivalence point noticed on the titration curves and was obtained from the plateau value of the titration curves (i.e., mEq n-butylamine/g catalyst) (Pizzio and Blanco 2003). There was an acceptable concordance between the theoretical and experimental amount of acid sites. It means that the procedure used to synthesize the catalysts was efficient. Expectedly, the cesium heteropoly had a lower amount of acid sites than the precursor acids. It was true for all the catalysts, regardless of the nature of Keggin anion. The effect of the level of protons exchanges on the strength and amount of acid sites was evaluated for the cesium phosphotungstate salts (Table 4SM; Fig. 5SM).

An increase of cesium load reduced the E_i value, as shows the titration curves, indicating that the acidity strength of salts was also lowered. However, independent of a total or partial cesium exchange, all the catalysts presented still very strong acid sites (Fig. 5SM). Table 4SM shows that the maximum acidity strength of the sites (i.e., Brønsted acidity of bulky) was reduced when the Cs content was increased.

The $Cs_3PW_{12}O_{40}$ catalyst presented the lowest number of acid sites (ca. 0.08 mmol H^+/g catalyst; Table 2SM). There was a satisfactory agreement between the theoretical and experimental values of the acid sites number of cesium salts. The dependence of the surface acidity and catalytic activity should be very important for this type of solid catalysts.

Porosimetry and BET analyses

The porosity of the cesium HPA salts was compared with those of parent acids (Table 5SM). It was found that the volume and size of pore presented by the cesium salts of HPAs containing 0.5 mol H^+/mol catalyst was higher than those displayed by their precursor HPAs, notwithstanding the addenda atoms (i.e., W or Mo) or heteroatom (i.e., P or Si) present in the Keggin heteropolyanion.

Keggin HPAs have a very low surface area (ca. 3.3–3.9 m^2g^{-1}, Table 5SM), nonetheless, when the protons were partially exchanged by cesium ions it became four times higher, independently of the nature of Keggin anion. This effect triggered by cesium exchange was confirmed, when we measured the surface area of the phosphotungstate salts that had a variable cesium load.

The isotherms of adsorption–desorption (Fig. 3) obtained from the cesium partially exchanged heteropoly salts were treated by the BET method providing the porosity and surface area of the solid catalysts (Table 6SM).
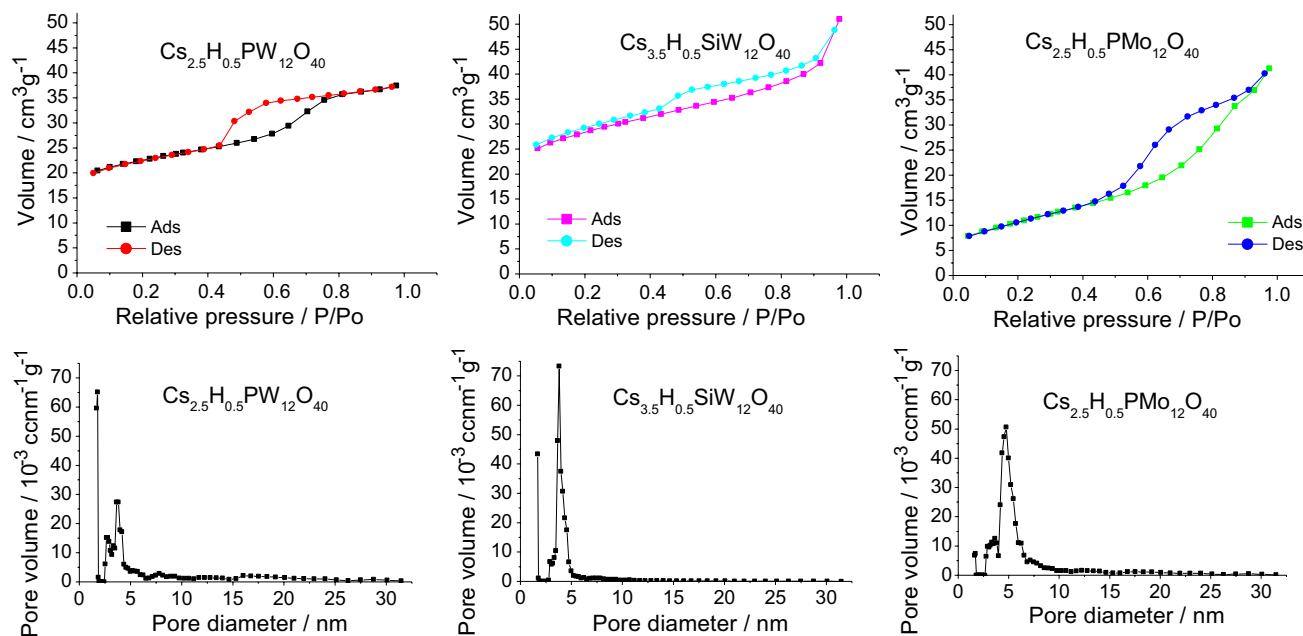

Fig. 3 Isotherms of adsorption/desorption of N2 and curves of pores diameter distribution obtained from Keggin HPAs and their partially exchanged salts with 2.5 mol of Cs

The quick initial increase corresponds to the formation of the first layer; therefore, an increase of pressure forms the second layer of the adsorbed molecules, followed by another layer. It was observed the irreversibility of the adsorption–desorption isotherms (i.e., presence of a hysteresis cycle) for all three catalysts. All these isotherms can be classified as Type IV, due to the hysteresis loop, which is usually observed for mesoporous materials. The sharp peaks appeared at 40 and 60 Å (Fig. 3) assure that these salts are mesoporous (Dias et al. 2004).

BET surface area of the cesium salts increased steeply as the Cs content was increased. A similar effect was reported by Dias et al. when synthesized cesium phosphotungstate salts (Dias et al. 2004). Comparing our results with others described in the literature, we can conclude that the increase of surface area depends on the different parameters, such as the method of the synthesis, the cesium source, the aging time and so on (Okuhara et al. 2000; Park et al. 2010; Dias et al. 2004; Pizzio et al. 2003).

SEM and EDS analyses

Figure 4 shows examples of the obtained SEM images for the phosphotungstic acid and their cesium partially exchanged salts. The images were selected to show whether an increasing in cesium load changed some morphological property of samples. SEM images were obtained with 1500 and 2000 magnifications, for the $H_3PW_{12}O_{40}$ and their Cs salts, respectively (Fig. 6SM).

$H_3PW_{12}O_{40}$ shows grains with sizes ranging from 1 to 100 μm and a layered structure. Cs exchange does not change very much the morphology, although the layered structure is not so clear, and the mean grain size is smaller. EDS spectra were recorded and confirmed that cesium load
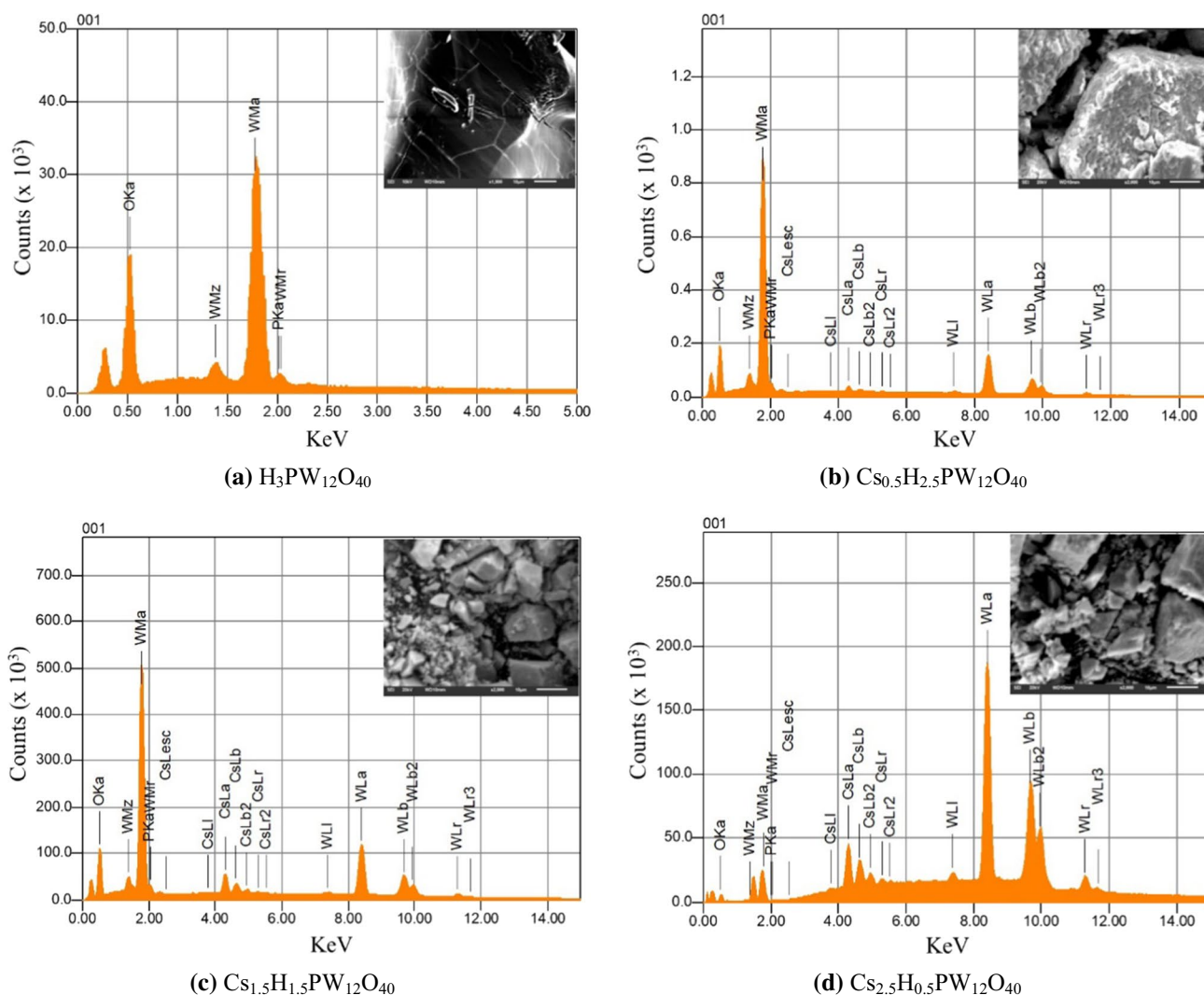

(a) $H_3PW_{12}O_{40}$

(b) $Cs_{0.5}H_{2.5}PW_{12}O_{40}$

(c) $Cs_{1.5}H_{1.5}PW_{12}O_{40}$

(d) $Cs_{2.5}H_{0.5}PW_{12}O_{40}$

Fig. 4 EDS spectra and SEM images (inset) of phosphotungstic acid and its cesium partially exchanged salts

incorporated into the phosphotungstic acid agreed with theoretical values. This effect can be evidenced by the change in the intensity of the Cs characteristic peaks between 4 and 6 keV, indicating the stoichiometry of reaction was successfully controlled. The contents of tungsten, phosphorus, and cesium were confirmed by ICP-MS analyses.

Catalytic tests

Screening of cesium exchanged Keggin heteropolyacid salt catalyst

The catalytic activity of HPA salts containing 2.5 mol of Cs was investigated (Fig. 5a) and compared to the parent acids (Fig. 5b). The reactions in the presence of the phosphotungstic catalysts achieved the highest conversions (ca. 100% and 85%, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and $H_3PW_{12}O_{40}$, respectively). Among the two kinds of catalysts studied, the phosphotungstic acid and their cesium salt were the most active.

When we compared the acidity of the soluble acids with the conversions achieved by them in reactions of β-pinene etherification, we conclude that apparently this feature did not the only responsible by their

catalytic performance; while the acidity strength obeyed the trends: $H_3PMo_{12}O_{40} \approx H_4SiW_{12}O_{40} > H_3PW_{12}O_{40}$ (Table 2), the conversions were as follows; $H_3PW_{12}O_{40} \approx H_4SiW_{12}O_{40} > H_3PMo_{12}O_{40}$ (Fig. 5b). The literature describes that even in acid-catalyzed reactions, not always the strongest acid catalyst is the most efficient (Essayem et al. 1995; Pizzio and Blanco 2003). It suggests that when the HPA catalyst is soluble, the heteropolyanion, and not only the proton, should play an important on this reaction. As reported in other acid-catalyzed processes, it is possible that the softness of heteropolyanion plays also an important role in this reaction (Rafiee et al. 2011).

Conversely, on the solid cesium heteropoly salts-catalyzed reactions, there was a different effect; the more acidic salt ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$) reached the highest conversion (Table 2; Fig. 5a). On the other hand, even though both silicotungstate and phosphomolybdate have an acidity strength practically equal (Table 4SM), the molybdenum salt was much more active. Once more, this result suggests that the acidity strength should not act alone on this process. For this reason, even at equal protons concentrations, the cesium salt catalysts with different anions reached distinct conversions.
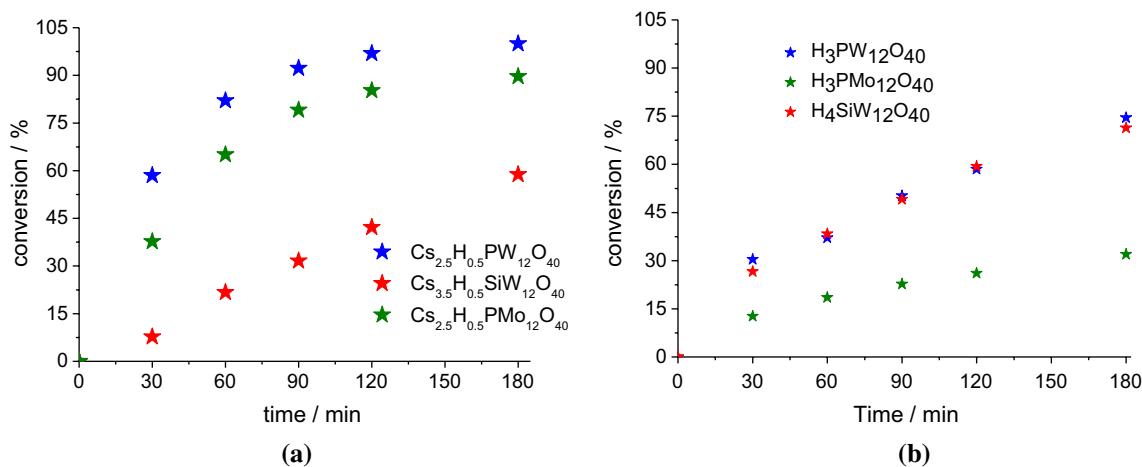

Fig. 5 Kinetic curves of alkoxylation of β-pinene with methyl alcohol in the presence of cesium heteropoly salt catalysts (**a**) and Keggin heteropolyacids (**b**). Reaction conditions: β-pinene (3.74 mmol), methyl alcohol (353 mmol, 10 mL), cesium catalysts (0.60 mol% of H^+ ions); HPA catalysts (0.60 mol% of H^+ ions), temperature (333 K)

Table 2 Acid sites of the heteropolyacids and their cesium salts determined by potentiometric titration with *n*-butylamine

Catalyst	E_i (mV)	Acidity strength	Theoretical acid sites (H^+ ions mmol/g catalyst)	Experimental acid sites (H^+ ions mmol/g catalyst)
$H_3PW_{12}O_{40}$	686	Very strong	1.14	1.13
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	554	Very strong	0.23	0.21
$H_3PMo_{12}O_{40}$	715	Very strong	1.52	1.47
$Cs_{2.5}H_{0.5}PMo_{12}O_{40}$	532	Very strong	0.16	0.15
$H_4SiW_{12}O_{40}$	718	Very strong	1.23	1.31
$Cs_{3.5}H_{0.5}SiW_{12}O_{40}$	529	Very strong	0.15	0.15

Our results agree with those described by Castanheiro et al., which investigated the methoxylation of α-pinene over silica-supported HPAs (Pito et al. 2010). Although the different substrate (i.e., α-pinene whereas β-pinene), the more active was also the phosphotungstic acid, regardless of has been used as a soluble or solid catalyst.

A pivotal aspect distinguishes the action of the HPAs in relation to their cesium salts; once that HPAs are completely soluble, they work in a homogeneous phase. Whereas, the insoluble cesium salt-catalyzed reactions proceed in heterogeneous conditions. The activity of the solid catalysts depends on different aspects such as surface area, porosity, surface acidity, which are absent in a homogeneous catalyst. The textural properties of cesium salts were similar (Table 6SM). Therefore, it is not the reason that justifies the different catalytic activity. Probably, other aspects not clearly understood yet should be responsible for different conversions achieved in the etherification reactions with these salts.

We suppose that in addition to the acidity strength (i.e., acids and their cesium salts) and the surface properties (i.e., cesium salts), the nature (i.e., composition) of the heteropolyanion plays also an essential role on the etherification reactions of β-pinene. Depending on the heteropolyanion, the stabilization of some reaction intermediates (see Scheme SM1) may be differently favored. Therefore, we will discuss the results obtained by the HPAs and their cesium salts analyzing the reaction selectivity of processes (Scheme 1).

The selectivity of these reactions depends on the stability and reactivity of carbocations formed in the solution. In general, the protonation of the double bond of the β-pinene is followed by the reactions of carbon skeletal rearrangement, and results on the formation of β-pinyl, α-terpinyl and bornyl carbocations (Scheme SM1).

The β-pinyl, α-terpinyl and bornyl carbocations may follow two distinct ways; release H^+ ions resulting in monoterpenes (i.e., limonene, α-terpinolene or camphene, respectively, Scheme SM1), or undergoes a nucleophilic attack by the hydroxyl group of the alcohol, resulting in alkyl ethers. These concurrent reactions (i.e., isomerization and carbon skeletal rearrangement) increase the number of products formed in HPA-catalyzed β-pinene reactions (Scheme 1), similarly to the reported for the α-pinene (Martins et al. 2018).

Table 3 summarizes the main result of the conversion and selectivity achieved in reactions in the presence of the Keggin HPAs or their cesium salts containing 0.5 mol of H^+ ions/mol catalyst. Regardless of the heteropoly catalyst, α-terpinyl methyl ether (**1a**) was always the majority
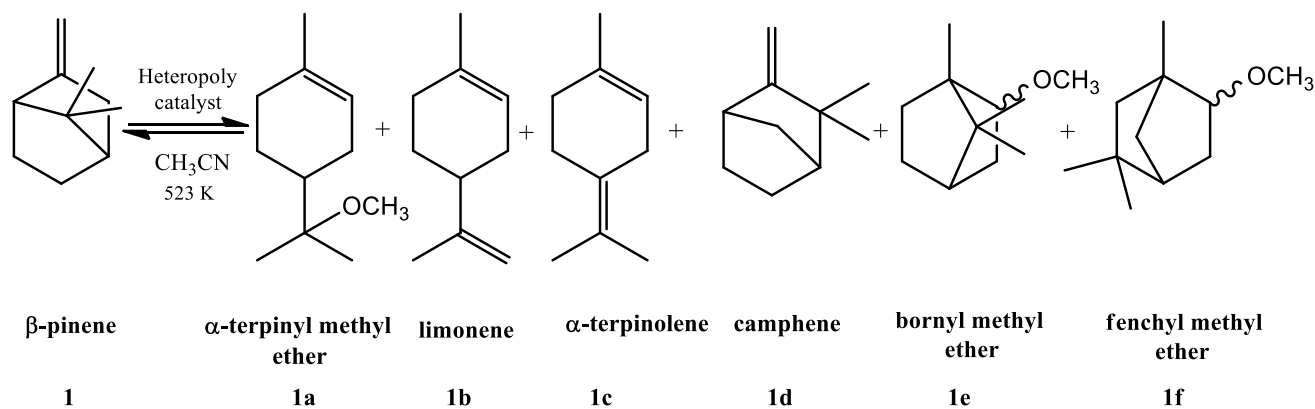
Scheme 1 Main products of heteropoly-catalyzed alkoxylation of β-pinene with methyl alcohol

Table 3 Conversion and selectivity of heteropoly-catalyzed β-pinene etherification with CH_3OH

Entry	Catalyst	Conversion (%)	Selectivity (%)					
			1a	1b	1c	1d	1e	1f
1	$H_3PW_{12}O_{40}$	82	50	18	14	3	11	4
2	$H_4SiW_{12}O_{40}$	79	47	20	15	3	10	5
3	$H_3PMo_{12}O_{40}$	38	51	17	13	4	10	5
4	$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	100	58	9	7	12	11	3
5	$Cs_{3.5}H_{0.5}SiW_{12}O_{40}$	60	52	10	6	17	11	4
6	$Cs_{2.5}H_{0.5}PMo_{12}O_{40}$	97	55	13	7	11	10	4

Reaction conditions: β-pinene (3.74 mmol), methyl alcohol (353 mmol, 10 mL), cesium catalysts (0.60 mol% of H^+ ions); HPA catalysts (0.60 mol% of H^+ ions), temperature (333 K)

product. This result can be assigned to the higher stability of the tertiary carbocation, which was formed by the carbon skeletal rearrangement of β-pinene (Scheme SM1). The α-terpinyl carbocation may undergo two reactions; a nucleophilic attack of alcohol gives the ether (**1a**) or, alternatively, the releasing of the H^+ ion, regenerating limonene (**1b**) or terpinolene (**1c**).

Table 3 shows that in addition to reach the highest conversion, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalyst gave the highest selectivity for α-terpinyl methyl ether (**1a**). The products formed from the α-terpinyl carbocation were predominant on the HPA-catalyzed reactions, indicating that the presence of H^+ ions in solution favor its formation. Conversely, the cesium salt catalysts favored the formation of camphene (**1d**), which is obtained from β-pinyl carbocation.

Figure 6 shows the conversion and regioselectivity of the reactions, with a special highlight for the α-terpinyl methyl ether (1a) product. Due to superior performance, the cesium phosphotungstate salt was selected to assess the effect Cs^+:H^+ molar ratio in the β-pinene etherification reactions.

Effect of Cs^+:H^+ proportion on the activity of cesium phosphotungstate catalysts in β-pinene etherification reactions with methyl alcohol

The Cs^+:H^+ proportion had a noticeable effect on the initial rate and conversion of the etherification reactions of β-pinene (Fig. 7). Apparently, there are two levels of substitution that affected the conversion; the first, a total removal, and the second, the partial exchange of protons. A total exchange of the protons by cesium ions drastically decreased the activity of the catalyst; the $Cs_3PW_{12}O_{40}$-catalyzed reaction achieved the lowest conversion (ca. 13%, Fig. 8).

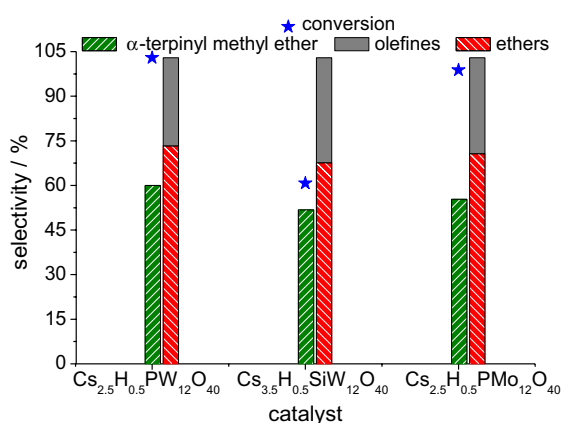On the other hand, if a small load of protons remains in the catalyst, it becomes very effective; the

$Cs_{2.5}H_{0.5}PW_{12}O_{40}$-catalyzed reaction was achieved an almost complete of β-pinene (ca. 100% conversion). As demonstrated previously, the $H_3PW_{12}O_{40}$ was less effective than $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalyst; the first achieved a conversion of 82%, while the second converted virtually 100% of β-pinene.

It is important to highlight that in all the runs with the cesium partially exchanged salt catalysts, the load of the H^+ ions remained constant (ca. 0.60 mol%). To do it, each catalyst was used with an adequate mass, which always gave 0.60 mol% of H^+ ions. Therefore, we can link the conversions achieved with two different aspects; the first,

Fig. 6 Conversions and regioselectivity of the products obtained in heteropoly-catalyzed β-pinene etherification reactions with methyl alcoho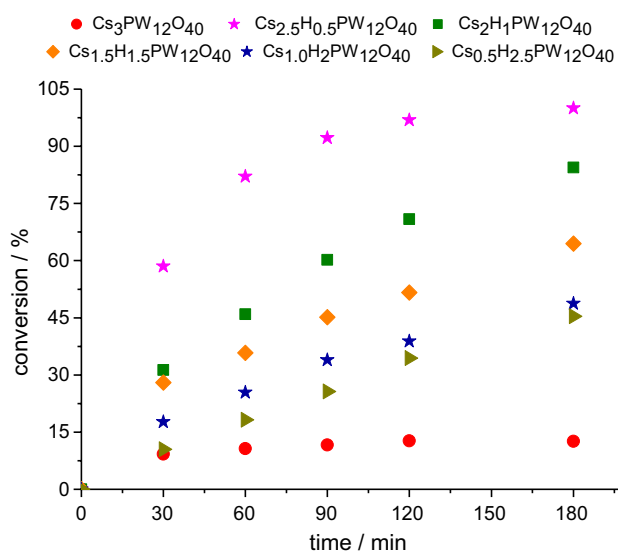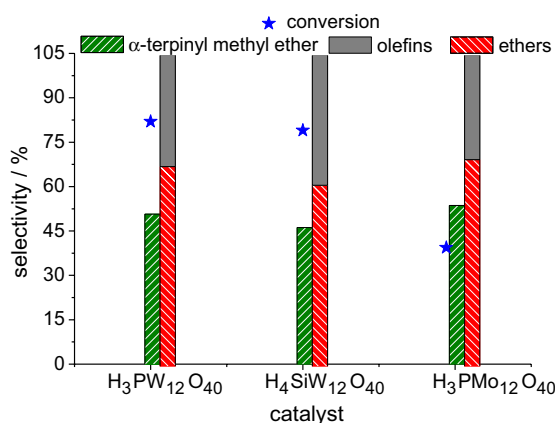l. Reaction conditions: β-pinene (3.74 mmol), methyl alcohol (353 mmol, 10 mL), cesium catalysts (0.60 mol% of H^+ ions); HPA catalysts (0.60 mol% of H^+ ions), temperature (333 K)
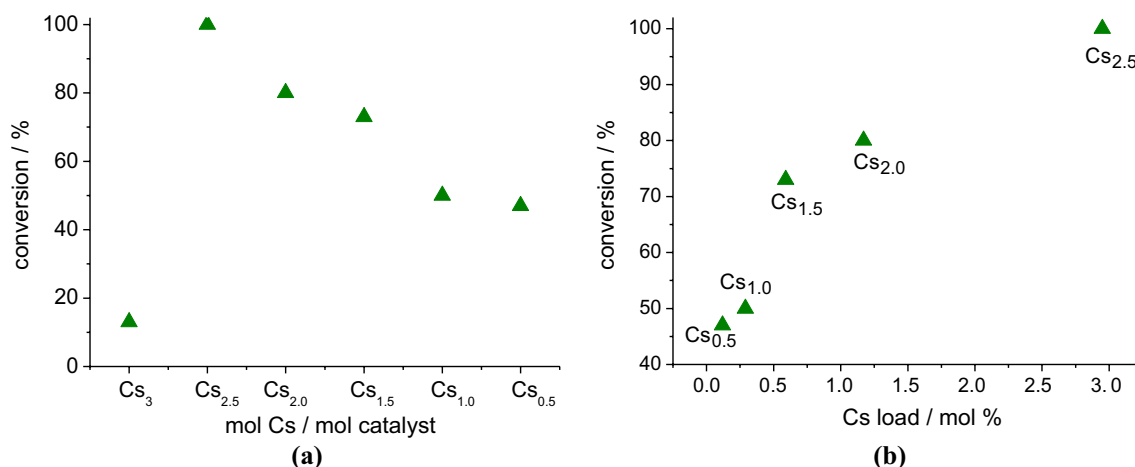
Fig. 8 Effects of Cs$^+$mol/catalyst mol proportion (**a**) and load of cesium partially exchanged salt catalyst (**b**) on the conversion of β-pinene etherification reactions with methyl alcohol. $Cs_3 = Cs_3PW_{12}O_{40}$; $Cs_{2.5} = Cs_{2.5}H_{0.5}PW_{12}O_{40}$; $Cs_{2.0} = Cs_{2.0}H_{1.0}PW_{12}O_{40}$; $Cs_{1.5} = C_{1.5}H_{1.5}PW_{12}O_{40}$; $Cs_{1.0} = Cs_{1.0}H_{2.0}PW_{12}O_{40}$; $Cs_{0.5} = Cs_{0.5}H_{2.5}PW_{12}O_{40}$
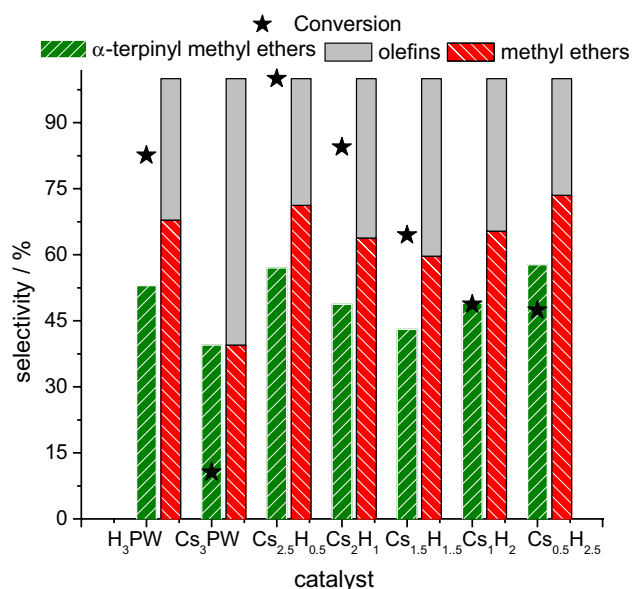
Fig. 9 Effects of cesium load on the conversion and selectivity of β-pinene etherification with methyl alcohol in the presence of H3PW12O40 catalyst or their partially cesium exchanged salts. Reaction conditions: β-pinene (3.74 mmol), methyl alcohol (353 mmol, 10 mL), cesium catalysts (0.40 mol% of cesium salts); temperature (333 K)

Fig. 10 Effect of the loading of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ on the kinetic curves of etherification of β-pinene with methyl alcohol. Reaction conditions: β-pinene (3.74 mmol), methyl alcohol (353 mmol), temperature (333 K)

the Cs content/mol of catalyst (Fig. 8a); the second, the total load of Cs (mol%) present in the reaction (Fig. 8b).

While Fig. 8a clearly shows that there is an "optimum load" of Cs per mol of catalyst (i.e., $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalyst), Fig. 9b shows that if a minimum of protons remains present in the catalyst, an increase on cesium load enhances the reaction conversion.
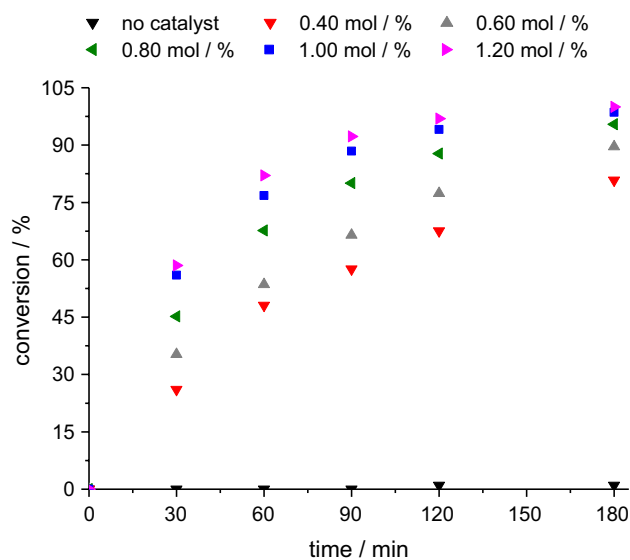
The effect of cesium load was also assessed on the reaction selectivity (Fig. 10). The Cs$^+$:H$^+$ molar ratio altered the reaction selectivity. In the presence only of protons (i.e., $H_3PW_{12}O_{40}$), the olefins selectivity was lower than that observed in the presence of $Cs_3PW_{12}O_{40}$. The opposite has occurred in relation to the ether's selectivity; they were more selectively formed using phosphotungstic acid than cesium phosphotungstate.

On the other, when both are present in the catalyst (i.e., cesium partially exchanged salts), we realize that there is two ranges of

concentration that differently affected the selectivity; on the first, the ethers selectivity increase as follows: $Cs_{1.5}H_{1.5}PW_{12}O_{40} < Cs_{2.0}H_{1.0}PW_{12}O_{40} < Cs_{2.5}H_{0.5}PW_{12}O_{40}$. Conversely, when a higher amount of H^+ ions is present, the ether selectivity increased as follows; $Cs_{1.0}H_{2.0}PW_{12}O_{40} < Cs_{0.5}H_{2.5}PW_{12}O_{40}$. This behavior demonstrated that the simultaneous presence of Cs^+ and H^+ in the catalyst improved the reaction selectivity.

The importance of the simultaneous presence of cesium and protons in the catalyst is may be clearly seen when comparing the selectivity of reactions; $Cs_{0.5}H_{2.5}PW_{12}O_{40}$ and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ achieved practically the same selectivity. Nonetheless, the conversion of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$-catalyzed reaction was remarkably higher than that observed in the presence of the $Cs_{0.5}H_{2.5}PW_{12}O_{40}$ catalyst (ca. 100 and 49%, respectively). It is evident that in terms of conversion, the cesium also plays an important role in these reactions.

Effects of the $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalyst load on the β-pinene etherification with CH_3OH

An increase of the catalyst load may contribute for the reaction achieve the maximum conversion more quickly. To assess this effect, the loading of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalyst was varied of 0.40–1.20 mol% (Fig. 10).

Within the range studied, an increase of the catalyst loading resulted in a higher initial rate and a higher conversion (Fig. 11). With 1.0 mol% catalyst, the β-pinene was virtually converted.

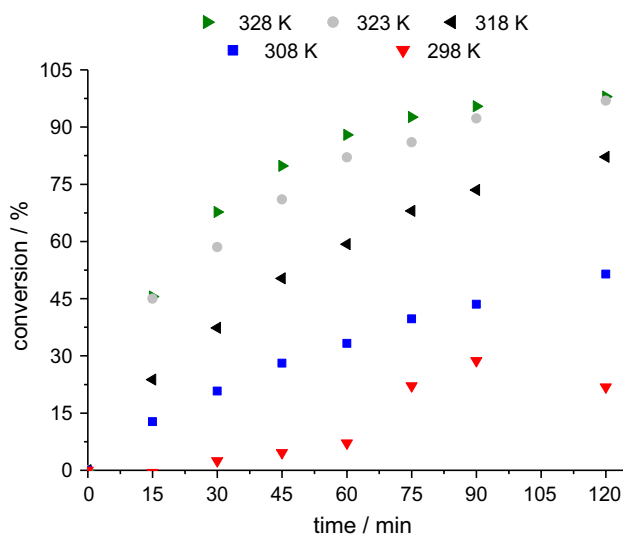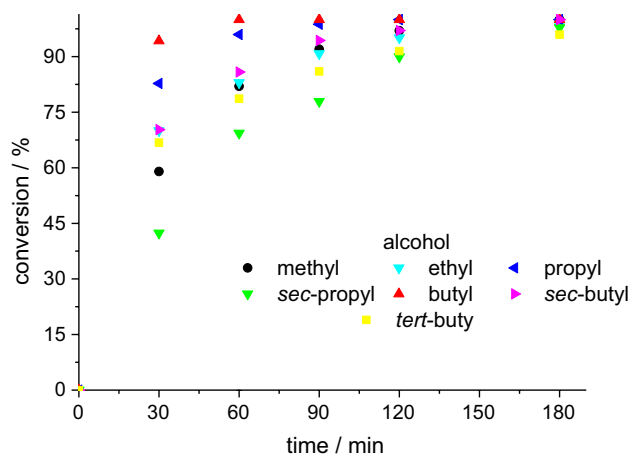Different from observed on the reaction conversions, the selectivity remained almost the same (Fig. 6SM).

Fig. 12 Kinetic curves of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$-catalyzed etherification reactions of β-pinene with different alcohols. Reaction conditions: β-pinene (3.74 mmol), $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (1.2 mol%), alkyl alcohol (353 mmol), temperature (333 K)

Regardless of the catalyst load, α-terpinyl methyl ether (1a) was always the major product with a high selectivity (ca. 60%); similarly, the selectivity of other reaction products remained practically the same. It means that when the H^+:Cs^+ proportion was remained constant at this level (ca. 2.5: 0.5 of Cs^+ to H^+), no significance change was observed on the reaction selectivity (Fig. 6SM). Nevertheless, with a higher load of the solid catalyst in suspension, a greater acid sites number becomes accessible (i.e., H^+ ions), consequently, a number higher of carbocations, which are the key intermediate of the reaction, are formed, leading to the higher and faster conversion of the β-pinene (Fig. 10).

Effects of temperature on the $Cs_{2.5}H_{0.5}PW_{12}O_{40}$-catalyzed β-pinene etherification with CH_3OH

To study effect of temperature can provide the activation energy of a reaction. However, once that herein there are several reactions happening (i.e., etherification, isomerization). No specific reaction can be separately assessed. Nonetheless, in addition to impact the reaction rate, the temperature may also affect the formation of carbocations, changing the reaction selectivity. To verify this effect, we carried out reactions varying the temperature of 298–328 K (Fig. 11).

Expectedly, an increment on temperature resulted in an equal effect on kinetic curves, resulting in higher conversions. However, the reaction selectivity (omitted herein by simplification) remained almost unaltered, suggesting that the stability of the reaction intermediate carbocations was not affected. Independent of reaction temperature, α-terpinyl methyl ether was always the main product.

Fig. 11 Effect of the loading of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalyst on the kinetic curves of etherification of β-pinene with methyl alcohol. Reaction conditions: β-pinene (3.74 mmol), $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (1.2 mol%), CH_3OH (353 mmol), temperature (333 K)

Effects of alcohol on the $Cs_{2.5}H_{0.5}PW_{12}O_{40}$-catalyzed β-pinene etherification reactions.

The carbon chain size as well as the steric hindrance on the hydroxyl group affect the alcohol reactivity (Rafiee et al. 2011). This effect was investigated herein, and the kinetic curves obtained in $Cs_{2.5}H_{0.5}PW_{12}O_{40}$-catalyzed β-pinene etherification reactions are displayed in Fig. 12.

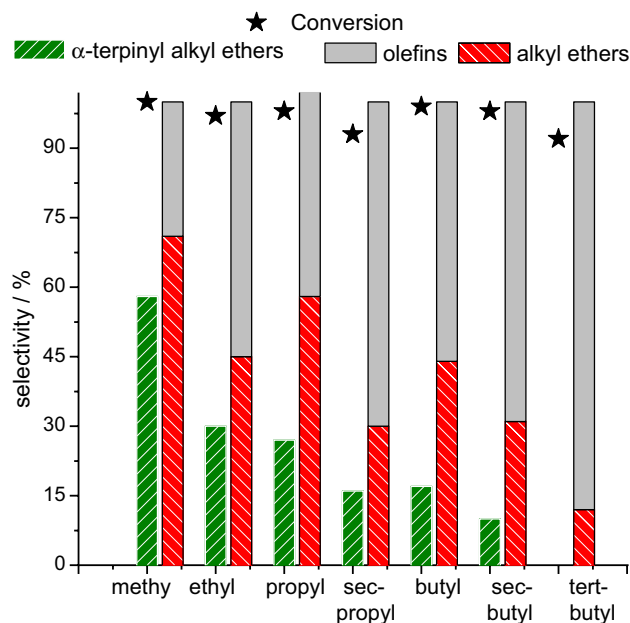The effect of hysteric hindrance on the hydroxyl group affected the alcohols reactivity as was expected; primary > secondary > tertiary. Nonetheless, it was expected that an increase of chain carbon size may decrease the alcohol selectivity. However, when we have observed the kinetic curves, we can realize that herein an opposite effect occurred; the reactivity of primary alcohols was as follows: $CH_3OH < C_2H_5OH < C_3H_7OH < C_4H_9OH$. The same effect also occurred for the reactions with the secondary alcohols; sec-propyl < sec-butyl. It is important to highlight that this comparison refers to the initial rate of the reactions, once that the reactions attained a very close final conversion.

The different initial rates observed for each alcohol suggest that it participate in the rate determining step of the reactions. Therefore, the double protonation of β-pinene, as well as the skeletal rearrangement reactions were less important for the velocity of the etherification reaction than nucleophilic attack of alcohol on the carbocation.

The reaction selectivity was drastically affected by the nature of alcohol. An increase on carbon chain resulted in a gradual decrease on the ethers selectivity, especially for the α-terpinyl alkyl ether. Conversely, the olefins selectivity was being progressively increased when alcohols with a higher carbon chain size were the substrates (Fig. 13).

Effect of the monoterpenes structure on the $Cs_{2.5}H_{0.5}PW_{12}O_{40}$-catalyzed etherification reactions of with methyl alcohol

α and β-pinene were the more selective substrates toward α-terpinyl methyl ether (Fig. 14); however, the exocyclic double bond of β-pinene apparently was more easily protonated than that trisubstituted endocyclic double bond of β-pinene. Consequently, the β-pinene etherification reaction achieved an almost complete conversion, while only 48% of β-pinene was converted.
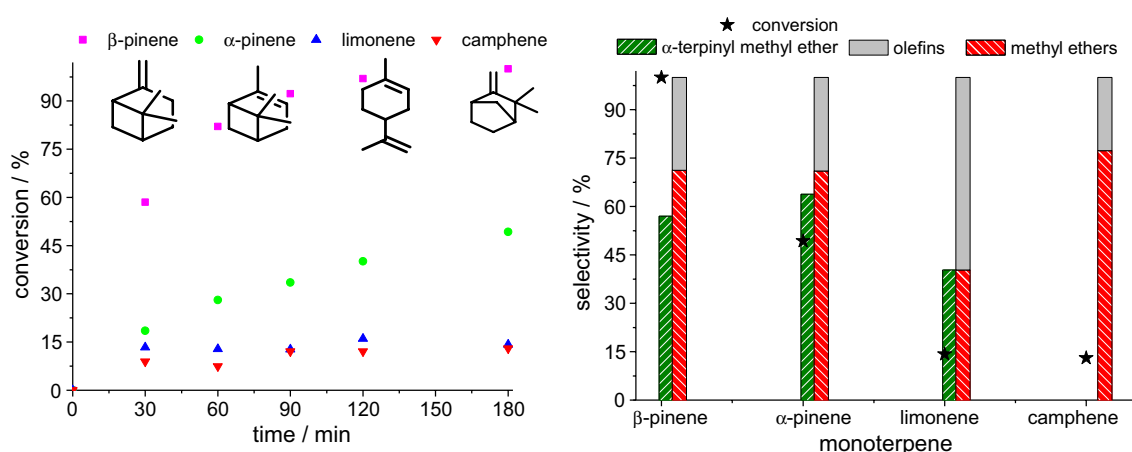

Fig. 13 Conversion and selectivity of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$-catalyzed etherification reactions of β-pinene with different alkyl alcohols. Reaction conditions: β-pinene (3.74 mmol), $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (1.2 mol%), alkyl alcohol (353 mmol), temperature (333 K)

Fig. 14 Kinetic curves and selectivity of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$-catalyzed monoterpenes etherification reactions with methyl alcohol. Reaction conditions: monoterpene (3.74 mmol), $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (1.2 mol%), methyl alcohol (353 mmol), temperature (333 K)

Although limonene has an exocyclic bond double that at principle, may has been protonated and thus generate a α-terpinyl carbocation and consequently α-terpinyl methyl ether, it was few reactive. Notwithstanding the high selectivity toward the α-terpinyl methyl ether (1a), only a poor conversion was achieved (ca. 17%, Fig. 14). It is suggestive that the reaction pathway to obtain the (1a) product involves lower energy when the substrate should be isomerized (i.e., α- and β-pinene) and generate the terpinyl carbocation, than when it should be directly protonated (i.e., limonene) to give the same tertiary carbocation. These substrates have also demonstrated a similar reactivity when were esterified over ion-exchanged and acid-activated clays or $H_3PW_{12}O_{40}$/SBA-15 (Silva et al. 2015; Castanheiro et al. 2017).

The reaction with camphene achieved the lowest conversion, due to the high steric hindrance exerted by two methyl groups on the double bond, as well as the presence of only one allylic hydrogen, which is hard to be abstracted. Consequently, although it has presented a high selectivity toward fenchyl and bornyl ethers, only a poor conversion was attained.

Catalyst reuse

The reusability of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalyst was assessed, performing successive cycles of recovery and reuse (Table 4). The high recovery rates achieved demonstrated that the procedure used was very efficient. The catalyst was reused without loss activity or selectivity toward the main product (i.e., α-terpinyl methyl ether). In addition, we carried out an experiment to verify there was a catalyst leaching and consequently some homogeneous contribution of solved catalyst could have happened.

Two experiments were performed to verify a possible leaching of the catalyst; a portion of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ solid catalyst was heated and stirred during 30 min in methyl alcohol; after removal of the solid salt by centrifugation and filtration, the β-pinene was added to liquid phase remaining and the reaction progress was followed by 3 h (i.e., exp. leaching 1, Fig. 15).

Table 4 Recovery rate and conversion of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalyzed-etherification reactions of of β-pinene with methyl alcohol

Exp	Cycle	Rate recovery (%)	Conversion (%)	Selectivity (1a)
1	Fresh	–	100	61
2	1	96	100	59
3	2	97	98	60
4	3	97	98	59

Reaction conditions: β-pinene (3.74 mmol), $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (1.2 mol%), methyl alcohol (353 mmol), temperature (333 K)

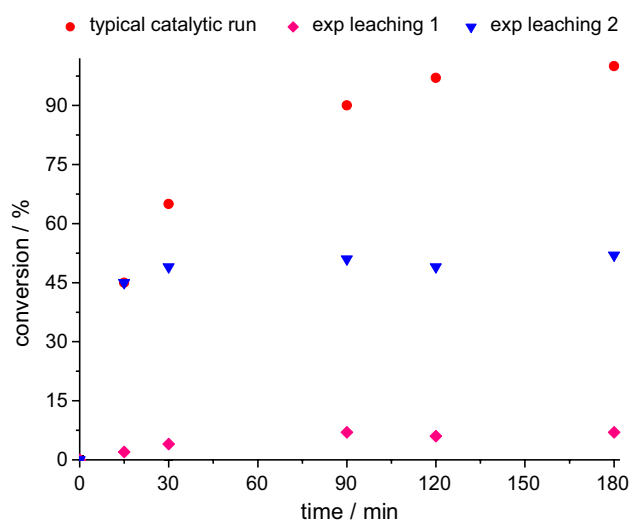**Fig. 15** Assessments on the leaching of the $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalyst in etherification reactions of β-pinene with methyl alcohol. Reaction conditions: monoterpene (3.74 mmol), $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (1.2 mol%), methyl alcohol (353 mmol), temperature (333 K)

No significant progress occurred when the reaction was carried in the solution originated from the leached phase of catalyst. In another experiment, we carried out the reaction with the $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ solid catalyst during 15 min; afterward, the catalyst suspension was centrifugated and the solid removed by filtration. The remaining solution was put in back in the reactor, and the reaction progress followed during 3 h (i.e., exp. leaching 2). We can realize the removal of the catalyst practically stopped the reaction progress; no significant increase in conversion was observed after the catalyst have been removed.

Conclusions

The activity of cesium exchanged partially Keggin heteropolyacid (HPAs) salts was investigated in etherification reactions of β-pinene. Among three salts with different heteropolyanions, the phosphotungstate anion was the most active and selective catalyst toward the synthesis of α-terpinyl methyl ether by etherification reactions of β-pinene with methanol. The effects of the level of protons exchanges were assessed for cesium phosphotungstate salts. The $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ solid catalyst was the most active and selective among them, achieving higher conversion and selectivity than soluble parent acid (i.e., $H_3PW_{12}O_{40}$). The influences of the main reaction parameters were studied (i.e., temperature, cesium load, protons load, time). We demonstrated that the simultaneous presence of the cesium ions and protons in the catalyst plays an essential role in these reactions, being the 2.5:0.5 molar ratio the optimum proportion. The reaction scope was

extended to the other alkyl alcohols and monoterpenes. An increase in carbon chain size favored the conversion of the reactions, however, compromised the selectivity of the terpinyl alkyl ether. The monoterpene structure was also a key aspect in the etherification reaction; the substrate conversion and selectivity for α-terpinyl methyl ether obeyed the trends: β-pinene > α-pinene > limonene > camphene. Finally, the $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalyst was efficiently recovered and reused without loss activity or selectivity. No significant leaching of the catalyst was verified.

Compliance with ethical standards

Conflict of interest There are no conflicts of interest to declare.

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