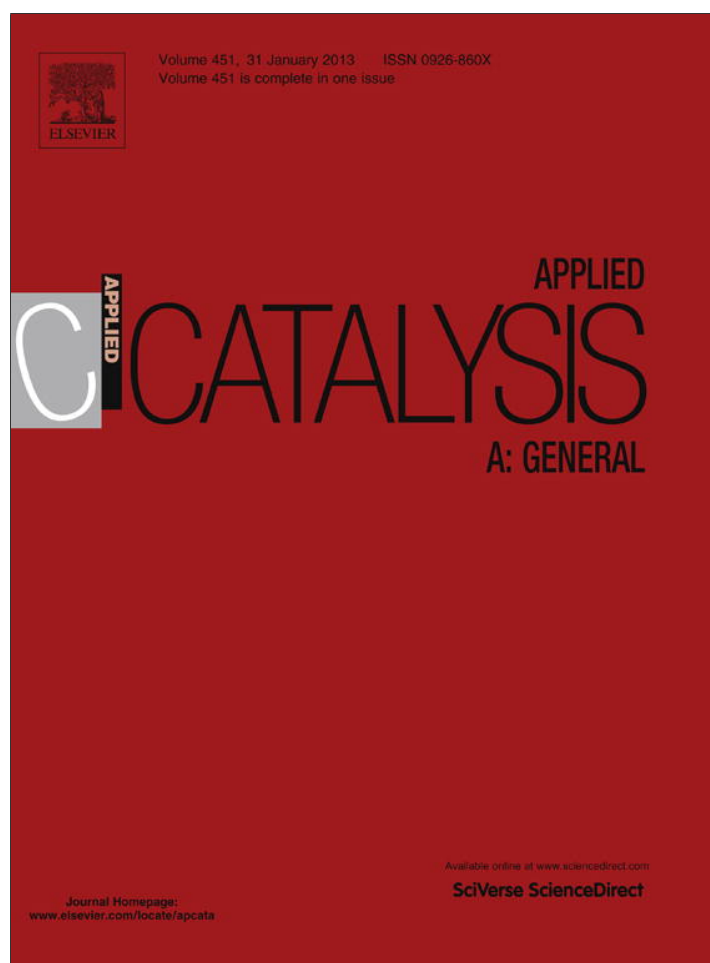


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## Applied Catalysis A: General

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## Alkoxylation of camphene over silica-occluded tungstophosphoric acid

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## ABSTRACT

Silica-occluded tungstophosphoric acid (PW-S<sub>sg</sub>) was used as an efficient, environmentally friendly heterogeneous catalyst for the liquid-phase alkoxylation of camphene into their more valuable alkyl isobornyl ether, which is used as perfume and cosmetic products, in the pharmaceutical industry, as well as in the food industry. The alkoxylation of camphene with C<sub>1</sub>–C<sub>4</sub> alcohols (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol and 2-butanol) to alkyl isobornyl ether was studied in the presence of PW-S<sub>sg</sub> (4.2% w/w) at 60–80 °C. Different linear and branched alcohols are compared in relation to their activity for the alkoxylation of camphene. The catalytic activity decreased with the increase of number of carbon atoms in the chain alcohol, which can be explained due to the presence of sterical hindrance and diffusion limitations inside the porous system of the catalyst. High selectivity of PW-S<sub>sg</sub> catalyst for the alkyl isobornyl ether was observed. The effect of various parameters, such as catalysts loading, initial concentration of camphene and temperature were studied to optimise the ethoxylation of camphene. The catalytic stability of PW-S<sub>sg</sub> in the ethoxylation of camphene was studied by performing consecutive batch runs with the same catalyst sample at the same conditions. After the third run, the catalytic activity stabilized. The catalyst can be recovered and reused without significant leaching of PW. The catalytic activity of PW-S<sub>sg</sub> was compared with the activity of tungstophosphoric acid immobilized on silica by impregnation method (PW-S<sub>im</sub>). The activity of PW-S<sub>sg</sub> is higher than that of PW-S<sub>im</sub> catalyst. After reaction, the PW-S<sub>im</sub> sample lost 20% of its heteropolyacid.

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## 1. Introduction

Monoterpenes are renewable feedstock for fine chemical industry and they are widely used in the pharmaceutical, cosmetic and food industry as active components of drugs and ingredients of artificial flavours and fragrances [1,2]. Acid-catalysed alkoxylation of terpenes is an important synthesis route to valuable terpenic ethers with many applications in perfumery and pharmaceutical industry [1]. Camphene is converted to alkyl isobornyl ether, which is used in formulation of cosmetic and perfumes, as well as in the industrial production of camphor. The alkoxylation of camphene is usually carried out in the presence of homogeneous catalysts, like sulphuric acid and silicotungstic acid [3]. However, the homogeneous catalysts lead to environmental problems and economical inconveniences. These problems can be overcome by the use of heterogeneous catalysts. Solid acid catalysts are preferable, offering easy

separation from the reactants and products by filtration, allowing continuous operation of reactors. They do less harm to the environment and have no corrosion or disposal of effluent problems. They are easily separable from the liquid products. Reusability of the catalyst is another advantage of using heterogeneous catalyst.

Heteropolyacids (HPAs) are Brønsted acids that are used as efficient catalysts for different reactions (Friedel-Crafts acylation, Fries rearrangement, etherification, esterification, isomerisation, hydration and hydrolysis) [4–6]. However, the low surface area (1–10 m<sup>2</sup>/g), the separation problem from reaction mixtures and low stability at relatively high temperatures are some disadvantages of HPAs. In order to overcome these disadvantages, the HPAs have been immobilized on different solid supports, like silica, activated carbons, zeolites, polymers, magnesia and alumina [4–6].

Heteropolyacids have been used as acid catalyst in reactions where terpenes are involved, such as hydration of  $\alpha$ -pinene [7–9], limonene [10] and camphene [11], isomerization of  $\alpha$ -pinene [12], acetoxylation of  $\alpha$ -pinene [9], limonene [9] and camphene [13], cyclization of pseudoionone [14] and methoxylation of  $\alpha$ -pinene [15].

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HPAs are promising catalysts for the alkoxylation reactions (high activity and selectivity, lack of side reaction such as sulphonation etc.). Heterogeneous catalysis is the most attractive option, but the standard bulk and supported HPA catalysts are not attractive because HPA can be readily solvated by the alcohol molecules and leached into solution. The silica-occluded HPA catalysts prepared by sol–gel method are stable towards leaching at moderate HPA loadings [16], hence are promising solid acid catalysts for the target reaction.

In our previous work, silica-immobilized PW has been applied as a heterogeneous catalyst for the methoxylation of  $\alpha$ -pinene [15]. The catalyst PW2.S (silica-occluded tungstophosphoric acid, with  $0.042 \text{ g}_{\text{PW}}/\text{g}_{\text{silica}}$ ) showed the highest activity.

In this work, we attempt to develop an efficient heterogeneous catalytic process for camphene alkoxylation with different alcohols (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol and 2-butanol) in the presence of silica-occluded tungstophosphoric acid (PW-S<sub>sg</sub>). Different parameters, such as initial concentration of camphene, temperature and catalyst loading are optimized. The catalytic stability of PW-S<sub>sg</sub> is also studied. The catalytic activity of PW-S<sub>sg</sub> is compared with that of tungstophosphoric acid immobilized on silica by impregnation method (PW-S<sub>im</sub>).

## 2. Experimental

### 2.1. Catalyst preparation

Tungstophosphoric acid (denoted PW, Aldrich) was immobilized in silica by sol–gel method, as described elsewhere [15,16]. A mixture of water (2.0 mol), 1-butanol (0.2 mol) and heteropolyacid ( $5.0 \times 10^{-4}$  mol) was added to tetraethyl orthosilicate (0.2 mol) and stirred at 80 °C during 3 h. The hydrogel obtained was dehydrated slowly at 80 °C for 1.5 h in vacuum (25 Torr). The obtained dried gel was extracted in a soxhlet apparatus using methanol as solvent during 72 h, and dried at 100 °C, overnight to give the catalyst denoted PW-S<sub>sg</sub>. The silica-occluded heteropolyacid was dried at 100 °C for 3 h prior to use in the catalytic reactions.

The PW was also supported on silica by impregnation method according to Pizzio et al. [17]; 1 g of silica gel (Aerosil 200, Degussa) was impregnated with 4 cm<sup>3</sup> of PW (Aldrich,  $m = 0.1 \text{ g}$ ) solution, using a solvent mixture consisting of ethanol and water (1:1 v/v), under constant stirring for 72 h. The slurry was evaporated to dryness, followed by calcination at 170 °C, during 4 h, to give the catalyst denoted as PW-S<sub>im</sub>.

### 2.2. Characterization techniques

The textural properties were determined from the nitrogen adsorption isotherms measured at 77 K using a Micromeritics ASAP 2000 instrument.

Powder X-ray diffraction (XRD) data were collected on a Bruker powder diffractometer with built-in recorder, using Cu K $\alpha$  radiation, nickel filter, 30 mA and 40 kV in the high voltage source, between 5° and 70° of  $2\theta$  at a scanning rate of 1° min<sup>-1</sup>.

FT-IR spectroscopy in KBr pellets was carried out on a Bio-Rad FTS 155 spectrometer. The spectra were recorded with a resolution of 4 cm<sup>-1</sup> in the range of 400–4000 cm<sup>-1</sup>, and running 1000 scans.

Tungsten amount in the catalyst was determined by inductively coupled plasma on a Jobin-Yvon ULTIMA instrument.

The <sup>31</sup>P MAS (magic angle spinning) NMR spectrum was recorded at 161.90 MHz on a 9.4 T Bruker Avance 400 spectrometer, with 40° pulses, a spinning rate of 15.0 kHz, and 70 s recycle delays (ambient temperature). Chemical shifts are quoted in parts per million from phosphoric acid.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out under nitrogen, with a heating rate of 10 °C min<sup>-1</sup>, using Shimadzu TGA50 and DSC50 systems.

Catalyst acidity was measured by potentiometric titration, according Pizzio et al. [17]. A small quantity of *n*-butylamine solution (0.05 N) in acetonitrile was added to a known mass (0.05 g) of solid suspended in acetonitrile (90 mL), and shaken for 3 h. Then, the suspension was potentiometrically titrated with the same solution of *n*-butylamine in acetonitrile. The electrode potential variation was measured with a Crison micropH 2001 instrument.

### 2.3. Catalytic experiments

The camphene alkoxylation reactions were carried out in a batch reactor, at 60–80 °C. In a typical experiment, the reactor was loaded with 15 cm<sup>3</sup> of alcohol (0.35, 0.26, 0.20, 0.20, 0.16 and 0.16 mol for methanol, ethanol, 1-propanol, 2-propanol, 1-butanol and 2-butanol, respectively) and 0.5 g of catalyst. The reactions were started by adding 1.5 mmol of camphene.

A blank experiment was carried out in the absence of catalyst, being kept all other conditions.

The stability tests for the PW-S<sub>sg</sub> catalyst were carried out by running five consecutive experiments, under the same reaction conditions. Between the catalytic experiments, the catalyst was separated from the reaction mixture by filtration, washed with ethanol and dried at 100 °C overnight.

A hot-filtration test was carried out for the catalyst PW-S<sub>sg</sub>. The reaction was carried out as described above; after 70 h (camphene conversion 50%) the catalyst was removed by hot-filtration. Sampling of the liquid was continued until 120 h, since the beginning of the experiment.

Nonane was used as the internal standard. The reaction progress was followed by gas chromatography (GC) using a KONIC HRGC-3000 C instrument equipped with a 30 m  $\times$  0.25 mm DB-1 column and a flame ionization detector.

The products were identified by gas chromatography mass spectrometry (GC–MS) using a FISON MD800 (Leicestershire, UK) instrument, equipped with a 30 m  $\times$  0.25 mm DB-1 column. Helium was used as carrier gas. The injector and detector temperatures were, respectively, 180 and 300 °C. The split ratio was fixed at 100. The oven temperature program was as follows: start at 80 °C (6 min), ramp at 6 °C min<sup>-1</sup> to 128 °C and ramp at 10 °C min<sup>-1</sup> to 300 °C.

The camphene conversion was expressed as the difference between the initial and final amount (mol) of the reactant divided by initial amount (mol) of the reactant.

Conversion (%)

$$= \frac{\text{initial amount (mol) of camphene} - \text{final amount (mol) of camphene}}{\text{initial amount (mol) of camphene}} \times 100$$

The selectivity for alkyl isobornyl ether was calculated using the following equation:

$$\text{Selectivity (\%)} = \frac{\text{amount (mol) of alkyl isobornyl ether}}{\text{total amount (mol) of product}} \times 100$$

## 3. Results and discussion

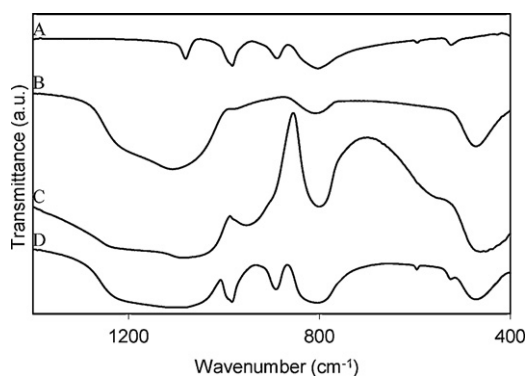
### 3.1. Catalysts characterization

Fig. S1 (supporting information) shows the nitrogen adsorption–desorption isotherms of silica, PW-S<sub>sg</sub> and PW-S<sub>im</sub> samples. While the silica and PW-S<sub>im</sub> materials exhibit type II isotherms (suggesting wide distribution of pore sizes), PW-S<sub>sg</sub> exhibits a type I isotherm which is characteristic of a microporous

**Table 1**  
Physicochemical characterisation of catalysts sample.

Sample	Amount HPA <sup>a</sup> (g <sub>HPW</sub> /g <sub>support</sub> )	W/P ratio	Surface area <sup>b</sup> (m <sup>2</sup> /g)	External Surface area <sup>c</sup> (m <sup>2</sup> /g)	Microporous volume <sup>c</sup> (cm <sup>3</sup> /g)	Total porous volume <sup>d</sup> (cm <sup>3</sup> /g)
Silica	–	–	153	148	0.02	0.46
PW-S <sub>sg</sub>	0.042	12	458	4.1	0.24	0.25
PW-S <sub>im</sub>	0.048	12	106	83.0	0.01	0.42

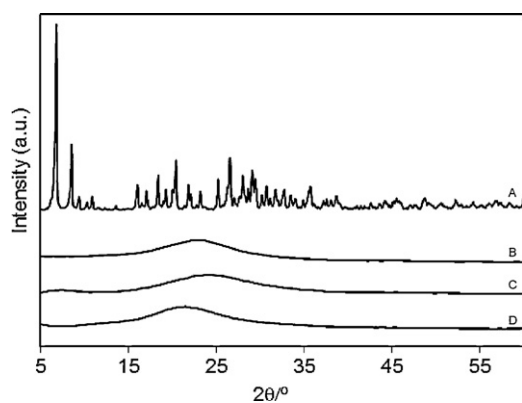
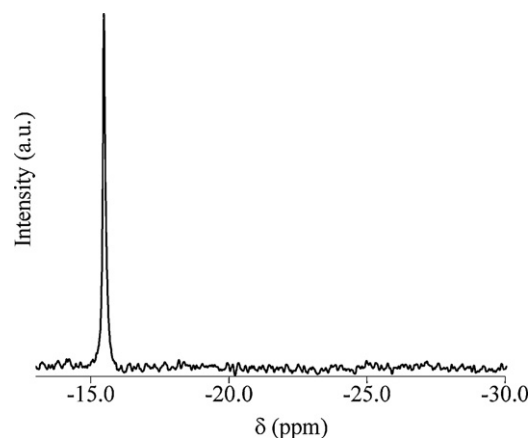
<sup>a</sup> ICP;  
<sup>b</sup> BET;  
<sup>c</sup> *t*-Method;  
<sup>d</sup> (*p/p*<sup>0</sup>) = 0.98.

**Fig. 1.** FTIR spectra: (A) PW; (B) silica; (C) PW-S<sub>sg</sub>; (D) PW-S<sub>im</sub>.

materials (according to IUPAC). Table 1 shows the textural parameters for the catalysts. The specific surface area ( $S_{\text{BET}}$ ) of the catalysts was determined using the BET method while microporous volume ( $V_{\text{micro}}$ ) and external surface area ( $S_{\text{ext}}$ ) were determined by the *t*-method, using a standard isotherm proposed by Gregg and Sing [18]. The total pore volume ( $V_{\text{p}}$ ) was estimated from the adsorption capacity at  $p/p^0$  of 0.98. The PW-S<sub>sg</sub> catalyst possesses higher  $S_{\text{BET}}$  and  $V_{\text{micro}}$  than the PW-S<sub>im</sub> (Table 1). Similar results were also observed by Kozhevinkova and Kozhevinkov [19].

The integrity of Keggin structure of PW was verified by FT-IR. Fig. 1 shows the FT-IR spectra of PW (Fig. 1A), silica (Fig. 1B), PW-S<sub>sg</sub> (Fig. 1C), and PW-S<sub>im</sub> (Fig. 1D). The symmetric and asymmetric vibrations of different W–O bonds are observed in the following regions of the vibration spectra: W–O<sub>d</sub> bonds (1000–960 cm<sup>-1</sup>), W–O<sub>b</sub>–W bonds (890–850 cm<sup>-1</sup>) and W–O<sub>c</sub>–W bonds (800–760 cm<sup>-1</sup>) [16]. It should be noted that in the spectral region 1000 and 1100 cm<sup>-1</sup> the heteropolyacid bands are masked by those of the silica.

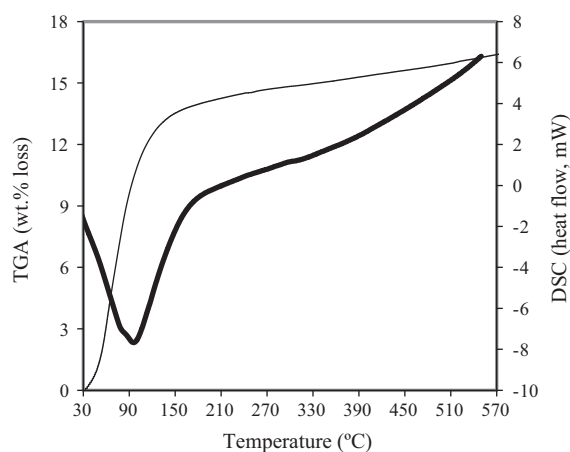
The XRD patterns of the PW, PW-S<sub>sg</sub> and PW-S<sub>im</sub> catalysts are shown in the Fig. 2. For the supported catalysts, there are no

**Fig. 2.** XRD patterns of (A) PW; (B) silica; (C) PW-S<sub>sg</sub>; (D) PW-S<sub>im</sub>.**Fig. 3.** <sup>31</sup>P solid-state MAS NMR spectrum of the PW-S<sub>sg</sub> catalyst.

evidences of crystalline phases related to the heteropolyacid, suggesting that the heteropolyacid particles are in the nano-size range and possibly well dispersed. A broad peak centered at ca. 25° 2θ (assigned to amorphous silica) is observed for PW-S<sub>sg</sub> and PW-S<sub>im</sub>. Similar results were reported by Molnár et al. [20].

The <sup>31</sup>P solid-state MAS NMR spectrum of the supported catalyst exhibits a single peak centred at ca. -15.5 ppm which corresponds to the tetrahedral coordination of PO<sub>4</sub> in the Keggin unit and indicates that the structure of the PW<sub>12</sub>O<sub>40</sub><sup>3-</sup> anion was retained during the preparation procedure (Fig. 3) [21–23]. These results are consistent with the FT-IR data.

Fig. 4 shows the TGA and DSC curves for the PW-S<sub>sg</sub> catalyst. The TGA shows a weight loss in the temperature range 30–150 °C which is probably due to the loss of physisorbed water. In fact, the DSC curve shows an endothermic peak in the same temperature range. Slight increase in weight loss from ca. 150–700 °C may be due to loss of water molecules of the hydrated catalyst, similar to that reported

**Fig. 4.** TGA and DSC curves of the PW-S<sub>sg</sub> catalyst.

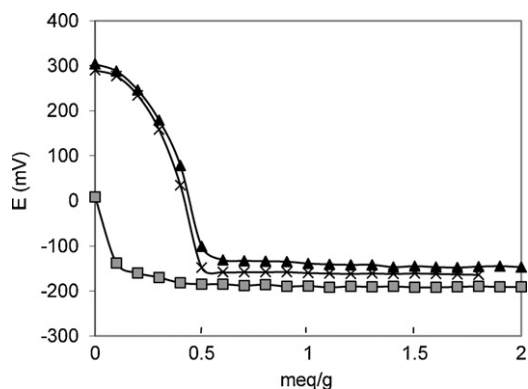


Fig. 5. Potentiometric titration with *n*-butylamine of the catalysts. (■) Silica; (▲) PW-S<sub>im</sub>; (×) PW-S<sub>sg</sub>.

in the literature for a similar type of material [19]. Although the thermal analyses do not evidence the thermal decomposition of the Keggin unit, one cannot rule out this possibility based on the literature data [19,24,25].

The acidity measurements of the catalysts were carried out by means of potentiometric titration with *n*-butylamine (Fig. 5, Table 2). The initial electrode potential ( $E_i$ ) indicates the maximum acid strength of the sites, which may be classified according to the following scale:  $E_i > 100$  mV (very strong sites),  $0 < E_i < 100$  mV (strong sites),  $-100 < E_i < 0$  (weak sites) and  $E_i < -100$  mV (very weak sites) [17]. The PW-S<sub>im</sub> catalyst shows higher maximum strength than the PW-S<sub>sg</sub> catalyst (Table 2), which may be at least partly related with differences in the amount of supported PW (Table 1).

### 3.2. Catalytic experiments

The camphene alkoxylation was carried out in the presence of PW-S<sub>sg</sub> at 60–80 °C. This reaction can be represented by Scheme 1. The protonation of camphene originates non-classical carbenium ion 2, which then undergoes a nucleophilic attack by an alcohol molecule to give alkyl isobornyl ether (3) and alkyl bornyl ether (4). Apparently, all these reactions are reversible [9,26].

In order to investigate the influence of the amount of catalyst, several experiments were set up by ranging the amount of catalyst from 0.25 to 0.75 g and the results are reflected in Fig. 6. Fig. 6A shows the effect of the PW-S<sub>sg</sub> catalyst loading on the camphene conversion. Different catalytic experiments were carried out at 80 °C. The initial concentration of camphene ( $0.10 \text{ mol dm}^{-3}$ ) was kept constant. When the catalyst loading increases, the equilibrium conversion is achieved more quickly. This can be explained due to the increase of the total number of active sites (Fig. 6A). Fig. 6B shows the initial reaction rates versus catalyst loading. It demonstrates that the rates based on the entire liquid phase volume are directly proportional to the catalyst loading. As the catalyst loading increases, the camphene conversion increases (Fig. 6A), probably due to the increasing the number of catalytic active sites.

Fig. 6C shows the effect of the amount of the PW-S<sub>sg</sub> catalyst on the selectivity to ethyl isobornyl ether. High selectivity values

Table 2

Potentiometric titration results of the catalyst sample.

Sample	Maximum acid strength (mmol/g)
Silica	0.001
PW-S <sub>sg</sub>	0.044
PW-S <sub>im</sub>	0.046

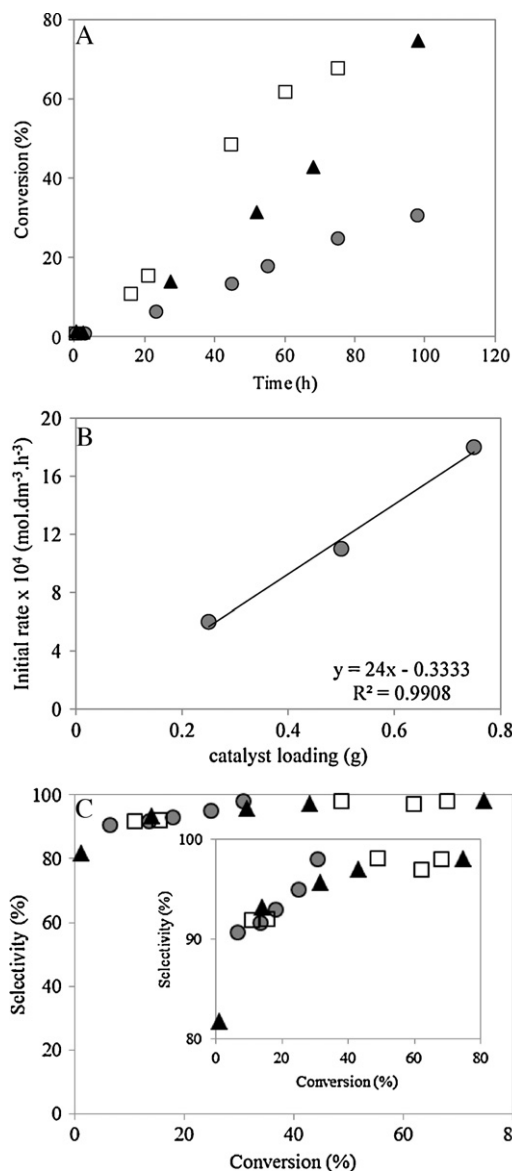
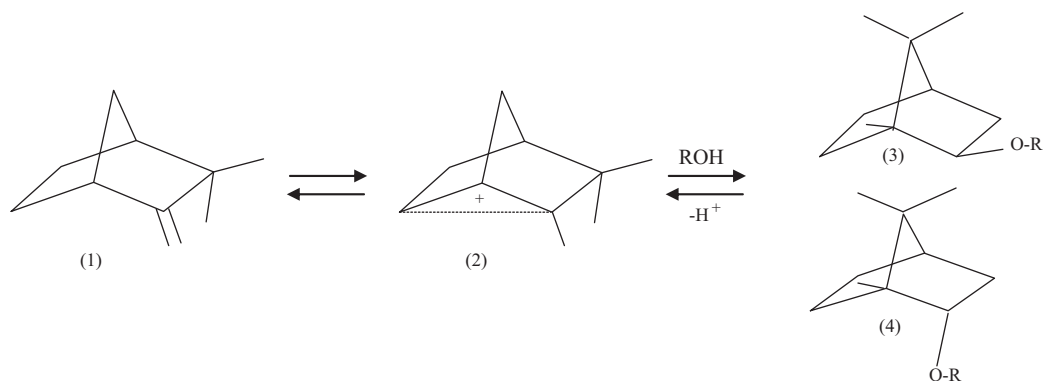


Fig. 6. Ethoxylation of camphene in the presence of PW-S<sub>sg</sub> catalyst. Effect of the catalyst loading. (A) Conversion versus time. (B) Selectivity for ethyl isobornyl ether. (●)  $m = 0.25$  g; (▲)  $m = 0.50$  g; (□)  $m = 0.75$  g. Reaction conditions: initial concentration of camphene =  $0.101 \text{ mol dm}^{-3}$ ; volume of ethanol =  $0.015 \text{ dm}^3$ ; temperature = 80 °C, amount of camphene = 1.52 mmol.

for ethyl isobornyl ether (about 95–98%) were obtained in all catalytic experiments over different PW-S<sub>sg</sub> amounts. However, the selectivity of PW-S<sub>sg</sub> catalyst decreased slightly with the amount of catalyst used in the reaction. This behavior can be explained due to the presence of high amounts of active sites, which can carry out the formation of by-products.

The effect of initial concentration of camphene on the PW-S<sub>sg</sub> catalytic activity on camphene ethoxylation was also studied. The initial concentration of camphene was varied from 0.05 to  $0.20 \text{ mol dm}^{-3}$ , while the reaction temperature ( $T = 80$  °C) and the catalyst loading ( $m = 0.5$  g) were kept constant. The results are shown on Fig. 7A. Increasing the concentration of camphene from 0.05 to 0.101 M leads to lower conversions at comparable reaction times; further increase in concentration to 0.2 M does not have a major influence on the reaction rate. Kinetic studies were carried out assuming pseudo-homogeneous reaction in an isothermal, perfectly stirred batch reactor.



Scheme 1. Alkoxylation of camphene (1).

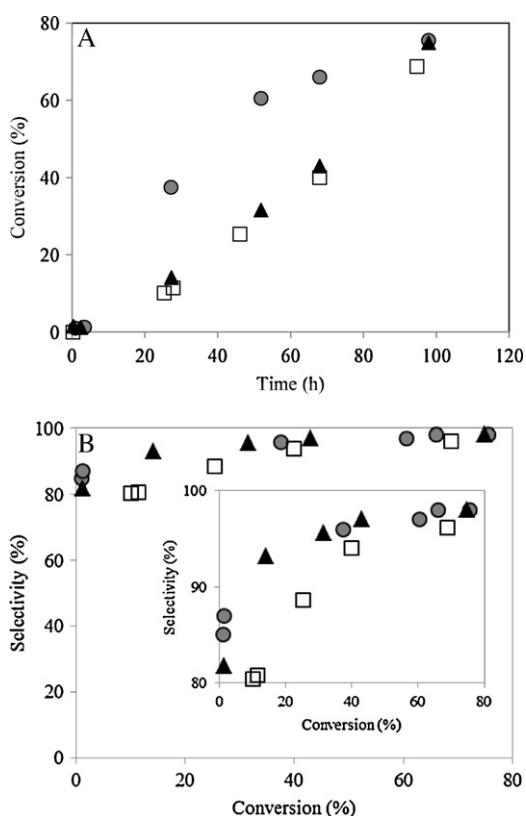


Fig. 7. Ethoxylation of camphene in the presence of PW-S<sub>sg</sub> catalyst. Effect of the initial camphene concentration. (A) Conversion versus time. (B) Selectivity for ethyl isobornyl ether. (●) C=0.050 mol dm<sup>-3</sup>; (▲) C=0.101 mol.dm<sup>-3</sup>; (□) C=0.203 mol dm<sup>-3</sup>. Reaction conditions: temperature=80 °C; catalyst loading=0.5 g, volume of ethanol=0.015 dm<sup>3</sup>.

The reaction order with respect to camphene, was determined assuming an irreversible reaction, and the rate equation:

$$-r_{\text{camphene}} = k \cdot [\text{camphene}]^\alpha \cdot [\text{alcohol}]^\beta \quad (1)$$

where  $\alpha$  is the order respecting camphene and  $\beta$  is the order respecting the alcohol. Since the alcohol was used in excess, one may assumed that the alcohol concentration remains essentially constant during the course of the reaction and Eq. (1) can be simplified to (2):

$$-r_{\text{camphene}} = k' \cdot [\text{camphene}]^\alpha \quad (2)$$

where

$$k' = k \cdot [\text{alcohol}]^\beta \quad (3)$$

The initial reaction rate is

$$-r_{\text{camphene}0} = k' \cdot [\text{camphene}]_0^\alpha \quad (4)$$

which can be represented in the following linearized form:

$$\ln(-r_{\text{camphene}0}) = \ln(k') + \alpha \cdot \ln([\text{camphene}]_0) \quad (5)$$

where the reaction order with respect to camphene is given by the slope ( $\alpha$ ).

From experimental results, the following equation was obtained,

$$\ln(-r_{\text{camphene}0}) = -8.79 + 0.68 \cdot \ln([\text{camphene}]_0) \quad (6)$$

with  $r^2 = 0.967$ .

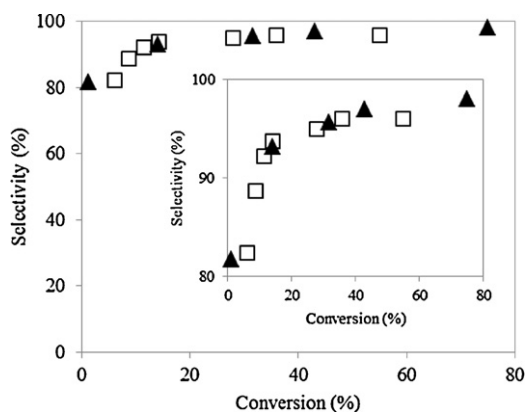
The reaction order with respect to camphene is 0.68.

High selectivity values for ethyl isobornyl ether were obtained in all reactions with different initial camphene concentration (Fig. 7B). When the initial camphene concentration increased, a decrease of the selectivity of PW-S<sub>sg</sub> for the desired product was observed. It seems that a high concentration of camphene in the vicinity of the active sites favors the formation of by-products. Similar results were also observed by Hensen et al. [27].

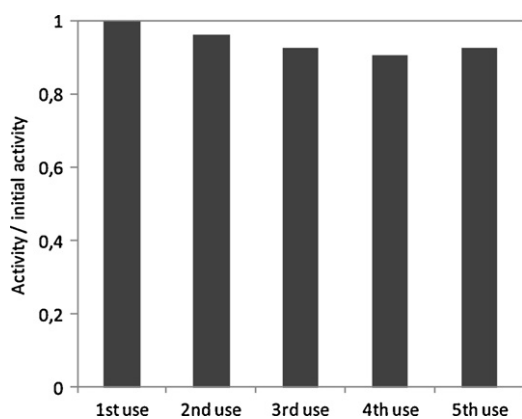
The temperature effect on the catalytic activity of PW-S<sub>sg</sub> in camphene ethoxylation was investigated by carrying out catalytic tests at 60 °C and 80 °C over PW-S<sub>sg</sub> catalyst, using the same initial concentration of camphene (0.10 mol dm<sup>-3</sup>) and the catalyst loading (m=0.5 g). As expected, the reaction carried at 80 °C was faster than at 60 °C. It was observed that the catalytic activity of PW-S<sub>sg</sub> at 80 °C is  $2.7 \times 10^{-5} \text{ mol h}^{-1} \text{ g}_{\text{cat}}^{-1}$ , and at 60 °C is  $1.8 \times 10^{-5} \text{ mol h}^{-1} \text{ g}_{\text{cat}}^{-1}$ . Very good selectivity values at high conversions were obtained in the studied range of reaction temperatures (Fig. 8). It seems that the temperature does not affect the selectivity of PW-S<sub>sg</sub> for ethyl isobornyl ether.

In order to study the catalytic stability of the PW-S<sub>sg</sub> on ethoxylation of camphene, consecutive batch runs with the same catalyst sample, under similar reaction conditions were carried out. The catalytic activity of PW-S<sub>sg</sub> catalyst decreased slightly from the first to fifth used (Fig. 9). This behaviour could be explained due to some adsorption of reactant and/or products on active sites of the catalyst. It was also observed that the selectivity for ethyl isobornyl ether is high, after the fifth utilization of PW-S<sub>sg</sub> (Fig. 10).

In order to examine any contribution of the homogeneous catalysis and confirm the catalyst stability, a hot-filtration experiment was performed with the catalyst sample PW-S<sub>sg</sub>. After 70 h of reaction the catalyst was separated from the reaction mixture, and its composition was followed for more 120 h. Fig. 11 compares the camphene concentration profiles obtained for the hot-filtration experiment and the normal catalytic experiment, both performed with the same catalyst sample. No further substrate conversion

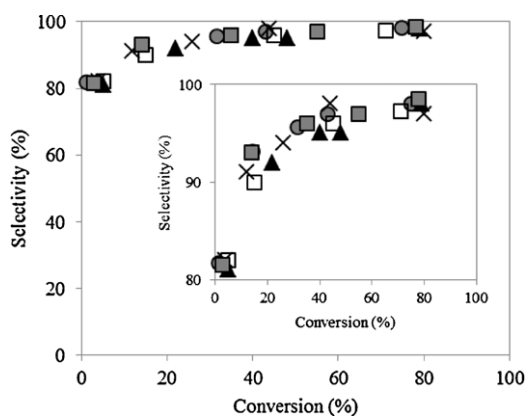


**Fig. 8.** Ethoxylation of camphene in the presence of PW-S<sub>sg</sub> catalyst. Selectivity for ethyl isobornyl ether. Effect of the reaction temperature. (▲)  $T=80^{\circ}\text{C}$ ; (□)  $T=60^{\circ}\text{C}$ . Reaction conditions: initial concentration of camphene =  $0.101\text{ mol}\cdot\text{dm}^{-3}$ ; catalyst loading =  $0.5\text{ g}$ , volume of ethanol =  $0.015\text{ dm}^3$ , amount of camphene =  $1.52\text{ mmol}$ .

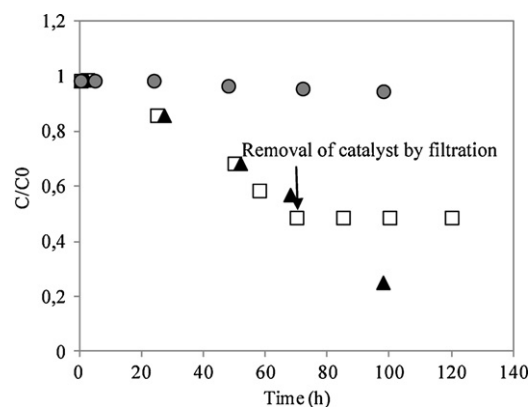


**Fig. 9.** Stability studies on PW-S<sub>sg</sub> catalyst sample on ethoxylation of camphene. Initial activities taken as the maximum observed reaction rate, calculated from the maximum slope of the camphene kinetic curve. Reaction conditions: initial concentration of camphene =  $0.101\text{ mol}\cdot\text{dm}^{-3}$ ; temperature =  $80^{\circ}\text{C}$ ; catalyst loading =  $0.5\text{ g}$ , volume of ethanol =  $0.015\text{ dm}^3$ , amount of camphene =  $1.52\text{ mmol}$ .

was observed in this experiment, which shows that the reaction occurs by heterogeneous catalysis and homogeneous catalysis does not play any significant role in our system, implying the absence of substantial PW leaching from silica under reaction conditions



**Fig. 10.** Stability studies on PW-S<sub>sg</sub> catalyst sample on ethoxylation of camphene. Selectivity for ethyl isobornyl ether. (●) 1st use; (□) 2nd use; (▲) 3rd use; (×) 4th use; (■) 5th use. Reaction conditions: initial concentration of camphene =  $0.101\text{ mol}\cdot\text{dm}^{-3}$ ; temperature =  $80^{\circ}\text{C}$ ; catalyst loading =  $0.5\text{ g}$ , volume of ethanol =  $0.015\text{ dm}^3$ , amount of camphene =  $1.52\text{ mmol}$ .



**Fig. 11.** Camphene concentration profile obtained for the blank experiment compared to that obtained with the catalyst sample PW-S<sub>sg</sub>. (□) hot-filtration test; (▲) normal experiment; (●) without catalyst experiment. Reaction conditions: initial concentration of camphene =  $0.101\text{ mol}\cdot\text{dm}^{-3}$ ; temperature =  $80^{\circ}\text{C}$ ; catalyst loading =  $0.5\text{ g}$ , volume of ethanol =  $0.015\text{ dm}^3$ , amount of camphene =  $1.52\text{ mmol}$ .

used. After reaction, the amount of the tungsten present in PW-S<sub>sg</sub> catalyst was determined by ICP. It was observed that the catalyst (PW-S<sub>sg</sub>) lost only 1% of the heteropolyacid. When the ethoxylation of camphene was carried out in the absence of catalyst, no camphene conversion was observed (Fig. 11).

The catalytic activity of PW-S<sub>sg</sub> on the camphene ethoxylation was compared with that of PW-S<sub>im</sub>. The initial activity was calculated as the maximum slope of the experimental kinetic curve of camphene divided by the catalyst amount. Table 3 shows the initial catalytic activity of PW-S<sub>sg</sub> and PW-S<sub>im</sub> at  $80^{\circ}\text{C}$ . It was observed that the activity of PW-S<sub>sg</sub> is higher than PW-S<sub>im</sub>, which may be due to the differences in texture properties (higher surface area and microporous volume in the former case, Table 1); the differences in catalytic activity do not correlate with the similar acid properties of the catalysts (Table 2 and Fig. 5). Similar results were reported by Molnar et al. [20] in the ester hydrolysis over heteropolyacids immobilized on a silica matrix. The selectivity of PW-S<sub>im</sub> catalyst to ethyl isobornyl ether is about 97%, at 78% of camphene conversion. After reaction, the amount of PW immobilized on silica was determined by ICP. It was observed that the catalyst (PW-S<sub>im</sub>) lost 20% of the initial amount of heteropolyacid.

The reaction can be carried out with other alcohols to obtain the corresponding alkyl isobornyl ethers. These ethers are also useful as fragrances similar to compound 3 (Scheme 1). Table 3 shows the catalytic activity of PW-S<sub>sg</sub> as catalyst in alkoxylation of camphene with different alcohols (methanol (C1), ethanol (C2), 1-propanol (1-C3), 2-propanol (2-C3), 1-butanol (1-C4) and 2-butanol (2-C4)) carried at  $60^{\circ}\text{C}$ . The catalytic activity decreased with the increase of the number of carbon atoms in the chain alcohol. These results may be due to diffusion limitations inside the pore structure of the catalyst, once it has been expected that in an electrophilic addition the longer-chain alcohols would be more reactive. Possibly, steric hindrance in the silica-occluded heteropolyacid pore structure is important in the case of longer-chain alcohols and the transition states do not easily form. The catalytic activity decreased from linear alcohols (1-propanol and 1-butanol) to branched alcohols (2-propanol and 2-butanol). This behavior can be also due to the presence of strong diffusion limitations of 2-propanol and 2-butanol inside porous system of the catalyst. A similar result was observed by Hensen et al. [27], in alkoxylation of limonene over beta zeolite.

Fig. 12 shows the selectivity for alkyl isobornyl ether obtained by reaction between camphene and various alcohols, in a batch reactor. For the tested alcohols high selectivity towards alkyl isobornyl ether were obtained. However, by increasing the chain length

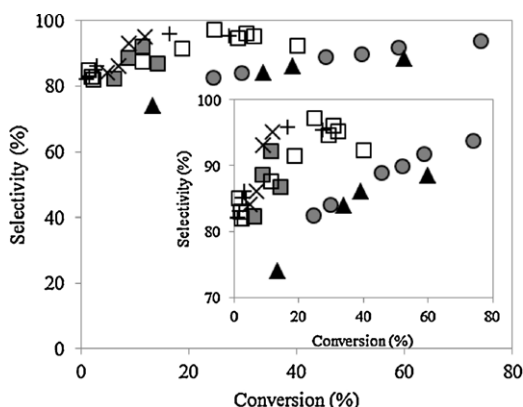
**Table 3**  
Alkoxylation of camphene in the presence of PW-S<sub>sg</sub> and PW-S<sub>im</sub> catalysts.<sup>a</sup>

Camphene (mmol)	Alcohol (mol)	Catalyst amount (g)	T (°C)	Time (h)	Conversion (%)	Selectivity to 3 (%)	Activity × 10 <sup>5</sup> (mol/h g <sub>cat</sub> )
1.52	Ethanol (0.26)	0.5 <sup>b</sup>	80	98	75	98	2.7
1.52	Methanol (0.35)	0.5 <sup>b</sup>	60	70	74	94	3.3
1.52	Ethanol (0.26)	0.5 <sup>b</sup>	60	98	60	88	1.8
1.52	1-propanol (0.20)	0.5 <sup>b</sup>	60	167	40	92	1.2
1.52	2-propanol (0.20)	0.5 <sup>b</sup>	60	189	28	95	0.27
1.52	1-butanol (0.16)	0.5 <sup>b</sup>	60	73	14	86	0.6
1.52	2-butanol (0.16)	0.5 <sup>b</sup>	60	131	12	95	0.3
1.52	Ethanol (0.26)	0.5 <sup>c</sup>	80	98	75	98	1.9

<sup>a</sup> Reaction conditions: initial concentration of camphene = 0.101 mol dm<sup>-3</sup>; temperature = 60 °C; catalyst loading = 0.5 g, volume of alcohol = 0.015 dm<sup>3</sup>.

<sup>b</sup> PW-S<sub>sg</sub> catalyst.

<sup>c</sup> PW-S<sub>im</sub> catalyst.



**Fig. 12.** Alkoxylation of camphene in the presence of PW-S<sub>sg</sub> catalyst. Selectivity for alkyl isobornyl ether. Effect of different alcohols. (●) Methanol; (▲) Ethanol; (□) 1-propanol; (+) 2-propanol; (■) 1-butanol; (×) 2-butanol. Reaction conditions: initial concentration of camphene = 0.101 mol dm<sup>-3</sup>; temperature = 60 °C; catalyst loading = 0.5 g, volume of alcohol = 0.015 dm<sup>3</sup>, amount of camphene = 1.52 mmol.

(more than two carbon atoms) of the linear alcohols, a decrease of selectivity was observed possibly due to steric hindrance effects discussed above [27].

Table 3 summarizes the results of camphene alkoxylation to give alkyl isobornyl ether (compound 3, Scheme 1) in the presence of PW-S<sub>sg</sub> at 60–80 °C.

#### 4. Conclusions

The alkoxylation of camphene with C<sub>1</sub>–C<sub>4</sub> alcohols (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol and 2-butanol) to alkyl isobornyl ether was successfully carried out in the presence of silica-occluded H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>. The alkyl isobornyl ethers are flavours and fragrances for perfume and cosmetic products, starting from a renewable biomass-based substrate.

The catalytic activity decreases with the increase of chain length of the linear alcohols, which can be explained due to the presence of diffusion restrictions in the porous system of catalyst and sterical hindrance.

High selectivity for alkyl isobornyl ether was obtained in the presence of silica-occluded heteropolyacid.

The catalyst (PW-S<sub>sg</sub>) can be recovered and reused without loss of activity and selectivity. The stability of PW-S<sub>sg</sub> catalyst towards metal leaching (less than 1%) is much greater than that of PW-S<sub>im</sub> which lost 20% of its initial amount of heteropolyacid, during the catalytic reaction.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcata.2012.11.007>.

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