Alkoxylation of camphene over silica-occluded tungstophosphoric acid

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ABSTRACT

Silica-occluded tungstophosphoric acid (PW-S_{sg}) 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_1–C_4 alcohols (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol and 2-butanol) to alkyl isobornyl ether was studied in the presence of PW-S_{sg} (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_{sg} 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_{sg} 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_{sg} was compared with the activity of tungstophosphoric acid immobilized on silica by impregnation method (PW-S_{im}). The activity of PW-S_{sg} is higher than that of PW-S_{im} catalyst. After reaction, the PW-S_{im} 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 Brönsted 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^2/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 α-pinene [7–9], limonene [10] and camphene [11], isomerization of α-pinene [12], acetoxylation of α-pinene [9], limonene [9] and camphene [13], cyclization of pseudoionone [14] and methoxylation of α-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 α-pinene [15]. The catalyst PW2_S (silica-occluded tungstophosphoric acid, with $0.042\,g_{PW}/g_{silica}$) 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_{sg}). Different parameters, such as initial concentration of camphene, temperature and catalyst loading are optimized. The catalytic stability of PW-S_{sg} is also studied. The catalytic activity of PW-S_{sg} is compared with that of tungstophosphoric acid immobilized on silica by impregnation method (PW-S_{im}).

2. Experimental

2.1. Catalyst preparation

Tungstophosphoric acid (denoted PW, Aldrich) was immobilised 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 (5.0×10^{-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_{sg}. 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 cm³ of PW (Aldrich, m = 0.1 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_{im}.

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 Kα radiation, nickel filter, 30 mA and 40 kV in the high voltage source, between 5° and 70° of 2θ at a scanning rate of 1° min⁻¹.

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⁻¹ in the range of 400–4000 cm⁻¹, and running 1000 scans.

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

The ³¹P 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⁻¹, 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 cm³ 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_{sg} 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_{sg}. 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 × 0.25 mm DB-1 column and a flame ionization detector.

The products were identified by gas chromatography mass spectrometry (GC–MS) using a FISONS MD800 (Leiccstershire, UK) instrument, equipped with a 30 m × 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⁻¹ to 128 °C and ramp at 10 °C min⁻¹ 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.

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

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

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

3. Results and discussion

3.1. Catalysts characterization

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