



Heteropoly acid catalysts in upgrading of biorenewables: Cycloaddition of aldehydes to monoterpenes in green solvents



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ABSTRACT

Acidic Cs salt of tungstophosphoric heteropoly acid, Cs_{2.5}H_{0.5}PW₁₂O₄₀ (CsPW), is excellent solid acid catalyst for liquid-phase cycloaddition reactions of biomass-based and easily available from essential oils monoterpene compounds, such as limonene, α -terpineol, α -pinene, β -pinene and nerol, with aldehydes, including benzaldehyde, crotonaldehyde as well as biomass-derived cuminaldehyde and *trans*-cinnamaldehyde. The reactions give oxabicyclo[3.3.1]nonene compounds potentially useful for the fragrance and pharmaceutical industries in good to excellent yields. The process is environmentally benign and can be performed in biomass-derived solvent 2-methyltetrahydrofuran and eco-friendly “green” organic solvents such as dimethylcarbonate and diethylcarbonate under mild conditions at low catalyst loadings without leaching problems. The solid CsPW catalyst can be easily separated from the reaction media and low-boiling solvents can be removed by distillation. Silica-supported H₃PW₁₂O₄₀ also demonstrated good performance in these reactions.

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1. Introduction

Mitigating the environmental impact of industrial chemical processes is one of the main topics in modern chemistry, in particular, catalytic chemistry. Although the use of catalytic rather than stoichiometric reactions is already among the requirements of green organic synthesis, the development of environmentally benign catalytic processes remains a challenge. In this connection, the use of renewable reagents and non-toxic biodegradable solvents (or no solvent at all) as well as heterogeneous catalysis, which allows facile catalyst separation and reduction of waste, is particularly important for the design of sustainable eco-friendly catalytic processes.

Numerous terpenic compounds found in essential oils (often as main constituents) are widely used in the fragrance, pharmaceutical and cosmetic industries [1–3]. Besides, terpenes can be chemically transformed into value-added products and therefore represent an abundant feedstock of renewable biomass-based substrates for chemical industry [1–8]. A variety of chemical reactions has been used for the catalytic upgrading of terpenes, such as hydroformylation, oxidation, epoxidation and hydrogenation

[4–8]. Acid-catalyzed transformations can also lead to various useful commercial chemicals starting from terpenes [6,9,10]. Most of these processes still use large amounts of mineral acids as catalysts and operate under homogeneous conditions with serious corrosion and waste problems.

Heteropoly acids (HPAs) due to their unique properties represent an attractive and environmentally friendly alternative to conventional acid catalysts such as mineral acids, ion-exchange resins, zeolites and clays [11–13]. First few examples of the application of heteropoly compounds (HPCs) for the transformations of terpenes were published in the 1990s [14–16]. Over the last decade, the interest to this promising topic has greatly increased [13]. HPAs usually show better catalytic activity and selectivity than the conventional acid catalysts and allow for higher turnover numbers to be obtained due to their stronger acidity. The important advantage of using HPAs in catalysis is the possibility to create heterogeneously-catalyzed processes in both non-polar and polar media. In non-polar solvents HPAs are insoluble and can be used directly as bulk and supported catalysts, e.g., HPA/SiO₂. In polar solvents, such as water, lower alcohols, acetone, etc., HPAs themselves are highly soluble; however, their acidic salts with large monovalent cations such as Cs_{2.5}H_{0.5}PW₁₂O₄₀ (CsPW) are insoluble and can be applied as heterogeneous acid catalysts. CsPW, possessing strong Brønsted acidity, large surface area and high thermal sta-

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bility, has been successfully used as a solid acid catalyst in several liquid-phase organic reactions [17–22].

Previously, we have applied HPCs as catalysts in various liquid-phase catalytic reactions of terpenes such as isomerization [21,23–26], etherification/esterification [27–29] and coupling with aldehydes [30,31]. In most of these reactions, HPCs have been used as heterogeneous catalysts in appropriate solvents; some of these reactions have been run under solvent free conditions [26], which is the most desirable within the green chemistry concept. As terpenes are highly reactive under acidic conditions, the use of solvents is usually required to avoid product and/or substrate oligomerization. Moreover, the reactions can be strongly dependent on the solvent nature, for example, α -pinene oxide isomerization [24] and coupling of terpenes with aldehydes [30,31].

The use of HPCs as catalysts for cycloaddition of aldehydes to terpenes has first been disclosed in our recent reports [30,31]. This chemistry represents a promising approach to the synthesis of oxygen-containing heterocyclic compounds [10,32–36], in particular, fragrance bicyclic ethers with oxabicyclo[3.3.1]nonene units [33,34,37]. The latter have attracted much attention as ligands for estrogen receptors involved in many physiological processes, e.g., cell growth regulation. Among the solvents used in the reactions of terpenes with aldehydes, satisfactory results have so far been obtained only in toxic and rigorously regulated solvents such as dichloromethane and 1,2-dichloroethane [30–35]. For this reason, our recent studies have been aimed at the search for environmentally friendly reaction media to substitute the chlorinated solvents. Another aim is to extend the scope of substrates to biorenewable aldehydes, i.e., to create processes in which both reagents are derived from biomass.

Recently, organic carbonates, in particular diethylcarbonate DEC and dimethylcarbonate (DMC), have attracted significant interest as green reagents and solvents in organic synthesis due to their biodegradability and low toxicity [38–40]. The production of DEC and DMC does not involve harmful reagents and their degradation does not produce toxic waste or emission of volatile organic compounds as their building block is carbon dioxide. DEC and DMC are both aprotic, weakly basic and low polar solvents (dielectric constant, $\epsilon = 2.8$ for DEC and 3.1 for DMC). Also they have relatively low boiling points compared to other organic carbonates, which allows for their easy distillation from reaction media (b.p. = 126 °C for DEC and 90 °C for DMC).

Here, we describe the cycloaddition reactions of monoterpenes with a series of aldehydes in the presence of silica-supported tungstophosphoric acid $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (HPW) and bulk CsPW as heterogeneous catalysts. Along with conventional 1,2-dichloroethane, these reactions were performed in non-toxic biodegradable “green” organic solvents such as diethylcarbonate and dimethylcarbonate, as well as biomass-derived 2-methyltetrahydrofuran (MeTHF). The following monoterpenes and monoterpene alcohols were used as the substrates: limonene (**1**), α -terpineol (**2**), α -pinene (**3**), β -pinene (**4**), linalool (**5**) and nerol (**6**). As the aldehydes, biomass-derived cuminaldehyde (**7**) and *trans*-cinnamaldehyde (**8**), available from essential oils of eucalyptus and cinnamon, respectively, were used along with crotonaldehyde (**9**) and benzaldehyde (**10**).

2. Experimental

2.1. Chemicals

All chemicals used for the preparation of catalysts and catalytic tests as well as reaction substrates were acquired from Aldrich, except Aerosil 300 silica, which was from Degussa.

2.2. Characterization techniques

The catalysts were characterized by ^{31}P MAS NMR (Bruker Avance DSX 400 NMR, room temperature, spinning rate of 4 kHz, 85% H_3PO_4 as the reference), X-ray diffraction (XRD, Rigaku Geigerflex-3034 diffractometer with $\text{CuK}\alpha$ radiation) and nitrogen physisorption (Micromeritics ASAP 2010 instrument). The content of tungsten and phosphorus in the catalysts was determined by inductively coupled plasma atomic emission spectroscopy (ICP) on a Spectro Ciros CCD instrument.

2.3. Catalyst preparation and characterization

Silica-supported $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (HPW/ SiO_2) was prepared by wet impregnation of Aerosil 300 (BET surface area of $300 \text{ m}^2 \text{ g}^{-1}$) with an aqueous HPW solution and dried at 130 °C/0.2–0.3 Torr for 1.5 h, as described previously [41]. The BET surface area of the prepared catalyst was $200 \text{ m}^2 \text{ g}^{-1}$, the pore volume $0.53 \text{ cm}^3 \text{ g}^{-1}$ and the average pore diameter 144 Å. The ^{31}P MAS NMR spectrum of HPW/ SiO_2 showed only one peak at ca. –15 ppm, characteristic of HPW [42]. As shown by XRD, only a small amount of HPW crystalline phase was present on the catalyst surface, with most of HPW being finely dispersed. The HPW content in the catalyst was 20 wt%.

$\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ (CsPW) was synthesized by dropwise addition of aqueous solution of cesium carbonate (0.47 M) to aqueous solution of HPW (0.75 M) at room temperature with stirring, as described previously [43]. The precipitated CsPW was aged in the aqueous mixture for 48 h at room temperature and dried in a rotary evaporator at 45 °C/3 kPa than in an oven at 150 °C/0.1 kPa for 1.5 h. The BET surface area of the prepared catalyst was $111 \text{ m}^2 \text{ g}^{-1}$, the pore volume $0.07 \text{ cm}^3 \text{ g}^{-1}$, and the average pore diameter 24 Å. The acid properties of the prepared catalysts, CsPW and HPW/ SiO_2 , have been studied calorimetrically by ammonia and pyridine adsorption and discussed previously [44,45].

2.4. Catalytic reactions

The catalytic tests were run under air in a 10 mL glass reactor equipped with a reflux condenser to avoid solvent evaporation. In a typical run, a mixture of the substrate (0.45–1 mmol), aldehyde (0.45–1.50 mmol), dodecane (GC internal standard, 0.30 mmol) and the catalyst HPW/ SiO_2 (10–20 mg, 0.70–1.40 μmol of HPW) or CsPW (10–30 mg, 3.0–9.0 μmol), in a specified solvent (3.0 mL) was magnetically stirred at 25–80 °C for a specified time. The reaction mixture was periodically analyzed by gas chromatography (GC, Shimadzu 17 instrument, Carbowax 20 M capillary column, flame ionization detector). Conversions and selectivities presented were obtained by GC and calculated based on the monoterpene substrate (limiting reagent) using dodecane as the internal standard. The difference in mass balance (if any) was attributed to high-boiling products (probably oligomers which could not be detected by GC). In order to control any contribution of homogeneous reactions and catalyst leaching, the catalyst was separated from the reaction mixture by centrifugation (20 °C, 18,000 rpm) and the reaction was allowed to proceed with another portion of monoterpene substrate. The lack of additional substrate conversion indicated the absence of any significant catalyst leaching. In addition, the tungsten content in supernatants was analyzed by atomic absorption spectroscopy (Hitachi-Z8200 spectrometer).

Reaction products were isolated by a column chromatography (silica gel 60) using mixtures of hexane and ethyl acetate as eluents and identified by GC–MS (Shimadzu QP2010-PLUS spectrometer, 70 eV), ^1H , and ^{13}C NMR (Bruker 400 MHz spectrometer, CDCl_3 , TMS).

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