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A Comparative Study of Solvent-Free and Highly Efficient Pinene Hydrogenation over Pd on Carbon, Alumina, and Silica Supports

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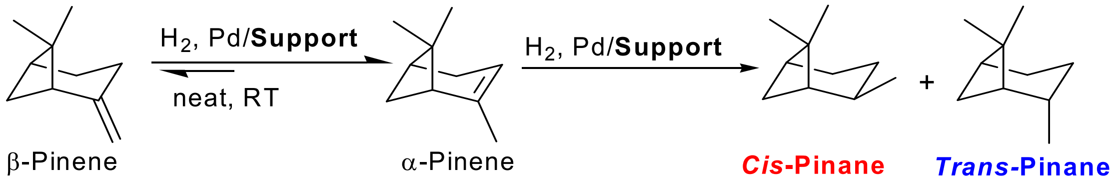
TABLE OF CONTENTS GRAPHIC



Support			Nb of Cycles
Charcoal	72	28	13
Alumina	78	22	14
Silica	88	12	01

ABSTRACT: Solvent free catalytic hydrogenation of pinene over Pd on carbon, alumina, and silica supports were compared. Despite the absence of solvent, Pd catalyst on all three supports yields to a quantitative conversion of pinene to pinanes and a higher selectivity for the *cis* isomer (72-89%). Temperature affected similarly the selectivity of the reaction for all three catalysts in favor of the *cis*-pinane isomer. However, recycling of the Pd on the three tested supports varied greatly. If Pd/C and Pd/alumina were successfully recycled thirteen and fourteen times respectively, Pd/silica could be used only once to convert pinenes into pinanes. Remaining very effective during all thirteen cycles, Pd/C was the best catalyst/support of the three tested ones for the solvent free hydrogenation of pinene. Influence of H_2 pressure on pinene conversion rates were investigated for Pd/C catalyst. An extremely low leaching rate of palladium in pinenes and pinanes determined by ICP/MS confirmed the heterogeneous nature of this catalytic solvent free reaction. The hydrogenation reaction presented in this paper is an alternate environmental friendly pathway for pinanes synthesis.

Keywords: α-Pinene, β-Pinene, Palladium, Heterogeneous catalysis, *Cis*-Pinane, *Trans*-Pinane.

1. INTRODUCTION

Some natural hydrocarbons with specific architectures, including pinanes, are of great interest for the pharmaceutical, bio energy, fine chemistry, and flavor industry[1-5]. The low abundance of the natural *cis*-and *trans*-pinane isomers in essential oils obliges the industry to use a synthetic alternative: a metal catalytic hydrogenation of α or β-pinene, the major constituents of turpentine oil from most conifers, logically leads to the desired pinane products[6]. However, the residual metal and solvent present at the end of the reaction represent an environmental and health concern. Due to their respective toxicities, regulatory agencies worldwide may require the control and elimination of these residues especially in drugs[7]. Green chemistry tools such as reusable catalyst, green solvent or solvent-free conditions may be used to prevent contamination of the final products.

The hydrogenation of α and β-pinene is an interesting model to investigate a greener reaction to obtain pinanes exempt from metal and solvent traces. The choice of solvent is critical especially in heterogeneous catalysis hydrogenation. It dictates the reaction selectivity and activity because of its interaction with the support and/or metal and also its assistance in adsorption and desorption steps. This behavior can be explained by the polarity and the geometry of the solvent[8, 9]. While ethanol has been used as solvent in general hydrogenation reaction and especially for pinenes hydrogenation[1, 10], *n*-octane has also been investigated as an alternate solvent[11,12]. In addition to the presence of solvent traces in the pinanes, the required energy costs for the solvent's evaporation must be considered. Moreover, the relative volatility of pinanes can cause losses during the evaporation step. It would be therefore advantageous both economically and environmentally to hydrogenate pinene without solvent. The solvent-free hydrogenation in general gives an interesting result as shown by the hydrogenation of 1-butene[8] and 2-butyne-1,4-diol[13]. To our best knowledge the solvent-free hydrogenation of pinenes has never been investigated

The hydrogenation of α and β-pinene has been studied intensively in several solvents either through heterogeneous[11, 14-18] and homogeneous[1,19,20] catalysis. Several supports such as alumina[1, 14], silica[15], and carbon[11, 16] with metals such as Ni[14, 17], Rh[1], Ru[20], Pt[16] and Pd[11] have been proposed. The low cost of palladium on activated charcoal made it widely used as catalyst in classic organic reaction[21], especially for hydrogenation and isomerization of alkenes[13]. To optimize the reactivity of palladium catalyst, the metal is usually dispersed on different supports such as activated carbon, alumina, organosilicate and other metal oxides. Catalyst concentration as well as its dispersion and its specific area play a crucial role in selectivity, activity and reusability[22]. Pd supported catalyst showed good results in recent hydrogenation studies of value-added chemical products[23]. As examples we can list the selective hydrogenation of ethyl cinnamate over polysilane-supported Pd/alumina[24], acrylic acid over Pd/alumina[25], and functionalized alkenes as well as *cis*-oleic acid or squalene over ultrasmall Pd nanoparticles encapsulated within an organosilica matrix.[26-28]

Herein, we described the first solvent-free heterogeneous hydrogenation of both α and β-pinene over Pd on carbon, alumina, and silica supports. The effects of pressure as well as reaction time and temperature were investigated.

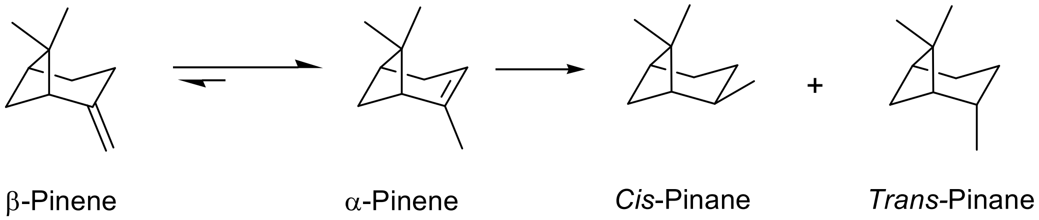
2. EXPERIMENTAL SECTION

β- and α-Pinene were purchased from Aldrich and Alfa Aesar. Palladium on carbon and alumina were purchased from Aldrich. Palladium on silica ‘’SiliaCat Pd(0)’’ was purchased from Silicycle Inc. H_2 (purity ≥ 99.9%) was purchased from Praxair Canada Inc. NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer. GC-MS analysis were recorded on an Agilent 6890 Series GC System coupled to an Agilent 5973Network Mass Selective Detector and capillary column (Zebron ZB-5MS, 30m X 0.25mm X 0.25um). Palladium content (Pd) in the obtained pinanes as well as in the used catalyst were determined using the Thermo Scientific iCAP-Q inductively coupled plasma mass spectrometer (ICP/MS; Bremen, Germany) interfaced with the ASX-520 auto sampler from CETAC Technologies (Omaha, USA).

In a 45 mL autoclave equipped with a glass liner containing a stirring bar, 5 g of pinene (36.7 mmol) and 0.5 g of Pd/C (10% wt, 4.69 mmol, 0.12 eq) or Pd/Alumina (10% wt, 4.69 mmol, 0.12 eq) or Pd/Silica (5% wt, 2.34 mmol, 0.063 eq) were placed. The autoclave was purged four times with hydrogen (1.38 MPa), pressurized to 2.75 MPa, and stirred. After 4hrs, the non-consumption of hydrogen indicated the disappearance of pinene. Hydrogen was vented from the autoclave, and the reaction mixture was filtered through a celite pad to obtain the pure pinanes. At low pressure (close to 1 atm), α- or β-pinene was hydrogenated in an empty flash chromatography cartridge connected with a balloon filled with hydrogen under a vigorous stirring at room temperature.

3. RESULTS AND DISCUSSION

Over Pd/C, under 2.75 MPa and at room temperature, the conversion of β-pinene was quantitative and the selectivity of *cis*-pinane was 71% after 4 hours (Scheme 1 and Figure 1a).



Scheme 1: Reagents and conditions: H_2 (2.75 MPa or low pressure), Pd/C, or Pd/Alumina, or Pd/Silica, RT.

^{1}HNMR and GC/MS analysis showed clearly the fast isomerization of β-pinene to α-pinene which occured after only 10 min. The ratio of β-pinene was then close to 1.5% and decreased to finally disappear at the end of the reaction (Figure 1a). The yield of this multigram reaction was quantitative, the pure product was obtained after only a filtration. ^{1}HNMR analysis of the obtained pinanes did not show any traces of the starting pinene: the absence of characteristic vinylic protons peaks at 5.2 ppm (α-pinene) and 4.6 ppm (β-pinene) confirmed a complete hydrogenation after 4 hours.

When the hydrogenation was conducted under the same conditions using α-pinene instead of β-pinene as an initial reactant (Figure 1b), pinene conversion was also complete after 4 hours and lead to a slightly lower selectivity of cis-pinane (68%). A fast isomerization between α and β pinenes was also observed: after only 5 min, the equilibrium between α and β isomers was reached and a 1.5% ratio of β-pinene was measured. Both α and β pinenes disappeared gradually until the complete conversion to pinanes.

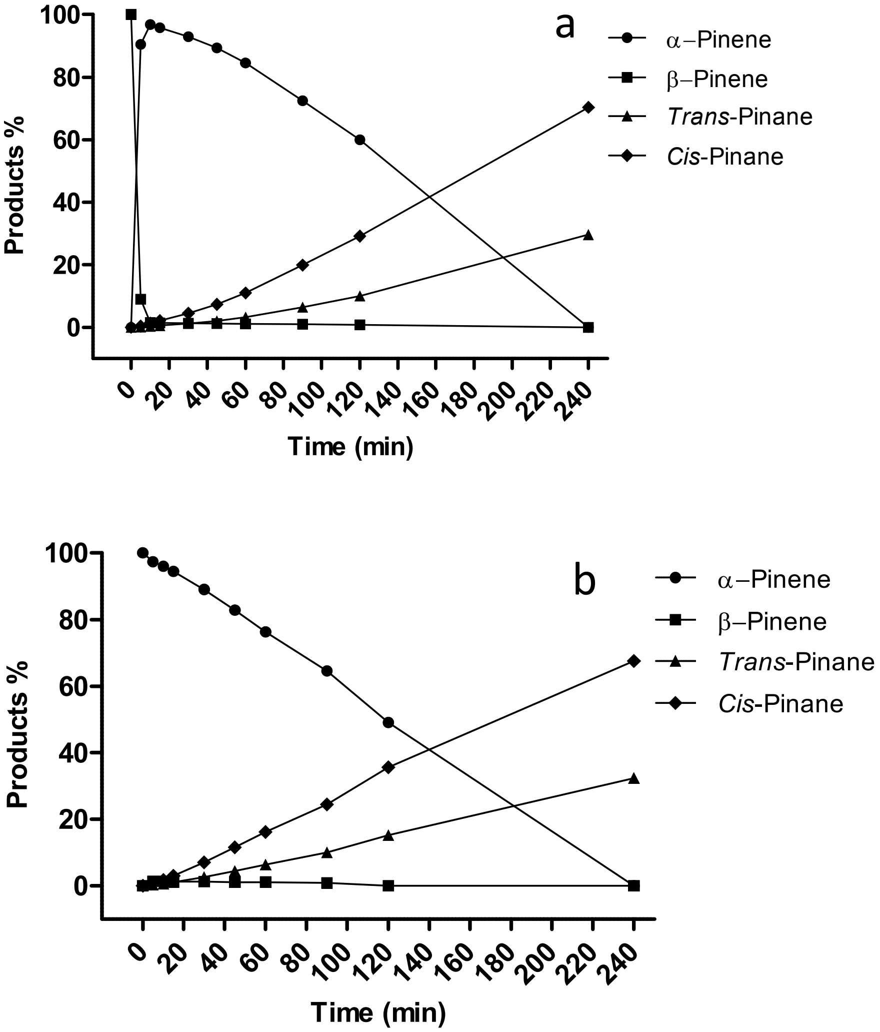


Figure 1. Hydrogenation of a) β-pinene and b) α-pinene over 10% Pd/C at 2.75 MPa and room temperature.

At a lower H_2 pressure, β and α pinenes conversion over Pd/C was slower but remained quantitative after 19 and 12 hours respectively (Figure 2). For both experiments, α and β isomerizations were slower: equilibrium at 1.5% ratio for β-pinene was reached after an hour. This ratio later slightly decreased until the reaction was complete. Hydrogenation of α and β pinenes also favored *cis*-pinane with respective selectivity of 61% and 64%. In comparison of the corresponding experiment realized at high pressure, a significant decrease of 7% was therefore observed in terms of *cis*-pinane selectivity. The selectivity of pinene asymmetric hydrogenation demonstrated to be pressure dependent. It could be affected by H_2 diffusion limitations into the liquid phase (i.e. H_2 gas-liquid mass transfer rate and access to the catalyst) as well as the sorption and by the kinetics of adsorption and desorption of both *cis/trans*-pinane from the catalytic sites[27].

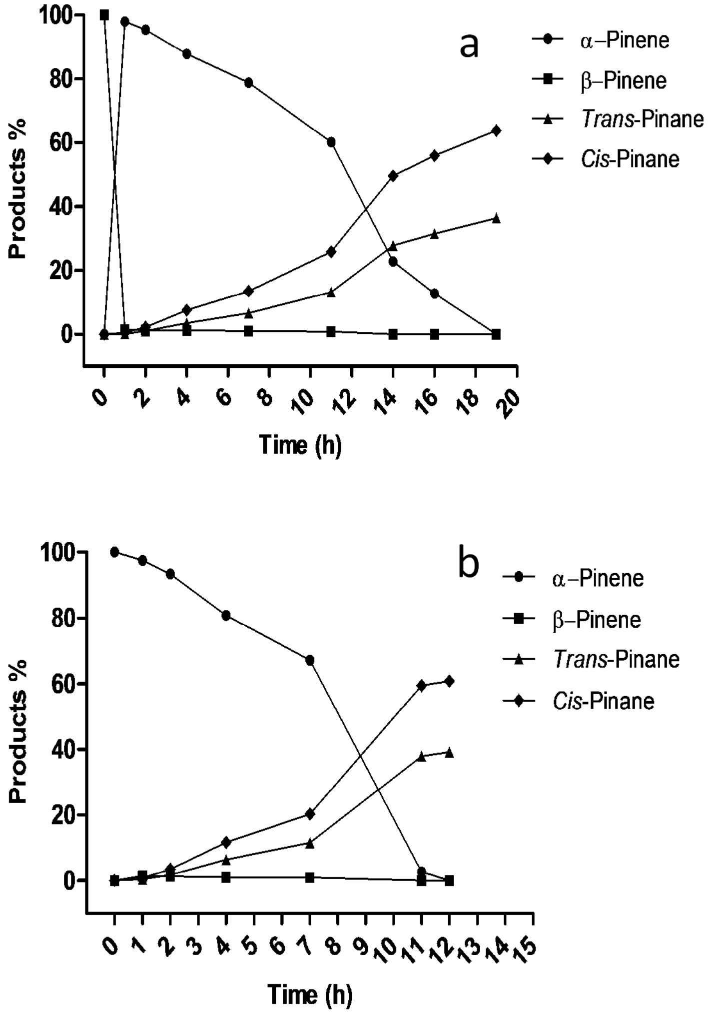


Figure 2. Hydrogenation of a) β-pinene and b) α-pinene over 10% Pd/C at low pressure and room temperature.

If all four previous time-series experiments supported the generic pinene hydrogenation mechanism (Scheme 1) with an apparent pseudo order of one for α-pinene[1], selectivities for *cis*-pinane were different, suggesting a kinetic control of this parameter. From the collected data, α-pinene conversion rates were calculated and plotted against the [*cis*-pinane]/ [*trans*-pinane] ratio, revealing a dependence between pinanes selectivity and α-pinene conversion rate (Figure 3).

Under high H_2 pressure and at the beginning of the reaction when high conversion rates were achieved, *cis*-pinane production was favored. Once the α-pinene conversion rate decreased (i.e at low H_2 pressure or towards the completion of pinene hydrogenation), cis-pinane production remained favored but to a lesser extent. Moreover, the conversion rates calculated at low and high H_2 conditions were not directly proportional to H_2 pressure suggesting that H_2 transport and sorption to the catalytic site may represent a kinetic limiting step of the proposed mechanism[29]. Further research is still needed to elucidate the kinetic parameters controlling solvent free pinene catalytic hydrogenation.

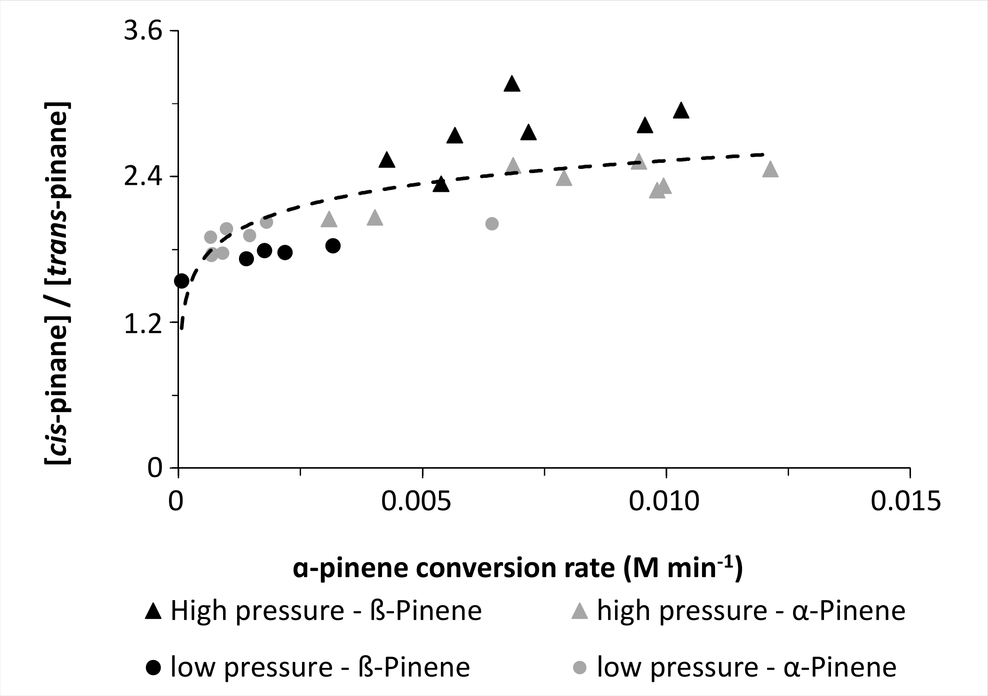


Figure 3. Pinanes selectivity vs α-pinene conversion rate measured at high (2,75 MPa) or low (≈ 0.1 MPa) H_2 pressure at room temperature.

When the hydrogenation was conducted on Pd/alumina, under 2.75 MPa and at room temperature, pinene conversion rate was comparable to the Pd/charcoal one. Hydrogenation over Pd/silica, which is made from highly dispersed Pd nanoparticles encapsulated within an organosilica matrix, under the same conditions, also lead to similar pinene conversion rate. For all three tested Pd supports, pinene isomerization was a fast process at room temperature leading to the preferential hydrogenation of α-pinene into *cis*-pinane.

The potential to recycle the Pd catalysts was tested by repeatedly adding fresh β-pinene into the reactor vessel once the hydrogenation of each cycle was complete. Pd/C was reused successfully thirteen times with no decline in activity. The *cis*-pinane selectivity increased significantly from 71% to 85% after the ninth run (Figure 4). Pd/ Alumina provided the highest selectivity and was reused for at least fourteen successive runs. However, pinene conversion decreased progressively after the fourth cycle to reach about 90% after 24 hours of reaction indicating a gradual loss of catalyst efficiency: longer reaction time were therefore applied to ensure complete hydrogenation of pinene (Figure 4). At the same concentration (10% wt, 0.235 mmol), Pd/Si was the least efficient catalyst: only 75% of pinene were converted into pinanes over 24 hrs of hydrogenation. This low activity may have resulted from a low catalyst dispersion and pinene hydrophobicity towards the silica phase. When concentration of Pd were halved (5% wt, 0.118 mmol), complete hydrogenation occured in only 4 hours. At this low concentration, the Pd/silica provided an interesting selectivity (88% for *cis*-pinane) but surprisingly we were not able to recycle this catalyst. A second hydrogenation of pinene on the same catalyst was intended and lead after 24 hrs of reaction to a mere conversion of 8% of β-pinene into pinanes. The Pd/silica catalyst became almost completely inactive after the first cycle

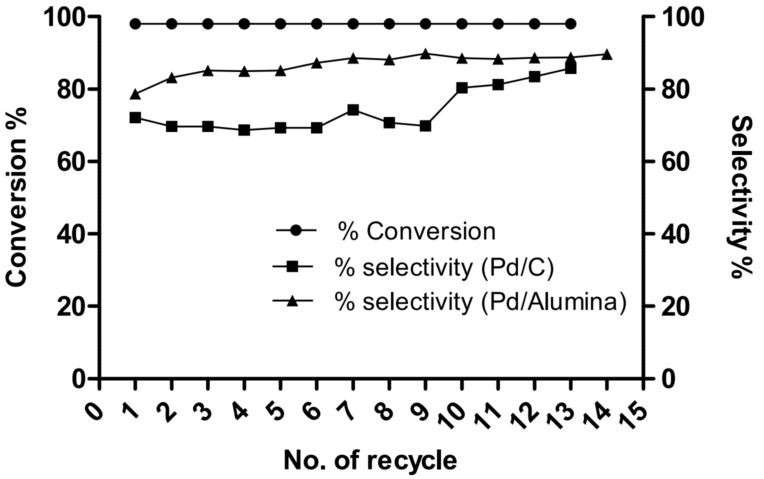


Figure 4. Catalyst recycling data for the hydrogenation of β-pinene over Pd/C and Pd/Alumina at 2.75 MPa and room temperature.

For both Pd/C and Pd/Alumina, the initial turnover frequency (TOF) was about 25 h^{-1} and significantly decreased with the number of cycles. After six cycles, TOFs were respectively about 12 and 3 h^{-1} for Pd/C and Pd/Alumina. The TOF decrease was more severe for Pd/ Alumina and reflected the longer reaction time necessary to complete pinene hydrogenation on this particular support. For this reason alone and despite a systematic lower *cis*-pinane selectivity, Pd/C was the best catalyst compared to the other two tested for pinene hydrogenation under neat conditions.

To confirm the heterogeneous nature of the catalysis, Pd leached from the Pd/C catalyst into the pinanes solution was measured by ICP/MS: it never exceeded 0.01% of the initial Pd amount throughout the 13 tested cycles. The concentrations of Pd measured in the pinanes obtained at the end of each cycle varied from <0.003 to 0.673 μg of Pd per g of produced pinanes and were extremely low compare to the quantity of Pd present in the catalyst (approx. 100 000 μg of Pd per g of Pd/C) which confirms that hydrogenation was indeed carried through heterogeneous catalysis. When the Pd/C was filtered after two hours of reaction, the hydrogenation of the filtrate without the filtered catalyst, at the same hydrogen pressure and temperature, failed which confirmed the lack of Pd catalyst in the filtrate and the heterogeneous catalytic nature of the reaction. The remaining pinene was not consumed and no additional pinanes were formed, even after 12 hrs as demonstrated by NMR and GC/MS.

For the three tested catalyst supports under neat conditions, the *cis*-pinane selectivities were within the range of the ones obtained in the presence of solvent such as ethanol[10]. In addition to the solvent choice, several other factors such as steric factor, sorption/desorption rate, pinene isomerization equilibria impacted pinanes selectivity[1]. By affecting directly the last 2 processes, the temperature is a major parameter to consider for the produced pinanes selectivity. For the 3 catalyst supports, the transformation of pinene was conducted at 0, 25 and 100 °C and pinanes selectivity was measured (Table 1). Likewise in presence of solvent, the influence of temperature on the reaction selectivity was revealed[10]: the lower the temperature was, the more *cis*-pinane was produced on the three palladised catalyst support.

α and β Pinenes exist as a mixture in natural source such as turpentine oil. From an economical point of view, the hydrogenation of a mixture could be therefore advantageous. The conversion of a mixture (1:1) of α and β pinenes was conducted over Pd/C at room temperature under 2.75 MPa: 98% of β-pinene has quickly isomerized to α-pinene and lead to a complete conversion into pinanes in less than 4 hrs. The selectivity of *cis*-pinane (68%) was similar to that obtained with the hydrogenation of α-pinene under the same conditions.

Table 1. Influence of the temperature on the catalytic activity in the hydrogenation of β-pinene (P_{H2} = 2.75 MPa)

Catalyst	*cis*/*trans*[a] at 0 °C	*cis*/*trans*[a] at 25 °C	*cis*/*trans*[a] at 100 °C
Pd/C[a]	81/19	72/28	65/35
Pd/alumina[a]	94/6	78/22	78/22
Pd/silica[a]	94/6	88/12	80/20

[a]Selectivity in final product evaluated by GC/MS analysis after 4h of hydrogenation.

The hydrogenation was also realized using turpentine oil. Under the same conditions, a complete pinene conversion and comparable *cis*-pinane selectivity (71%) were observed. The pinane obtained from α/β pinenes was tested as a bio-based alternative solvent for the extraction of natural products. The *cis*-rich pinane extracted a higher amount of carotenoids from carrots compared to n-hexane and also showed comparable potential to the petrochemical solvent to extract oil from rapeseeds and aromas from caraway seeds[30]. Consequently, pinanes could be an interesting solvent to replace petroleum-origin solvents for the extraction of several natural products widely used in food and pharmaceutical industry

4. CONCLUSIONS

In this study, for the first time a solvent free hydrogenation of α and β-pinene over Pd on various supports was investigated. Under neat conditions, pinene hydrogenation was proven to be a heterogeneous catalytic reaction through an isomerization to a predominantly α-pinene and produced a *cis*-pinane enriched mixture up to 89% at room temperature. As in the presence of a solvent, the hydrogenation was pressure and temperature dependent in term of efficiency and selectivity. The catalyst support was also crucial under neat condition, Pd/silica was active for only a single cycle while Pd/C and Pd/alumina were recycled thirteen and fourteen times respectively.

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Notes

The authors declare no competing financial interest.

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