A Practical Approach for Ambient-Pressure Hydrogenations Using Pd on Porous Glass


A Pd on porous glass catalyst system was used in the liquid-phase hydrogenation of terpenoid substrates with dihydrogen at room temperature and atmospheric pressure. A multitude of substances were hydrogenated selectively with yields of 90–100%. In all experiments, only C–C, C–N, and N–N double bonds were hydrogenated. Studies revealed that carbonyl and aromatic double bonds are inert towards catalytic reduction with dihydrogen under the conditions employed. In some cases, hydrogenation was accompanied by isomerization, so that treatment of β-pinene, for example, afforded isomeric α-pinene, which was subsequently hydrogenated to pinane.

Introduction

In the last years, the application of catalytic methods has increased in order to reduce production costs, minimize waste, and improve selectivities.[1] The liquid-phase hydrogenation of unsaturated compounds is an important step in the preparation of fine chemicals in different areas, such as pharmaceuticals, human and animal nutrition, or the flavor and fragrance industry.[2] Low-priced catalytic systems with simple preparation procedures are necessary for an application in modern chemistry. Different metals (e.g. Pd, Pt, Ru, Rh, Ni) can be used directly as catalysts, in complexed form or as precursors for preparation of the catalytic systems. Heterogeneous catalysts can be divided into two groups: bulk and supported catalysts. The anchoring of metals on solid supports is one of the most important methods to obtain supported catalysts. There are several advantages of heterogeneous catalysis compared to homogenous catalysis.[3] Especially important is the ease of separation of the catalyst from the reaction mixture and the temperature stability of heterogeneous systems. Temperature stability of supported catalysts is also important, as the reactions are often carried out at elevated temperatures or the preparation requires calcination steps to yield the active component in the desired oxidation state. Inorganic (silica, alumina, zeolites, nanotubes) as well as organic materials (PEG, chitin, chitosan) can serve as support materials in heterogeneous catalysis.[4] Using silica as support material is advantageous with respect to its thermal and chemical stability. The possibility for influencing the pore structure and pore size distribution during the synthesis of silica or porous glasses is another benefit for the use of silica-containing supports.[5, 6] Because of their temperature stability, inorganic supports are often used in hydrogenations at elevated temperatures in the gas phase. The supports can either be impregnated with the metal compound or the metal precursor can be fixed through anchoring groups to the surface.

The hydrogenation of terpenes is an important area of research. Terpenes are a class of natural products that can be transformed into compounds important for industrial production of pharmaceuticals, perfumes, flavors and fragrances, as well as vitamins.[1a, 2c, 7] More than 8000 terpenes and nearly 30000 terpenoids are known, and most of them occur naturally. The structure of terpenes and terpenoids is based on isoprene units, and their biosynthesis follows the so-called isoprene rule.[8] Furthermore, it is of special interest in organic chemistry to chemoselectively reduce double or triple bonds in the presence of other functional groups.[9]

Herein, we present our studies on the hydrogenation of a multitude of compounds using a catalytic system comprised of palladium on porous glass (Pd/glass). The Pd/glass catalyst is a stable system that can be prepared in a few straightforward steps. The catalyst based on the porous glass TRISOPOR as support material was previously used for hydrogenation reactions and was also found to catalyze C–C coupling reactions (Suzuki, Heck).[6, 10] In the present study, specific parameters of the support (particle and pore size, pore volume, specific surface area) were varied and the results are compared to previous findings.[6, 10][a] Also, we investigate the application of the Pd/glass catalyst in the liquid-phase hydrogenation of various substances. Most of the chosen reactants belong to the class of terpenes or contain characteristic functionalities such as C=–C (alkenyl, aryl), C=O, C=N, or N=N bonds.
Results and Discussion

The Pd on porous glass (Pd/glass) catalyst system was used in the heterogeneously catalyzed liquid-phase hydrogenation of reactants containing different types of double bonds (Tables 2 and 3). Some molecules contain aromatic double bonds in different ring systems. Thus, we were able to test the selective hydrogenation of different bonds for a broad range of molecules. The carrier material for the Pd/glass catalyst consisted of over 95% SiO\textsubscript{2} with minor impurities of Al\textsubscript{2}O\textsubscript{3}, Na\textsubscript{2}O, and K\textsubscript{2}O. The support material TRISOPOR (VitraBio GmbH, Steinach, Germany) has an average pore size of 50 nm, a particle size of 100–200 μm, and an average specific surface area of 98.2 m\textsuperscript{2} g\textsuperscript{-1}. The catalyst was prepared by a wet impregnation method, which requires subsequent calcination of the system to immobilize the Pd(OAc)\textsubscript{2} precursor on the support. Thermal treatment led to the formation of PdO (see below).\textsuperscript{8,11} Reduction of the catalyst to the correct oxidation state was carried out in situ at the beginning of the hydrogenation reactions. Hydrogenations were performed in ethyl acetate (AcOEt) as solvent with dihydrogen as the hydrogenation reagent, at room temperature and atmospheric pressure. In all experiments, only C−C, C−N, and N−N double bonds were hydrogenated; hydrogenation of carbonyl bonds and of aromatic double bonds did not take place.

X-ray photoelectron spectroscopy (XPS) was used to identify the oxidation state of palladium at the surface of the catalyst. XPS profiles for the Pd 3d core level of the catalysts, representing the three states in the preparation/reaction process (before calcination, before application, and after application) are shown in Figure 1 (see also Table 1). To identify the oxidation state of the Pd species anchored on the catalyst surface, the region in the XPS spectra representing the Pd 3d core level was analyzed by a high-resolution scan (335–343 eV). Comparison of the peak maxima for Pd 3d\textsubscript{5/2} and Pd 3d\textsubscript{3/2} is shown in Table 1.

![Scheme 1. Hydrogenation of β-pinene (8)](image)

**Scheme 1.** Hydrogenation of β-pinene (8)

![Figure 1. XPS spectra of the Pd 3d core level (E\textsubscript{g}; binding energy) for the Pd/porous glass catalyst before calcination (a), before application (b), and after application in the hydrogenation of 1 (c).](image)

![Table 1. Pd 3d core level XPS data for the catalyst used.](table)

<table>
<thead>
<tr>
<th>Pd/glass</th>
<th>Binding energy [eV]</th>
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<tr>
<td>Pd 3d\textsubscript{5/2}</td>
<td>Pd 3d\textsubscript{3/2}</td>
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<tr>
<td>before calcination\textsuperscript{[a]}</td>
<td>335.2</td>
</tr>
<tr>
<td>after calcination\textsuperscript{[b]}</td>
<td>336.1</td>
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<tr>
<td>after application\textsuperscript{[c]}</td>
<td>335.3</td>
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[a] Pd/glass (1 wt %; for spectral data, see Figure 1). [b] Calculated at 300 °C for 2 h. [c] After hydrogenation of 1 (15 mmol, 0.24 mol % Pd/glass, 60 mL ethyl acetate, room temperature, atmospheric pressure).

Compounds that need only one equivalent of dihydrogen for complete hydrogenation are shown in Table 2. Benzaldehydoxime (7) showed no conversion under the tested experimental conditions, thus implying that hydrogenation of the C−N(OH) double bond requires rigorous reaction conditions. Compounds 1–6 (Table 2) were converted quantitatively within 40 and 240 min to give the desired products in 90–100% yield.

As a model reactant, we used benzalacetophenone (1), because it contains three different types of double bonds. During our studies, different types of support materials (porous glass: TRISOPOR) were investigated using 1 as substrate. Previously published results showed that with other charges of TRISOPOR, small amounts of the hydroxy derivative (1,3-diphenylpropanol) were generated after 30 h reaction time resulting from attack of the hydroxyl on the carbonyl group.\textsuperscript{10}

The product of the hydrogenation of hydroxybenzylidenacetone (2) is the so-called "raspberry ketone", an important intermediate in the flavor and fragrances industry owing to its characteristic odor.\textsuperscript{11} The hydrogenated product of azobenzene (5) dissociates to yield aniline during the reaction because of the instability of the N−N single bond. The hydrogenation of α-pinene (4) is an important step in the production of linalool, which is an intermediate in the vitamin A synthesis.\textsuperscript{14,15} In the case of 4, a quantitative conversion was obtained after 210 min and two products, cis- and trans-pinane (4a), were observed in a ratio of 66:34, besides small amounts of bornane (selectivity < 2%). Similar results were found in previous studies.\textsuperscript{14,15} The heterogeneous hydrogenation of 4 with Pt/C, Pd/C, or Ni catalysts leads to a selectivity for cis-4a of 49–99% depending on H\textsubscript{2} pressure and the reaction temperature. In situ
reduction with hydrogen (Li/C\textsubscript{2}H\textsubscript{5}NH\textsubscript{2}) yields a product mixture that contains 56–57% of cis-4a\textsuperscript{[16]}. Verbenone (3) showed the shortest reaction time (40 min) and the best conversions under our reaction conditions. Hydrogenation afforded cis-verbenone (3a) with a selectivity of 100%, as also found previously for hydrogenations using Pt/SiO\textsubscript{2} as catalyst\textsuperscript{[17]}. In contrast to the hydrogenation of 3 with Pt/SiO\textsubscript{2}\textsuperscript{[17]} or PtO\textsubscript{2}\textsuperscript{[18]} and in accordance to the other results presented herein, longer reaction times do not lead to a reduction of the C=O group to yield verbanol. In similar fashion to the hydrogenation of 4, the formation of cis-3a is favored as a result of the less-hindered geometrical arrangement of the molecule (bulky groups are opposite the adsorption plane) on the catalyst surface\textsuperscript{[15,16]}. The higher reactivity of 3 compared to 4 is attributed to the strained ring system which is based on the carbonyl group in this molecule. In addition, \( \beta \)-pinene (8; Scheme 1) was used as a reactant. Here, a rapid and complete isomerization of 8 to 4 during the first few minutes of the reaction was observed in accordance with previous studies\textsuperscript{[10,16,19]}. No isomerization took place in the absence of hydrogen. In the second step, the intermediate 4 was hydrogenated to afford cis- and trans-4a (66:34) in 330 min with a conversion of 97%. The reason for the longer time required for quantitative hydrogenation from 4 (compared to pure 4) to cis- and trans-4a is not yet understood.

Compounds 9–15, which need one or two equivalents of dihydrogen for complete hydrogenation, are shown in Table 3. In addition to the reduction of the double bonds, isomerization hydrogenation depended on the conversion of 9.

Compounds with two double bonds, which can be hydrogenated under our reaction conditions, were also chosen as substrates. Citral (12), \( \beta \)-citronellene (13), limonene (14), and ZZ-1,5-cyclooctadiene (15) need two equivalents of molecular hydrogen for quantitative hydrogenation of their C=C double bonds. All reactants offer a broad variety of isomers and intermediates during their hydrogenation. Citral (3,7-dimethyl-2,6-octadien-1-ol) was chosen as a model compound to study the hydrogenation of \( \alpha,\beta \)-unsaturated aldehydes whereupon three double bonds could be reduced: conjugated C=C and C=O bonds, and isolated C=C double bonds\textsuperscript{[18]}. Hydrogenations of 12 were performed with a conventional available mixture of 9:1 and Z-12 (3:2). The reaction network for reduction of 12 is very complex (Scheme 3). In the first step of hydrogenation, citronellal (10) and its isomers were generated as the main intermediates\textsuperscript{[20]}. The results revealed that the hydrogenation of the \( \alpha,\beta \)-unsaturated double bond is favored and an attack of the carbonyl group did not occur. A selectivity for 10 of 78% was obtained for critral conversions of 40% (Figure 2). These results are comparable with previous findings, which reported selectivities for 10 of 70%, 88%, 68%, and 70–82% using Pd/SiO\textsubscript{2}, Pd/polymer, Pd/C, and NiB/SiO\textsubscript{2}, respectively\textsuperscript{[18,21]}. The most important product from an industrial viewpoint is 10 as it is a basic intermediate in the fine chemical industry, for example, for the production of menthol and fragrances in soaps and perfumes\textsuperscript{[22]}. After 270 min, 12 was quantitatively converted into 3,7-dimethyloctanal (10a).
The acyclic monoterpene \( \beta \)-citronellene (13) was quantitatively converted after 40 min. The terminal double bond was hydrogenated first, and during the reaction course many different isomers were formed and identified by GC-FID and GC-MS. The monocyclic terpene limonene (14) was converted after 90 min with a selectivity of 97% for the products cis- and trans-\( p \)-menthane as well as for \( p \)-cymene.\[^{10a, 23}\] Limonene (14) was first hydrogenated on the less-hindered exocyclic double bond, and in the second step the remaining double bond was reduced. Many intermediates such as terpinolene, \( p \)-1-menthene, \( p \)-3-menthene, and \( \gamma \)-terpinene were detected during the reaction. Furthermore, the hydrogenation of limonene generated the terpene \( p \)-cymene with a yield of 6%, thus offering an aromatic ring system as reaction product. A comparison with other studies revealed that the formation of \( p \)-cymene with different types of Pd-impregnated silica depends on the reaction temperature and the Pd loading.\[^{10a, 24}\] After the hydrogenation of the second double bond, a product mixture consisting of cis- and trans-\( p \)-menthane (14a) was obtained.

Cyclooctene was produced by partial hydrogenation of the twofold unsaturated ring system \( Z, Z \)-1,5-cyclooctadiene (15) with a selectivity of 95% after 90 min.
Our results are comparable with previous studies in which high cyclooctene selectivities were found but only when the reaction was carried out in a temperature regime of 40–70 °C and with a hydrogen pressure of 2–10 bar.\(^\text{[2a, 24]}\)

Cyclooctene was subsequently reduced to afford the saturated product cyclooctane (15a). In accordance with previous reports, the reaction of cyclooctene is slow compared to the formation of cyclooctene from 15.\(^\text{[15, 26]}\)

The hydrogenation of 1 (model reaction) was also used for recycling experiments. The catalyst was reused after the reaction (three reaction cycles), employing two different methods of catalyst treatment: 1) after separation of the catalyst from the reaction mixture by filtration (recovery > 96%), the spent catalyst was washed and air-dried before its reuse (Figure 3), or

2) the washed catalyst was oven-dried for 2 h at 300 °C (Figure 4). In both cases, the catalyst activity decreased significantly from the first reaction cycle to the second, but with air-drying the catalytic activity was higher (35% 1 after 210 min) than for the re-calcined catalyst (60% 1 after 210 min). Clearly, the calcination step causes a decrease in conversion of 1 during the hydrogenation because of a loss in the active surface of the catalyst owing to sintering processes in the SiO\(_2\) framework of the catalyst.

Conclusions

In summary, Pd on porous glass is an inexpensive catalyst system with a wide range of application. The advantages of this system include the simple catalyst preparation method and the mild reaction conditions used for performing selective hydrogenation reactions. Studies revealed that aliphatic C=C, C=N, and N=N bonds can be reduced with dihydrogen at room temperature and atmospheric pressure using Pd on porous glass as catalyst. Product selectivities strongly depend on the substrate used in the reaction. Nevertheless, we were able to generate selectively a multitude of different products that are important building blocks in the fine chemicals industry. The combined results indicate that the Pd on porous glass catalyst is unable to promote the attack of carbonyl bonds.

Experimental Section

General Remarks: All substrates and solvents were purchased from Sigma–Aldrich and used as received without further purification. The purity of all compounds was checked by capillary gas chromatography. Analyses of the reaction mixtures were carried out by GC-FID (HP 6890) and GC-MSD (HP 6890 N/5973 MS). GC-FID (for compounds 1–3, 5–7); HP 5, 30 m \( \times 0.25 \text{ mm} \times 0.25 \text{ μm}, \text{He 15 psi, program: } 60 \text{ °C (hold for 1 min), } 25 \text{ K}\text{min }^{-1} \text{ up to } 280 \text{ °C (hold for 12 min), detector temperature: } 280 \text{ °C, detector temperature: } 300 \text{ °C. GC-FID (for all compounds investigated): } \text{HP 5, } 30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ μm, He 15 psi, program: } 35 \text{ °C (hold for 1 min), } 4 \text{ K}\text{min }^{-1} \text{ up to } 80 \text{ °C, } 4.5 \text{ K}\text{min }^{-1} \text{ up to } 90 \text{ °C, } 35 \text{ K}\text{min }^{-1} \text{ up to } 280 \text{ °C (hold for 3 min), detector temperature: } 250 \text{ °C, detector temperature: } 280 \text{ °C. GC-MSD (for all compounds investigated): } \text{HP 5, } 30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ μm, He 7 psi, program: } 55 \text{ °C (hold for 1 min), } 5 \text{ K}\text{min }^{-1} \text{ up to } 150 \text{ °C, } 20 \text{ K}\text{min }^{-1} \text{ up to } 280 \text{ °C (hold for 5 min), detector temperature: } 280 \text{ °C, Ei (70 ev). The products were identified by comparing both their retention times and mass spectra with authentic samples. Hence, GC was used to monitor the course of the reaction. All product yields reported herein are yields determined by GC and not those of isolated compounds. Yields and conversions were calculated from the corrected peak areas using hexadecane as internal standard. All presented results are the averages of at least two experiments. XPS spectra were recorded with a Quantum 2000 (PHI Co., Chanhassen, MN, USA) apparatus with a focused mono-
Standard Preparation of Catalyst: The main component of the porous glass support TRISOPOR (VitraBio, Steinach, Germany; pore size: 50 nm, particle size: 100–200 μm) was dissolved in dichloromethane (50 mL) in a round-bottomed flask (100 mL), and the porous glass support (1 g) was then added to the mixture. After removal of the solvent in vacuo, the catalyst precursor was calcined for 2 h at 300 °C in a muffle furnace (mls 1200 pyro; MLS GmbH, Leutkirch, Germany), to afford a catalyst with a loading of 1 wt% Pd.

Experimental Setup: The selected substrate (15 mmol) and hexadecane (200 μL; internal standard) were dissolved in ethyl acetate (60 mL) and introduced into a Schlenk flask. The catalyst (400 mg; 0.24 mol%) was added, and then a sample of the reaction mixture was taken (500 μL). The Schlenk flask was connected to the dihydrogen reservoir by a plug valve, and the reaction vessel was flushed with dihydrogen (3 L/C up to 400 mL). The liquid-phase hydrogenations were repeated two times (i.e. three reaction cycles).

Recycling Experiments: After hydrogenation, the catalyst was separated from the reaction mixture by filtration and washed with ethyl acetate and ethanol. The spent catalyst system was either air-dried (Figure 3) or calcined for 2 h at 300 °C (Figure 4). These procedures were repeated two times (i.e. three reaction cycles).

Keywords: fragrances · hydrogenation · palladium · supported catalysts · terpenoids


A more detailed study including characterization of the catalyst system including TEM, TGA, and chemisorption studies is in preparation and will be presented elsewhere.


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