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Study on selectivity of β-myrcene hydrogenation in high-pressure carbon dioxide catalysed by noble metal catalysts

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Hydrogenation of monoterpenes, such as β-myrcene, in high-density carbon dioxide over 0.5 wt.% Pd, or Rh, or Ru supported on alumina was investigated. Hydrogenation catalysed by Rh and Ru is generally faster in a single supercritical (sc) phase (gaseous reagents and solid catalyst) than in a biphasic system (liquid + gas reactants + solid catalyst). The reaction catalysed by Pd occurs faster in two phases. The final composition of the reaction mixture is strongly dependent on the noble metal catalyst used for the reaction. Palladium gives mainly 2,6-dimethyloctane (≈95%), rhodium produces 2,6-dimethyloctane with a yield higher than 40%, and around 40% of 2,6-dimethyloct-2-ene, while ruthenium gives around 10% of 2,6-dimethyloctane and 50% of 2,6-dimethyloct-2-ene leaving the highest amount of unreacted β-myrcene. The Pd catalyst is highly active with an excellent selectivity in enabling the one-pot synthesis of 2,6-dimethyloctane through β-myrcene hydrogenation in the presence of $scCO_2$. The overall activity of the noble metal catalysts decreased in the order Pd > Rh > Ru. The problem of leaching of the active metal from the catalyst rod was also investigated.

Introduction

Hydrogenation of organic compounds is a process of overriding chemical importance.[1] A propitious route for the production of oxygenated derivatives commercially essential in the pharmaceutical, perfume and flavour industries begins with the hydrogenation of monoterpenes.[2] Terpenes are a significant class of naturally occurring compounds widely employed in organic synthesis either as a core of chiral auxiliaries or as starting materials for optically pure molecules or asymmetric ligands exploited in enantioselective transformations.[3]

β-Myrcene, an acyclic polyunsaturated monoterpene with three carbon–carbon double bonds, two of them being conjugated, is one of the core raw materials for the synthesis of terpene alcohols and aldehydes, which are appropriate intermediates in the production of vitamins A and E.[4]

Research on the catalytic hydrogenation of β-myrcene over Pd–charcoal, Raney® nickel and Adams platinum catalysts dates from the mid-1930s, when the partial hydrogenation of β-myrcene gave 2,6-dimethyloct-2-ene.[5] Hydrogenation of β-myrcene in ethyl acetate over Pd on a porous glass support,[6] over sol–gel Pd/SiO_2,[7] and over Ru, Cr, Ir and Rh complexes led to a complex mixture of mono-, di- and trihydrogenated products.[8] Gaseous H_2 is a relatively cheap and versatile reagent for hydrogenation, but it can be difficult to use in practice. Laboratory-scale hydrogenation is commonly slow because H_2 is scarcely soluble in most solvents. Supercritical fluids due to their complete miscibility[9] with H_2 have already been utilised[10] for hydrogenation and other related reactions. The role of the supercritical fluid is almost certainly more complex than slightly enhancing the concentration of H_2. Supercritical hydrogenation has several advantages over traditional solvent-based hydrogenation.[1a,11,12] Mass transport limitations are minimised, CO_2 reduces viscosity or increases diffusion rates compared to traditional solvents and access to catalytic centres can be enhanced. Furthermore, changing the supercritical conditions can alter the selectivity of reactions as well.[13] The disadvantage, however, is the need for specialised equipment and bulky gas cylinders.[14]

Apart from the aforementioned advantages, carbon dioxide also plays another role in supercritical hydrogenation. Hydrogen has a surprisingly low solubility in most organic solvents, whereas it is completely miscible with supercritical carbon dioxide. Thus, at a given pressure of gas the effective concentration of H_2 in a supercritical solution can be nearly an order of magnitude higher than in a conventional solvent. As a consequence, the hydrogen concentration at the catalyst surface is greatly increased, leading to extremely high reaction rates compared to the normal liquid phase operation. In addition the solvent-power of the $scCO_2$ can be easily tuned by changes in both temperature and pressure.[15]

The present work is a continuation of our previous study on the employment of supercritical carbon dioxide in the heterogeneous catalysis of monoterpenes ($C_{10}H_{16}$), such as α-pinene[16] (one carbon–carbon double bond) and limonene[13,17,18] (two carbon–carbon double bonds). The Pd[16a] and Pt[16b] catalysed hydrogenation of α-pinene turned out to be faster in a two phase system than when a single phase is in contact with the

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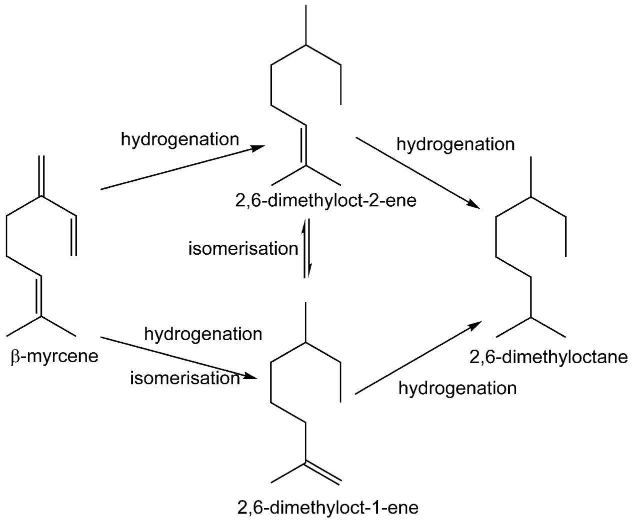
catalyst. The reaction rate was controlled by the adsorption of α-pinene at the catalyst surface.[16] Previous work published in *Green Chemistry* about the hydrogenation of limonene with different catalysts demonstrates that hydrogenation occurred rapidly in supercritical, one-phase conditions, while only one of the double bonds was selectively hydrogenated in certain conditions in a biphasic mixture.[13] Analysing the effect of the hydrogen partial pressure on Pd catalysed hydrogenation in biphasic conditions, the rate-controlling factor was found to be the concentration of limonene in the liquid phase that wets the catalyst.[17a]

Herein, we report the results of a study on the hydrogenation of β-myrcene ($C_{10}H_{16}$, three carbon–carbon double bonds) using noble metal catalysts (Pd, Ru, Rh) supported on alumina in high-density carbon dioxide. $scCO_2$ is receiving considerable and growing interest as an environmentally benign reaction medium for organic synthesis. Applications of $scCO_2$ to hydrogenation reactions involving heterogeneous catalysts[12,19] are particularly attractive. Furthermore, the careful design of solid catalysts to capitalise the unique solvent properties of $scCO_2$ may afford greater advantages, resulting in diverse activity and selectivity. The Pd catalyst was selected as the most active, while Ru and especially Rh catalysts were used to check the catalysts which were reported as less active.[20] The present investigation aims to achieve diverse selectivities dependent on the active metal used. As far as we are aware, this is the first report on hydrogenation of β-myrcene where supercritical carbon dioxide is used, either in an expanded-liquid solvent system or in a single supercritical phase. Note that whenever authors use the text term "biphasic", it means, the system contains a liquid terpene, gaseous CO_2 and H_2, and a solid catalyst. The one phase system refers to a terpene gas phase together with CO_2 and H_2, and a solid catalyst. The hydrogenation of β-myrcene involving the key compounds is presented in Scheme 1.



Scheme 1

Experimental

Chemicals: Hydrogen and carbon dioxide were supplied by Air Liquide, with a stated purity of 99.998 mol%. β-Myrcene (purity: 90%) was supplied by Fluka. 2,6-Dimethyloct-2-ene (purity > 95%), 2,6-dimethylocta-2(*Z*),6-diene (purity > 95%), 2,6-dimethylocta-2(*E*),6-diene (purity > 95%) were delivered from ChemSampCo. *Cis-p*-menthane (purity: ≥ 97%) was supplied by Fluorochem Limited, β-citronellene (purity > 98.5%) by Fluka, and 2,6-dimethyloctane (purity > 90%) by TCI Europe. β-Myrcene was purified by distillation and the final purity of β-myrcene was ≥ 99.0% as determined by GC. All the other terpenes were used as received without any further purification.

The qualitative identification of terpenes was performed by GC/TOFMS using a few representative reaction samples. The separation was performed with a 30 m × 250 μm i.d. fused silica capillary column coated with a 0.25 μm thickness film of 5% phenyl groups in the dimethylpolysiloxane (CP-Sil 8 CB) from Varian Inc. Helium was used as carrier gas at a flow rate of 1.0 mL min^{-1}. The oven temperature was programmed from 50 °C, held for 1 min, to 250 °C at 5 °C min^{-1}, held for 5 min. Injector and detector temperatures were set at 250 °C. 1 μL of sample was injected in split mode, with a split ratio of 30.

The presented retention indices (linear retention indices—LRIs) were calculated according to van den Dool and Kratz[21] using a mixture of C_8 to C_{27} hydrocarbons (AccuStandard, New Haven, CT, USA) in pentane. The hydrocarbons C_9–C_{12} were used for the calculations based on the GC/TOFMS results. The obtained LRIs were compared with the literature data (*cis-m*-menthane)[22] or predicted data (2,6-dimethyloct-4(*Z*)-ene, 2,6-dimethyloct-1-ene, 2,6-dimethyloct-4(*E*)-ene) using the method proposed by Heinzen *et al.*[23] The targeted terpenes were thus tentatively identified using the LRI calculations and matching their individual spectra with the NIST 2005 MS library using ChemStation software.[22]

Catalysts: 0.5 wt.% Pd/Al_2O_3, 0.5 wt.% Rh/Al_2O_3, and 0.5 wt.% Ru/Al_2O_3 as pellets were bought from Aldrich.

Samples of the fresh catalysts, used in the biphasic and the single phase reaction were analysed using Scanning Electron Microscopy/Energy Dispersive X-Ray Spectroscope (SEM/EDS) equipped in an Oxford light elements detector. First, the sample of the catalysts were gold coated in a Polaron E-5100 sputter coater, and then observed in a Hitachi S-2400 scanning electron microscope, using 25 kV accelerating voltage. The images of Pd, Rh and Ru on alumina catalysts are shown in Fig. 1.

Moreover, the BET apparent surface area (S_{BET}) was determined according to the BET theory using the already mentioned microscope. The S_{BET} were 170, 166, 182 m^2 g^{-1} for fresh Pd, Rh and Ru catalysts respectively. The specific surface areas of the Pd, Rh and Ru catalysts after the biphasic reactions were as follows: 140, 154, 178 m^2 g^{-1}. The BET analyses of the catalysts after a one-phase reaction gave the following results: 110, 142 and 169 m^2 g^{-1} for Pd, Rh and Ru catalysts correspondingly.

The presence of catalyst metals in the solutions was tested using the Atomic Absorption Spectroscopy (AAS) technique by means of a ThermoElectron Atomic Absorption Spectroscope S Series.

Equipment for hydrogenation: The hydrogenations were performed in an apparatus with a sapphire-windowed cell connected by a pump to a tubular reactor which encloses a catalyst. This apparatus has already been described in detail in the literature.[13,17,18] The reactants (either CO_2-expanded liquid terpene or a single supercritical phase, where liquid and gases

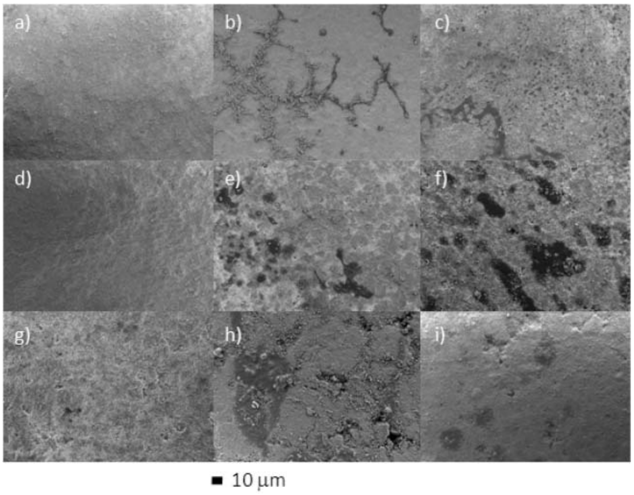


Fig. 1 The SEM images of Pd, Rh and Ru catalysts (white or grey spots) supported on alumina (darker or grey areas); (a) fresh Pd catalyst, (b) Pd catalyst after biphasic reaction, (c) Pd catalyst after single phase reaction, (d) fresh Rh catalyst, (e) Rh catalyst spent in biphasic reaction, (f) Rh catalyst after one-phase reaction, (g) fresh Ru catalyst, (h) Ru catalyst used in biphasic reaction, (i) Ru catalyst after the reaction in the single phase.

produce one gas phase) circulate continuously from the bottom of the view cell, through the catalyst bed, and back to the upper entrance of the cell. The flow rate of 3.3 mL/min employed guarantees that during 1–2 min the whole reaction mixture recirculates at least once. Due to this, the feed composition that simulates the process performed in the batch mode changes rapidly. The reaction samples were taken at regular intervals through the HPLC valve equipped with a 100 µl sampling loop. The contents of the loop were dissolved in a measured amount of pentane with nonane used as an internal standard for the sample analysis. CO_2 was vented to the atmosphere. For each reaction 1.5 g of the fresh catalyst and 2 mL of β-myrcene were used. The qualitative identification of products was based on comparisons between the obtained GC-FID LRIs and those obtained by GC/TOFMS, and authentic samples. Quantitative analysis was carried out by gas chromatography by means of a HRGC-3000C gas chromatograph. Column: 30 m × 0.32 mm i.d. fused silica capillary column coated with a 0.25 µm thickness film of 5% phenyl groups in the dimethylpolysiloxane (CP-Sil 8 CB), from Varian Inc., was used. Oven temperature program: 60-80 °C, ramp at 1 °C min^{-1}, and 80–240 °C, ramp at 20 °C min^{-1}. Injector and FID detector temperature was 250 °C. The response factor for the analysed terpenes was determined as follows: β-myrcene – 1.41, 2,6-dimethyloct-2-ene – 1.34, 2,6-dimethylocta-2(*Z*),6-diene – 1.39, 2,6-dimethylocta-2(*E*),6-diene – 1.39, *cis*-*p*-menthane – 1.44, β-citronellene – 1.35, and 2,6-dimethyloctane – 1.29. The response factors for the other identified terpenes: 2,6-dimethyloct-4(*Z*)-ene, 2,6-dimethyloct-1-ene, and 2,6-dimethyloct-4(*E*)-ene were arbitrarily judged to be at the level of 1.37, while for *cis*-*m*-menthane – 1.43.

Safety warning! The handling of pressurised gases and supercritical fluids requires the use of suitable high-pressure equipment and must be carried out under rigorous safety conditions only.

Results

Products distribution

The hydrogenation of β-myrcene was examined using Ru, Rh and Pd on alumina catalysts in CO_2. β-Myrcene and other terpenes referred to in this work are presented in Fig. 2. The hydrogenation of β-myrcene was performed either in biphasic (4 MPa of H_2 and 12.5 MPa of total pressure) or single supercritical phase (4 MPa of H_2 and 16 MPa of total pressure) conditions. Figs. 3 and 4 show the concentration profile for the products of the reaction catalysed by 0.5 wt.% Pd/Al_2O_3 in biphasic and monophasic conditions, respectively. The reaction performed in biphasic conditions (Fig. 3) in the batch mode indicates that the product distribution profile does not change after 80 min of the reaction. The highest yield of the fully hydrogenated product, 2,6-dimethyloctane (Fig. 2 structure 2), was obtained for the experimental conditions of 12.5 MPa of total pressure, with a total yield of 95%. In the initial stage of the reaction, two of the dihydrogenated products: 2,6-dimethyloct-2-ene (Fig. 2 structure 5), 2,6-dimethyloct-1-ene (Fig. 2 structure 6) are noticed in considerable quantities. Other mono- {β-citronellene (Fig. 2 structure 9)}, di- {2,6-dimethyloct-4(*Z*)-ene (Fig. 2 structure 7), 2,6-dimethyloct-4(*E*)-ene (Fig. 2 structure 8)}, fully hydrogenated {*cis*-*p*-menthane (Fig. 2 structure 3),

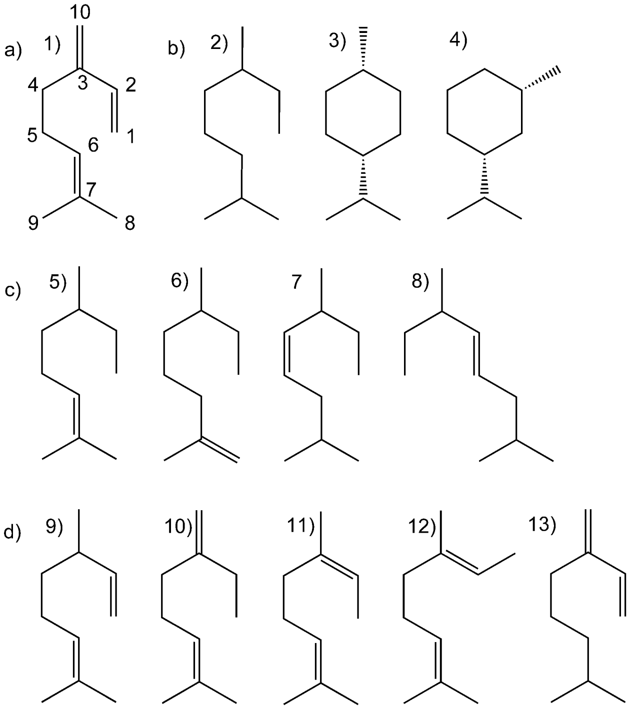


Fig. 2 Terpenes referred to in the manuscript: (a) (1) 7-methyl-3-methyleneocta-1,6-diene (β-myrcene); (b) Fully hydrogenated: (2) 2,6-dimethyloctane, (3) *cis*-*p*-menthane, (4) *cis*-*m*-menthane; (c) Hydrogenation of 2 carbon–carbon double bonds: (5) 2,6-dimethyloct-2-ene, (6) 2,6-dimethyloct-1-ene, (7) 2,6-dimethyloct-4(*Z*)-ene, (8) 2,6-dimethyloct-4(*E*)-ene; (d) Hydrogenation of 1 carbon–carbon double bond: (9) 3,7-dimethylocta-1,6-diene (β-citronellene), (10) 2-methyl-6-methyleneoct-2-ene, (11) 2,6-dimethylocta-2(*Z*),6-diene, (12) 2,6-dimethylocta-2(*E*),6-diene, (13) 7-methyl-3-methyleneoct-1-ene. The carbon numbering system in the hydrocarbon skeleton is presented for the β-myrcene structure.

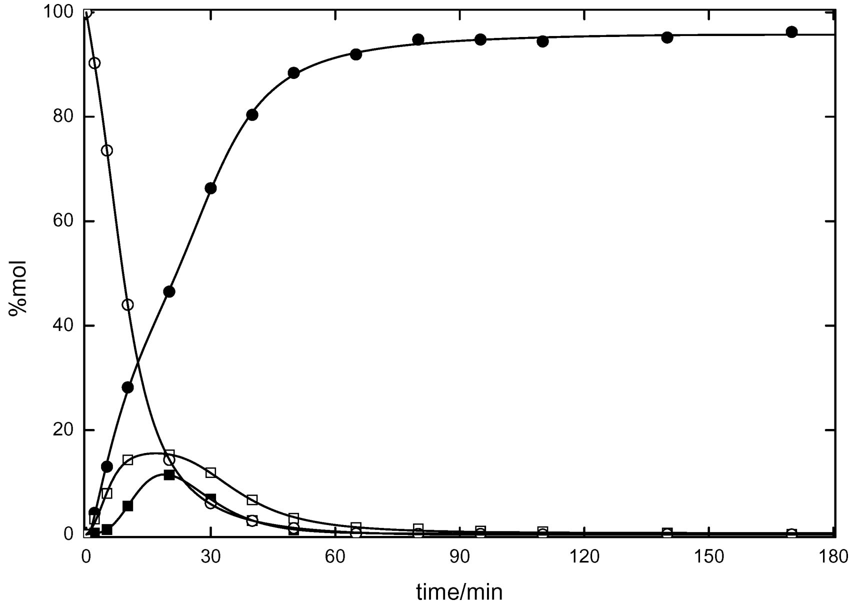


Fig. 3 Profile of the hydrogenation of β-myrcene over Pd/Al_2O_3 catalyst, expressed as mole percentage of β-myrcene (○), 2,6-dimethyloctane (●), 2,6-dimethyloct-1-ene (■),2,6-dimethyloct-2-ene (□) as a function of time, at 323.15 K, 4 MPa of H_2 and 12.5 MPa of total pressure (two phases). Other identified (β-citronellene, 2,6-dimethyloct-4(*E*)-ene, 2,6-dimethyloct-4(*Z*)-ene, *cis*-*m*-menthane, 2,6-dimethylocta-2(*Z*),6-diene, 2,6-dimethylocta-2(*E*),6-diene) terpenes are not presented in the figure.

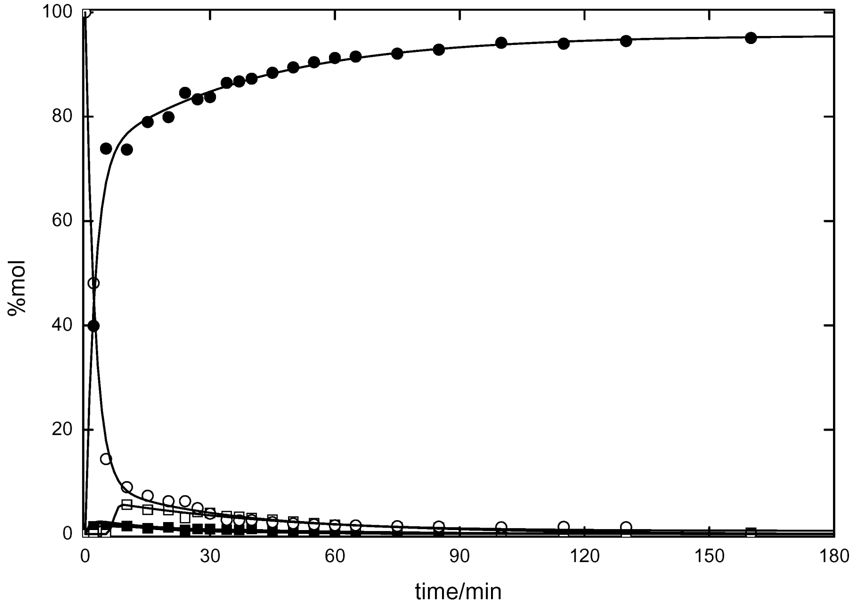


Fig. 4 Profile of the hydrogenation of β-myrcene over Pd/Al_2O_3 catalyst, expressed as mole percentage of β-myrcene (○), 2,6-dimethyloctane (●), 2,6-dimethyloct-1-ene (■), 2,6-dimethyloct-2-ene (□) as a function of time, at 323.15 K, 4 MPa of H_2 and 16.0 MPa of total pressure (supercritical phase). Other identified (β-citronellene, 2,6-dimethyloct-4(*E*)-ene, 2,6-dimethyloct-4(*Z*)-ene, *cis*-*m*-menthane, 2,6-dimethylocta-2(*Z*),6-diene, 2,6-dimethylocta-2(*E*),6-diene) terpenes are not presented in the figure.

cis-*m*-menthane (Fig. 2 structure 4)}, and an unidentified product in a total yield not higher than 4% are detected as well.

Fig. 4 presents the profile of the products obtained in the course of hydrogenation of β-myrcene at 16 MPa of total pressure in a single phase catalysed by 0.5 wt.% Pd/Al_2O_3. The outcome of the reaction is in general agreement with the reaction profile obtained for the reaction carried out in two phases. The only difference is that there are less mono- and dihydrogenated products and their isomers observed at the beginning of the reaction in one phase compared to the two-phase reaction depicted in Fig. 3.

Hydrogenation of β-myrcene over 0.5 wt.% Rh/Al_2O_3 was performed in biphasic conditions (Fig. 5) and in a single phase (Fig. 6). The first remark on the outcome of the reactions catalysed by rhodium is the lack of further hydrogenation of the intermediate to 2,6-dimethyloctane. This effect caused by the activity of the catalyst is discussed later. The concentration

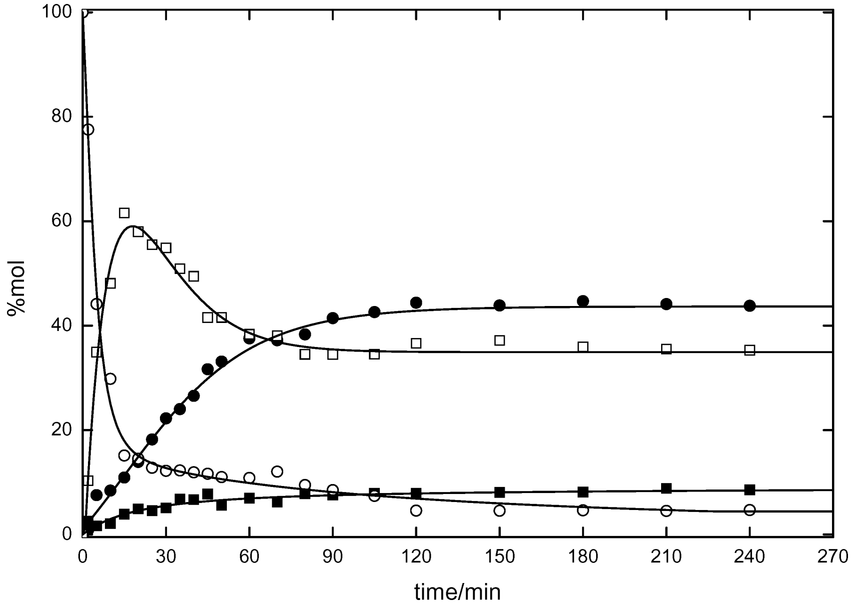


Fig. 5 Profile of the hydrogenation of β-myrcene over Rh/Al_2O_3 catalyst, expressed as mole percentage of β-myrcene (○), 2,6-dimethyloctane (●), 2,6-dimethyloct-1-ene (■),2,6-dimethyloct-2-ene (□) as a function of time, at 323.15 K, 4 MPa of H_2 and 12.5 MPa of total pressure (two phases). Other identified (β-citronellene, 2,6-dimethyloct-4(*E*)-ene, 2,6-dimethyloct-4(*Z*)-ene, *cis*-*m*-menthane, *cis*-*p*-menthane, 2,6-dimethylocta-2(*Z*),6-diene, 2,6-dimethylocta-2(*E*),6-diene) terpenes are not presented in the figure.

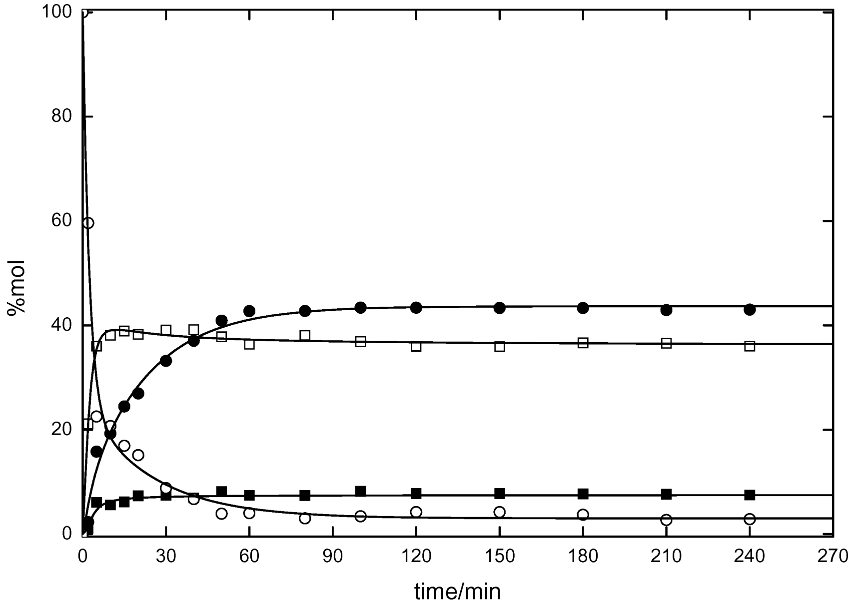


Fig. 6 Profile of the hydrogenation of β-myrcene over Rh/Al_2O_3 catalyst, expressed as mole percentage of β-myrcene (○), 2,6-dimethyloctane (●), 2,6-dimethyloct-1-ene (■),2,6-dimethyloct-2-ene (□) as a function of time, at 323.15 K, 4 MPa of H_2 and 16 MPa of total pressure. Other identified (β-citronellene, 2,6-dimethyloct-4(*E*)-ene, 2,6-dimethyloct-4(*Z*)-ene, *cis*-*m*-menthane, *cis*-*p*-menthane, 2,6-dimethylocta-2(*Z*),6-diene, 2,6-dimethylocta-2(*E*),6-diene) terpenes are not presented in the figure.

profile of the dihydrogenated product 2,6-dimethyloct-2-ene (Fig. 5) obtained for the reaction performed in two phases exhibits an interesting feature. During the first 15 min of the reaction, the concentration of dihydrogenated intermediate rises to 61.6 mol% and after that, decreases during the next 65 min to the level of 34.5 mol%. Careful analysis of this stage of the reaction shows that between 15 and 80 min of reaction, the concentration of β-myrcene drops from 15.1 mol% to 9.5 mol% and the concentrations of the fully hydrogenated 2,6-dimethyloctane and disaturated product 2,6-dimethyloct-1-ene increase by 27.4 mol% and 3.9 mol%, respectively. The other identified and unidentified products keep the concentration generally constant. This suggests that a relationship exists in the system, which can be described by the following equation: $n_{\text{2,6-dimethyloct-2-ene}} + n_{\beta\text{-myrcene}} = n_{\text{2,6-dimethyloctane}} + n_{\text{2,6-dimethyloct-1-ene}}$, where *n* is the number of moles of a certain terpene at the constant total volume. The characteristic shape of the curve designating the other monounsaturated product: the 2,6-dimethyloct-2-ene

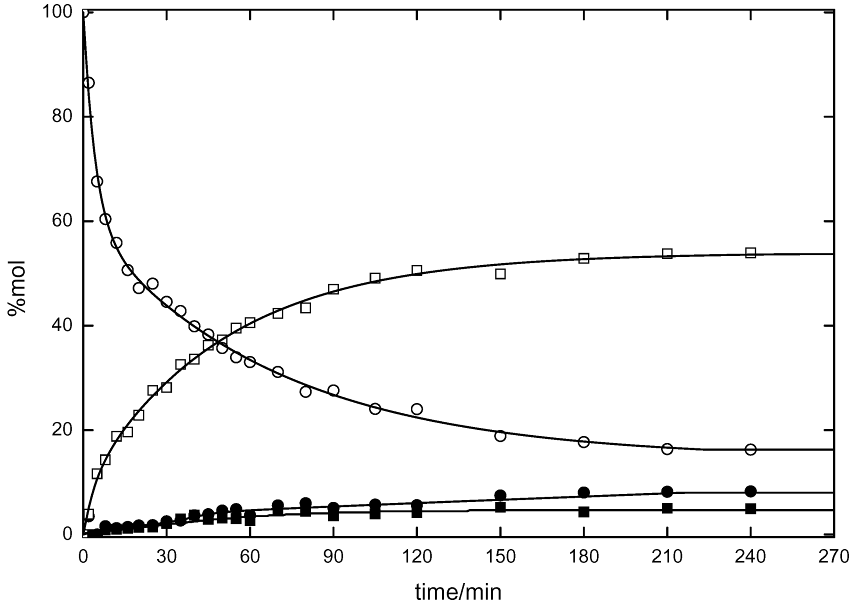


Fig. 7 Profile of the hydrogenation of β-myrcene over Ru/Al_2O_3 catalyst, expressed as mole percentage of β-myrcene (○), 2,6-dimethyloctane (●), 2,6-dimethyloct-1-ene (■), 2,6-dimethyloct-2-ene (□) as a function of time, at 323.15 K, 4 MPa of H_2 and 12.5 MPa of total pressure (two phases). Other identified (β-citronellene, 2,6-dimethyloct-4(*E*)-ene, 2,6-dimethyloct-4(*Z*)-ene, *cis*-*m*-menthane, *cis*-*p*-menthane, 2,6-dimethylocta-2(*Z*),6-diene, 2,6-dimethylocta-2(*E*),6-diene) terpenes are not presented in the figure.

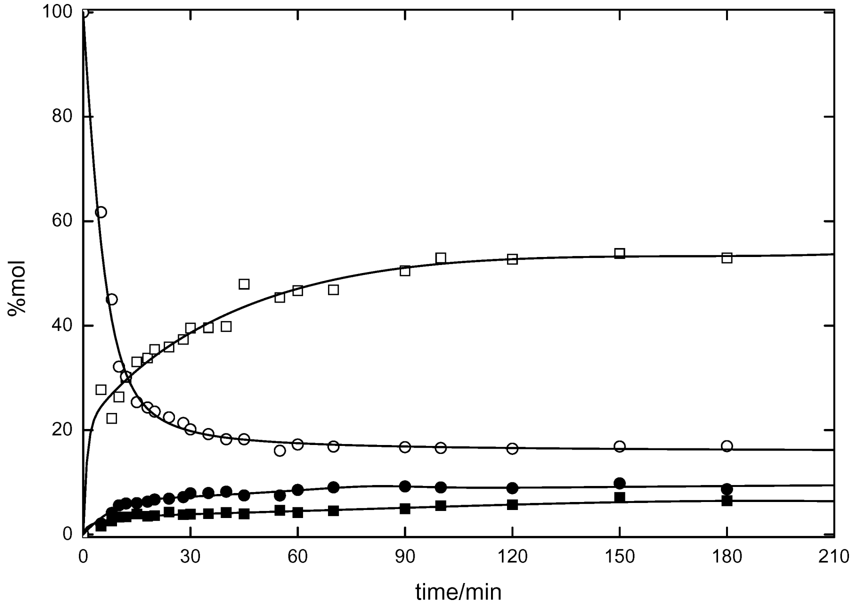


Fig. 8 Profile of the hydrogenation of β-myrcene over Ru/Al_2O_3 catalyst, expressed as mole percentage of β-myrcene (○), 2,6-dimethyloctane (●), 2,6-dimethyloct-1-ene (■),2,6-dimethyloct-2-ene (□) as a function of time, at 323.15 K, 4 MPa of H_2 and 16 MPa of total pressure (one phase). Other identified (β-citronellene, 2,6-dimethyloct-4(*E*)-ene, 2,6-dimethyloct-4(*Z*)-ene, *cis*-*m*-menthane, *cis*-*p*-menthane, 2,6-dimethylocta-2(*Z*),6-diene, 2,6-dimethylocta-2(*E*),6-diene) terpenes are not presented in the figure.

profile, is only slightly noticeable in the reaction performed in a single phase (Fig. 6).

Hydrogenation of β-myrcene catalysed by 0.5 wt.% Ru/Al_2O_3 in two (Fig. 7) and one phase (Fig. 8) systems, reveals that the main product of these reactions is dihydrogenated 2,6-dimethyloct-2-ene with a concentration slightly above 50 mol%. Nevertheless, an insignificant amount of the fully hydrogenated product is found. The other characteristic feature of the reaction performed with this catalyst is the level of the unreacted β-myrcene that is much higher than in the case of the other catalysts. This can be explained by the activity of the catalyst which is discussed later.

Catalyst stability

The analysis of the SEM images (Fig. 1) for Pd, Rh and Ru catalysts supported on alumina illustrates that the surface of the catalysts changed during the reactions performed in biphasic and monophasic conditions. This observation leads us to check the probability of leaching of the catalyst metal. For this purposes the SEM/EDS technique has been employed. Although due to the low concentration of the noble metal catalyst on the catalyst surface this technique does not provide indisputable results in this area. In the next step, the AAS technique has been used to confirm the changes observed on the catalyst surfaces presented in Fig. 1. The obtained results confirmed the removal of the catalyst metals from the surface of the rods. The leaching is generally smaller in the case of employment of the catalyst in two phases than in one phase. This is true for all the catalysts used in the reactions; although the AAS analyses show that the highest metal content is found in the sample from the reaction carried out over Pd catalyst. The concentration of palladium detected in the samples collected from the reactions executed in one and two phases are not higher than 21.5 mg L^{-1} and 14.5 mg L^{-1}, respectively. Rhodium catalyst is slightly more stable. Rh content is found at the level of 19.3 mg L^{-1} and 12.4 mg L^{-1} in the samples from the reactions in single and biphasic conditions, correspondingly. Our analyses show that Ru catalyst is the most stable and gives the lowest metal concentration in the reaction samples. The data obtained for the samples after the reaction in one and two phases show that the concentration of Ru metal reaches the levels of 16.3 mg L^{-1} and 5.9 mg L^{-1}, respectively, which affirms the conclusions gained from SEM analyses.

Discussion

Mechanism of the hydrogenation of β-myrcene

β-Myrcene is a $C_{10}H_{16}$ hydrocarbon with three C=C double bonds, where two of them are conjugated and one is isolated. Both conjugated C=C double bonds are terminal and undergo hydrogenation much faster. The third, isolated C=C double bond between the sixth and seventh carbons in the hydrocarbon skeleton is generally less susceptible to hydrogenation.[24] This is due to the presence of two terminal methyl groups linked with the seventh carbon of the hydrocarbon skeleton.

Hydrogenations of β-myrcene catalysed by Pd catalysts gave mostly the fully hydrogenated product. Other, mainly dihydrogenated compounds like: 2,6-dimethyloct-2-ene (Fig. 2, structure 5), 2,6-dimethyloct-1-ene (Fig. 2, structure 6) were noticed as well. The appearance of 2,6-dimethyloct-2-ene could be explained by the favourable hydrogenation of two conjugated C=C double bonds between carbons in positions 1–2, and 3–10.[25] As has already been reported "in the hydrogenation of compounds containing carbon–carbon conjugation, there is a strong tendency for both double bonds to be hydrogenated at about the same rate".[26] Moreover, at the half-hydrogenation step, the mixture may contain considerable amounts of unreacted terpene, disaturated products with possible dihydrocompounds.[26] In our research, this refers to the monosaturated 2,6-dimethylocta-2(*Z*),6-diene (Fig. 2 structure 11) and 2,6-dimethylocta-2(*E*),6-diene (Fig. 2 structure 12). These compounds are observed at the beginning of the reaction in small, however noticeable amounts. In the classical Pd/charcoal catalysed hydrogenation of β-myrcene without supercritical CO_2, the main product is formed by 1,10-addition of hydrogen to the conjugated system (2,6-dimethylocta-2(*Z*),6-diene, or 2,6-dimethylocta-2(*E*),6-diene) and some of the 1,2-dihydrocompound (2-methyl-6-methyleneoct-2-ene (Fig. 2 structure 10)—not detected by us) is also obtained. Additionally, neither the 3,10-dihydro product (β-citronellene), nor the isolated double bond attacked to form 7-methyl-3-methyleneoct-1-ene (Fig. 2 structure 13) is observed.[5]

The results obtained by Dupont *et al.*[5] are substantially different if compared to the hydrogenation catalysed by Pd/Al_2O_3 with supercritical CO_2 presented in this work. Our results show that Pd/Al_2O_3 promotes the formation of monosaturated products (2,6-dimethylocta-2(*E*),6-diene and 2,6-dimethylocta-2(*Z*),6-diene) only in minor amounts. Dupont *et al.*[5] discovered that both stereoisomers are the products of hydrogenation, while in the reaction with supercritical CO_2 the main product is the fully saturated 2,6-dimethyloctane. Furthermore, the other monosaturated 2-methyl-6-methyleneoct-2-ene is not detected by us in the reaction mixture. After 20 min of the reaction, the dihydrogenated 2,6-dimethyloct-1-ene with a yield of 10% is discovered as an effect of the allylic isomerisation of 2,6-dimethyloct-2-ene occurring in the course of the reaction.

The product composition and the appearance of the isomers in the reaction catalysed by palladium can be explained by the mechanism of the reaction. The mechanism of the hydrogenation showed the facile double bond migration and formation of π-allyl complexes.[25] Gault *et al.* proposed a mechanism of hydrocarbon reaction which assumes π-allyl adsorption.[27] Augustine *et al.* presented "that the peculiar catalytic behaviour of palladium can best be accounted for by invoking the intermediacy of a π-allyl-adsorbed species".[20] More recent work in this field presents the mechanism of β-myrcene hydrogenation catalysed by Pd/SiO_2. This mechanism involves σ-alkyl and/or η^3-intermediates formed by the reaction of the terminal C=C double bonds with the metal catalyst.[7] The reaction performed in cyclohexane as a solvent shows that the selectivity of the reaction towards monosaturated or the fully saturated product is dependent on the temperature and catalyst. At the lowest investigated temperature (60 °C) Pd/SiO_2 was very active and quantitatively gives the fully saturated product. In the course of the reaction investigated by us, 2,6-dimethyloctane, the fully hydrogenated olefin, is obtained as well.

Hydrogenation of β-myrcene catalysed by Rh/Al_2O_3 gives substantially different results than that obtained for Pd catalysed reactions as mentioned above. The difference can be explained by the mechanism of the reaction. The mechanism of Rh catalysed hydrogenation of olefins is mechanistically comparable to platinum catalysed reactions.[28] This suggests that the hydrogenation of terpene catalysed by Rh occurs *via* a 1,2-σ_2 adsorption of the Horiuti–Polanyi mechanism, contrary to the formation of π-allyl complexes present in the case of the palladium catalysed hydrogenation.[29]

Results gained for the Rh catalysed reactions performed in one phase are similar to those obtained for the two-phase reaction. This indicates that in both cases reaction occurs *via* the same mechanism, although high hydrogen availability in one phase speeds up further the hydrogenation to the completely saturated product 2,6-dimethyloctane.

Hydrogenation of terpenes catalysed by Ru was investigated very rarely and the mechanism of the reaction is not yet indisputably determined. Indeed, Speziali *et al.*[8] suggested the mechanism of the hydrogenation of β-myrcene without CO_2 catalysed by complexes of ruthenium, or rhodium in a homogenous liquid phase. The mechanism of β-myrcene hydrogenation catalysed by Ru[8] is identical to that previously reported for Pd/SiO_2 catalysed hydrogenation of β-myrcene.[7] The very same mechanism suggested by Speziali *et al.*, in principle explains the results gained for Ru or Rh complexes, although the results are very different from those obtained for Pd/SiO_2 published earlier by them. The results obtained by us for Rh and Ru catalysts do not match those presented by Speziali *et al.*[8] This proves that further investigations in this field should be performed.

Activity of the catalyst

The outcome of the hydrogenation of unsaturated olefins varies mostly with the catalyst metal. The activity of many catalysts is greatly affected by small traces of impurities, acting as poisons or promoters that lead to many discrepancies between the results of different literature reports.[26]

Pd catalyst is an active metal catalyst, as is also observed in our work. The high activity of the catalyst metal leads to the predominant formation of the fully hydrogenated product. As the final outcome 2,6-dimethyloctane, the fully saturated compound, is obtained in 95% yield, while the other minor constituents are present only in very small quantities.

The previous study from our laboratory for other terpenes (α-pinene and limonene) demonstrated that Pd catalyst is a very active metal, which leads to high conversion of the investigated terpenes and good selectivity towards the fully hydrogenated products in reactions performed in biphasic conditions.[11a,12b]

Based on the results obtained for the reaction catalysed by Rh, it can be stated that rhodium catalyst is less active than palladium. The composition of the final mixture contains slightly above 40% of the completely saturated 2,6-dimethyloctane. The remaining 60% is constituted by other mono- and dihydrogenated products and unreacted β-myrcene at levels of 5%. Relatively low concentrations of 2,6-dimethyloctane and the presence of unreacted β-myrcene proves that Rh catalyst is less active towards hydrogenation of terpene in the presence of CO_2.

As reported in the literature, the hydrogenation of unsaturated olefins catalysed by ruthenium is generally very slow. It is caused by the 50 to 150 times lower activity of ruthenium catalyst compared to platinum, palladium or rhodium.[20] The noticeable, however not so large reduction of activity can be concluded from the reactions performed by us in biphasic (Fig. 7) and single phase (Fig. 8) conditions as well.

A very low level of 2,6-dimethyloctane, a high concentration of the unreacted β-myrcene and a relatively high number of the partially hydrogenated intermediates or their isomers with a concentration higher than observed in other reactions, demonstrates that ruthenium catalyst is less active than rhodium and even more than palladium.

Summarising, it can be stated that the catalyst metal determines the activity of the catalyst towards the hydrogenation of β-myrcene. Additionally, it controls the conversion of β-myrcene and the selectivity of the obtained products.

The effect of total pressure on the reaction outcome

The pressure of CO_2 strongly affects the reaction conditions. At lower total pressure (12.5 MPa), reactions were carried out in biphasic (liquid + gas) conditions, while 16 MPa of total pressure shifted the reaction mixture towards a one-phase region. The pressure tuning changes not only the number of phases, but also controls the concentration of the reagents in the vicinity of the catalyst. This in turn determines the rate of the reaction.

The ordinate units in the concentration profiles are mole percentage of the total amount of terpenes and taking into account the solubility of CO_2 in β-myrcene at the reaction conditions, the initial volumes of the CO_2-expanded liquids were calculated.[30] The obtained results allow the calculation of the initial reaction rate constants (k) and the initial volumes of the liquid phase for the initial stage of the reactions in each experiment. From the calculated volumes of the liquid phase and the known total initial amount of β-myrcene, its initial concentration (in mol/vol) was calculated. In addition, the mol% of β-myrcene was used to calculate the concentration (mol/vol) of β-myrcene as a function of time due to the fact that each molecule of product is produced from one molecule of β-myrcene. Moreover, the reactions were carried out in a semi-continuous way, and the high recirculation rate used allowed the composition of the feeds to alter continuously, influencing the kinetics like in a batch process. Indeed, with the applied 3.3 mL/min flow rate of the reaction mixture, the entire liquid is recirculated at least once every 2–3 min. Postulating the disappearance of β-myrcene as a first order reaction, plots of ln[β-myrcene] as a function of time showed straight lines for the initial stages of the reaction. In $scCO_2$ the reaction kinetics exhibited a first-order reaction rate *i.e.* for limonene[17a] and citral[31] hydrogenations. The obtained results indicate that the hydrogenation of the first double bond is always faster in one phase than in two phases as presented in Table 1. Moreover, the experimental results show that the initial reaction rate constant depends on the activity of the catalyst used for the reaction, and it decreases with diminishing catalyst activity.

The faster first double bond hydrogenation is associated with a faster achievement of equilibrium in the case of the reactions catalysed by Rh (compare Fig. 5 and 6) and Ru (compare Fig. 7 and 8). It can be concluded that hydrogenation of further double bonds is faster in one phase than in two phases for these two catalysts. Similar results were obtained in the hydrogenation of limonene, the full hydrogenation of the two double bonds of the limonene molecule was faster in supercritical, monophase conditions. When the hydrogenation was performed in a biphasic system, only one of the double bonds was selectively hydrogenated.[13]

Table 1 The initial reaction rate constant (10 k/min) for the hydrogenation of the first C=C double bond of β-myrcene carried out over Pd, Rh or Ru catalyst in one or two phases conditions

	10 k/min		
	Pd	Rh	Ru
one phase	3.89	3.00	1.03
two phases	0.92	1.00	0.81

For the Pd/Al_2O_3 catalyst presented in this work, the results of hydrogenation of β-myrcene demonstrate the opposite behaviour. While the first double bond is hydrogenated faster in one phase than in two phases, the next two double bonds are hydrogenated slower in monophasic conditions. This leads to a longer reaction time which is essential in achieving equilibrium in the existing system, as presented in Fig. 3 and 4. It proves that reactions performed in biphasic conditions, in some particular cases, are faster than hydrogenations in one supercritical phase. Examples of fast hydrogenations performed in biphasic mixtures containing high-pressure carbon dioxide are described by Hitzler *et al.*[32] The results from our laboratory also showed that hydrogenation rates of (liquid) α-pinene in biphasic conditions, at lower CO_2 pressure, is as high or in certain conditions even higher than rates in supercritical mixtures, at higher CO_2 pressure.[16] Milewska *et al.*[16b] interpreted their data based on the assumption that the rate is controlled by the adsorption of pinene, and not hydrogen, at the catalyst surface. The authors reasoned that, if the adsorption of pinene at the catalyst surface is related to the limiting rate step, a biphasic system may lead to higher rates, because α-pinene is more concentrated in the liquid around the catalyst than when diluted in a single supercritical phase. Chouchi *et al.*[11a] found that the CO_2 pressure effects α-pinene conversion. They noticed that at constant H_2 pressure and lower total pressure the conversion of α-pinene increases. Our investigation on limonene hydrogenation[12b] agreed with this conclusion. The study on the effect of hydrogen pressure on the hydrogenation of limonene in biphasic conditions over Pd demonstrated that the initial rate of hydrogenation increases with hydrogen partial pressure. The rate-controlling factor is the concentration of limonene in the liquid phase that in turn is controlled by the volume expansion of the liquid phase induced by carbon dioxide.[12b]

The results of the hydrogenation of terpenes presented in previous reports and in this work show that relatively small changes in pressure tune the reaction conditions and affect the outcome of the analysed reactions.

Conclusions

Hydrogenation of the terpene, β-myrcene, over palladium, rhodium and ruthenium in a carbon dioxide atmosphere was performed. Reactions were carried out in biphasic conditions, at lower CO_2 pressure and compared with the outcome of the hydrogenation reactions executed in one, supercritical phase. Reactions over Rh and Ru catalysts performed in a single supercritical phase reach equilibrium generally faster than hydrogenation carried out in biphasic conditions. In the case of Pd, the reaction performed in the supercritical phase is slightly slower than in biphasic conditions. The final composition of the reaction mixture is significantly dependent on the noble metal catalyst used for the reaction. Palladium catalyst is the most active metal, next Rh and the least active catalyst is Ru. Palladium catalyses the hydrogenation of β-myrcene to the completely saturated, 2,6-dimethyloctane, product. The rhodium catalyst is less active and selective leading to the formation of monounsaturated 2,6-dimethyloct-2-ene in only slightly smaller amounts than the saturated 2,6-dimethyloctane. Ruthenium, as the least active catalyst, gives dihydrogenated 2,6-dimethyloct-2-ene in the main, leaving close to 20 mol% of the unreacted starting terpene. None of the catalysts is stable under the reaction conditions and the metal is removed in noticeable amounts over the course of the reactions.

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