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Density-Dependent Formation of the Pure *trans*-Isomer of the Unsaturated Alcohol by Selective Hydrogenation of Citral in Supercritical Carbon Dioxide

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Abstract: Selective hydrogenation of citral to unsaturated alcohol [geraniol (*trans*) + nerol (*cis*)] was carried out in supercritical carbon dioxide ($scCO_2$) using an MCM-41 supported plantinum catalyst (~ 1 wt% Pt). A remarkable rate of isomerization of the unsaturated alcohol [nerol (*cis*) to geraniol (*trans*)] during the hydrogenation of citral was achieved simply by tuning the density of CO_2. Optimum reaction conditions were developed to obtain only geraniol (*trans*) with a selectivity of 98.8% and citral conversion of 99.8%. A significant change in the *cis*:*trans* ratio of the product (1:82.3) from the substrate (1:1.3) was observed depending on the various reaction parameters like carbon dioxide and hydrogen pressure, reactant concentration, reaction time and, particularly, the total selectivity for unsaturated alcohol [geraniol (*trans*) +nerol (*cis*)]. It has been observed that the presence of hydrogen is necessary for isomerization. Our results were explained in terms of a density-dependent, two-step model. The kinetic behaviour shows that the rate of isomerization was higher in $scCO_2$ compared to other organic solvents and the pure form of geraniol (*trans*) was obtained exclusively. A probable reaction pathway was proposed in order to explain the isomerization during hydrogenation of citral in $scCO_2$ medium.

Keywords: density; *cis/trans* isomerization; mesoporous material; selective hydrogenation; supercritical carbon dioxide

Introduction

The selective hydrogenation of α,β-unsaturated aldehydes represents an important class of industrially relevant reactions, useful in the specialty and fine chemicals fields.[1] The primary target of this type of reaction is the hydrogenation of a specific unsaturated bond (C=O, C=C) leaving the other untouched. For instance, citral is an unsaturated aldehyde, mainly obtained as the mixture of *cis* and *trans*-forms with an isolated C=C along with conjugated C=O and C=C bonds. Hydrogenation of the conjugated C=O leads to *cis*- and *trans*-isomers of the unsaturated alcohol (nerol and geraniol, respectively). The *trans*-isomer of the unsaturated alcohol (geraniol) having a rose-like odour, mainly used in perfume can also act as an allelochemical or secondary metabolite, which are indispensable for the life process,[2] for antimicrobials, fungicides and insecticides in the pharmaceutical, cosmetic and flavour manufacturing industries.[3] In addition to that geraniol (*trans*) is the starting material for the synthesis of Phomactin, which is a biological active platelet-activating factor (PAF) antagonist and lipid mediator.[4] Moreover, in the course of unsaturated alcohol formation, a mixture of *cis*- and *trans*-isomers was also obtained along with different types of hydrogenated products and loss of the quality of the desired product. Thus, the synthesis of only the *trans*-isomer of the unsaturated alcohol from the *cis/trans* mixture of the reactant is a challenging task.

Selective hydrogenation of citral has been widely investigated, focusing particularly on the synthesis of the unsaturated alcohol [geraniol (*trans*) + nerol (*cis*)] using noble metals on different supports, bimetallic catalysts[5–7] or by addition of promoters and basic catalysts[8] in various organic solvents.[9] However, the production of the unsaturated alcohol has suffered from the disadvantages of complex processes leading to low yields, use of environmentally hazardous organic solvents, transition metal catalysts, problems associated with catalyst-product separation and side reactions such as decomposition, which take place during distillation.

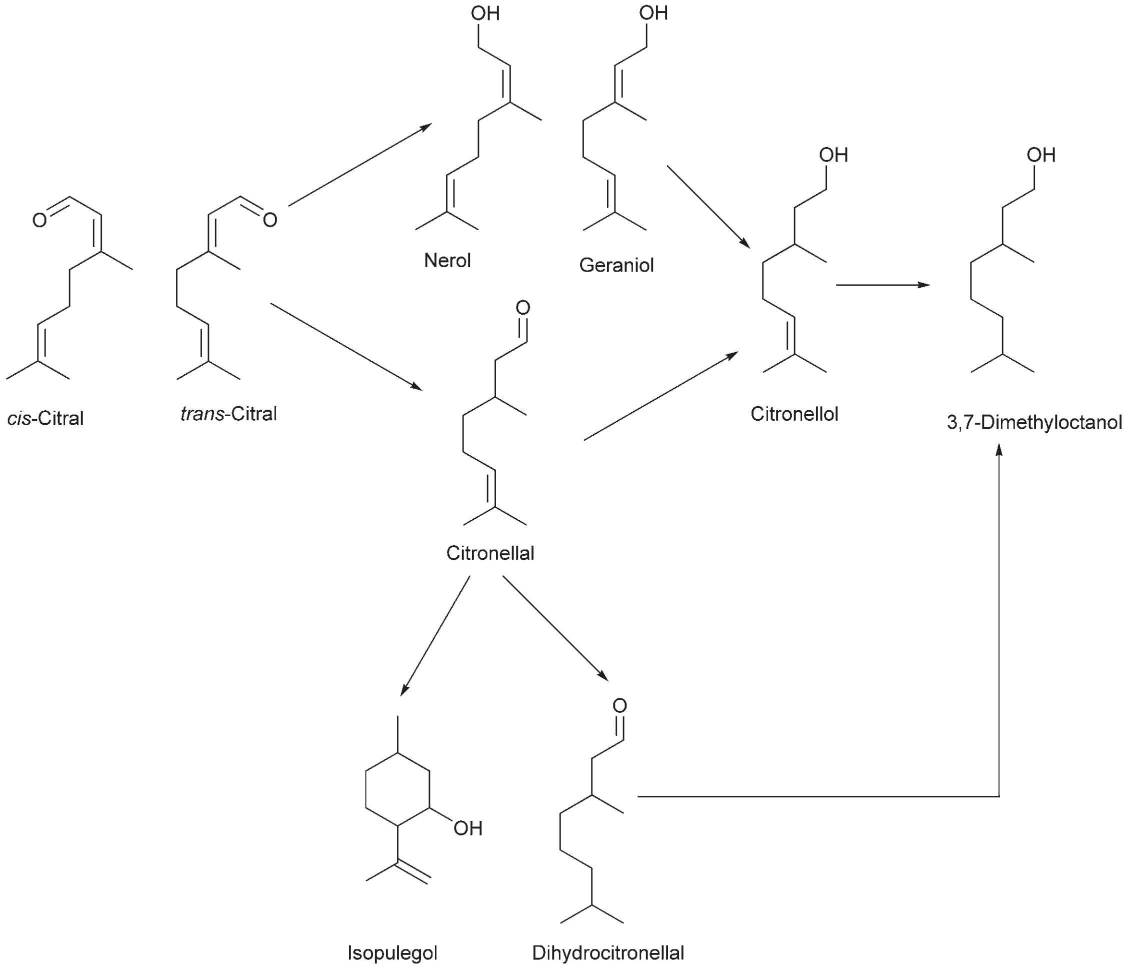
Supercritical carbon dioxide ($scCO_2$) regarded as a "green" reaction medium offers important advantages over conventional organic solvents. The high miscibility of $scCO_2$ with many reactant gases can help to avoid mass transfer limitations.[10] Moreover, the high compressibility of $scCO_2$,[11] could result in a significant change in the chemo-, regio- and stereoselectivity. Fine tuning of the solvent strength by minor changes in pressure (larger density variations) can have a strong impact on chemical equilibrium and reaction rates in highly compressible supercritical medium, and results in a strong control over selectivity in contrast to conventional organic solvents. Recently, pressure-dependent product selectivity was achieved in the hydrogenation of citral in $scCO_2$ using various types of noble metals[12] and transition metal catalysts.[13–15] However, most of the studies are based on the feasibility of the process, performance of the catalyst regarding selectivity to the unsaturated alcohol (neglecting the isomerization) and comparison with the conventional process.

The objectives of this work is (1) to optimize the reaction conditions to obtain only the *trans*-isomer of the unsaturated alcohol and (2) to understand the probable reaction pathway responsible for the significant stereoselectivity of the unsaturated alcohol, which is a difficult task especially for a heterogenous catalytic system in $scCO_2$ medium. From our previous studies[15] we have observed that citral hydrogenation is strongly influenced by the nature of the metal ions and Pt is more favourable for the selective hydrogenation of C=O in $scCO_2$. Thus, Pt-containing mesoporous material was chosen to obtain high selectivity for geraniol (*trans*) + nerol (*cis*).

Results and Discussion

Catalytic Activity

Citral hydrogenation is a complex network process. Scheme 1 displays a possible hydrogenation product under the studied reaction conditions [$T = 35–80\,°C$; $P_{H_2} = 0.5–4$ MPa; $P_{CO_2} = 4–17$ MPa; reaction time = 4–6 h; amount of catalyst = 0.025–0.2 g and reactant = 1.6–12.24 mmol] using a 50-mL autoclave. In the first part, we will try to find out the optimum reaction conditions such as CO_2 and H_2 pressures, temperature, amount of citral, weight of the catalyst and also the reaction time for the formation of geraniol (*trans*).



Scheme 1. Probable reaction pathway of citral hydrogenation in supercritical carbon dioxide.

The next part will cover the probable reaction pathway to the formation of the geraniol (*trans*) in $scCO_2$ using Pt-MCM-41 catalyst.

Optimization of Reaction Conditions

Effect of CO_2 Pressure

The influence of CO_2 pressure on the conversion and selectivity for the hydrogenation of citral is illustrated in Figure 1 (top). All results are under standard conditions (temp. = 70 °C, P_{H_2} = 4 MPa, time = 4 h) unless otherwise noted. The product selectivity result shows that the geraniol (*trans*) + nerol (*cis*) was obtained as the principal product. At low pressure (density) of CO_2, the hydrogenation of the C=C bond also occurred and consequently the partially saturated aldehyde (citronellal) and the saturated alcohol (citronellol) were formed. No dihydrocitronellal, dimethyloctanol and ring closure products like isopulegol were detected. As the pressure (density) of $scCO_2$ increased the selectivity for citronellal and citronellol was subsequently suppressed and geraniol (*trans*) + nerol (*cis*) was obtained with significantly higher selectivity (98.8% + 1.2%). A closer look at the selectivity for the unsaturated alcohol shows a clear correlation between CO_2 density and the *cis*:*trans* ratio [nerol (*cis*); geraniol (*trans*)] [Figure 1 (bottom)]. In accordance with the result, when the density of CO_2 is low (4–6 MPa) and it is in the gas phase, the *cis*:*trans* ratio (substrate 1:1.3) does not change. However, the ratio decreases significantly (*cis*:*trans* = 1:82.3) when CO_2 is in the liquid phase. A similar pressure effect was obtained during the *cis/trans* isomerization of olefins in $scCO_2$.[16] This finding was explained by the formation of the *trans*- isomer in the liquid phase conditions due to the restricted withdrawl of the reaction products from the catalyst surface which leads to further reaction of the adsorbed species. Moreover, Pt-containing mesoporous Si was used as catalyst. Density-dependent adsorption of CO_2 with different solutes on the catalyst surface is a well known phenomenon.[17–19] We are aware that the density of the supercritical medium changes substantially either by changing the pressure or temperature. For example, a change in pressure from 4 to 14 MPa the density changes from 1.6181 to 10.406 mol/L (NIST Chem web book) and the solubility of the citral increases. According to the phase behaviour studies the solubility of citral increases with CO_2 pressure (density) and the single phase was obtained above 10.0 MPa at 70 °C. So, the CO_2 pressure above 10 MPa was favourable for the adsorption of the reactant to the catalyst acitve site. As the loading of the reactant increases with increasing pressure, the conversion as well as selectivity was enhanced and consequently the *cis:trans* ratio was changed. But above 14 MPa the solubility as well as adsorption does not change much leaving conversion and selectivity nearly constant. Dillow et al. proposed a two-step model to explain the density related *cis*,*trans*-isomerization in $scCO_2$.[20] According to the model, the *cis*-isomer will be converted to the *trans*-isomer *via* an intermediate (not in the classical sense). In the first step the solvent shelled *cis* will undergo a structural change by overcoming the energy barrier through the formation of an intermediate species before concominant rearrangement of the solvent shell. In the second step, a rearrangement will occur to stabilize the new species and which is density dependent. An increase in conversion from 34.3% to 99.8% was observed with the increase in pressure and a S-type curve was obtained (Figure 1, top). The steep part of the S-type curve can be attributed to the change in citral-rich two phases at lower pressure (4–8 MPa) to a single phase at higher pressure (> 10 MPa). This phase transition obviously augmented the conversion due to the increase in concentration of citral in the CO_2 phase.[21] Hence, the density variation can have a strong impact on the conversion and

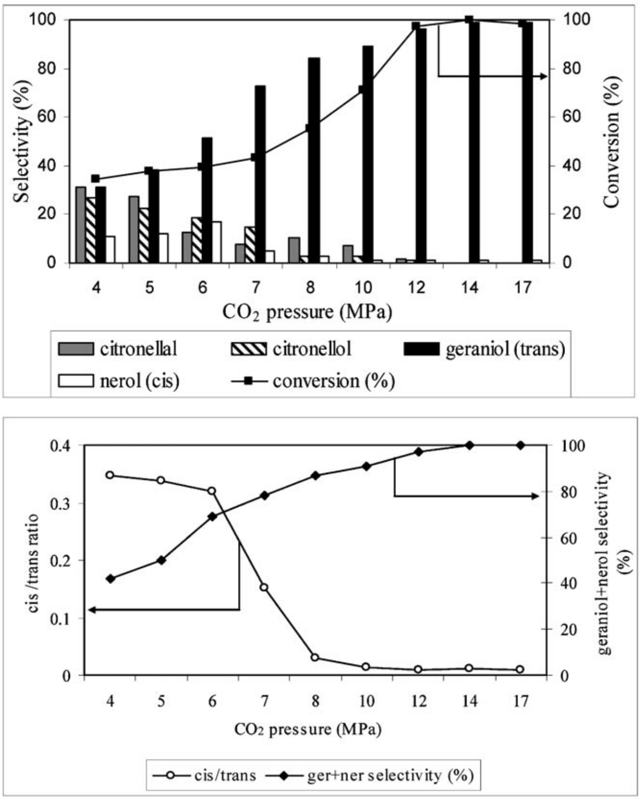


Figure 1. (*top*) Effect of CO_2 pressure on the conversion and the product distribution of citral hydrogenation. (*bottom*) Variation of *cis/trans* ratio with the selectivity of unsaturated alcohol. *Reaction conditions:* T = 70 °C; reaction time = 4 h; P_{H_2} = 4 MPa; amount of catalyst = 0.1 g; reactant = 6.24 mmol.

selectivity along with the *cis:trans* ratio of the unsaturated alcohol and the maximum *trans*-selectivity was obtained above 10 MPa of CO_2 pressure.

Effect of Reaction Time

Figure 2 displays the effect of time on the hydrogenation of citral under the standard reaction conditions. The results indicate that there is a rapid hydrogenation of citral during the first few minutes to citronellal, citronellol and geraniol (*trans*)+nerol (*cis*). An initial TOF of 0.152 s^{-1} to the formation of citronellal was observed. However, after 2 h, a decrease in the selectivity for citronellal and citronellol accompanied with the substantial increase in the selectivity for geraniol (*trans*)+nerol (*cis*) occurred. Initially, geraniol (*trans*)+nerol (*cis*) was obtained with 79% selectivity and reached a maximum during 4 h of reaction. The high selectivity for geraniol (*trans*)+nerol (*cis*) in $scCO_2$ medium can be explained by a specific interaction between CO_2 and the Lewis base groups like the C=O group of the reactant molecule, which favoured the formation of C–H--O with the hydrogen atom attached to the carbonyl carbon. Consequently, the reactivity of the C=O bond increases followed by the hydrogenation of the C=O bond.[22] Thus, from the molecular point of view $scCO_2$ medium was adding extra advantages regarding the selective hydrogenation of C=O.[23] Following the selctivity for geraniol (*trans*)+nerol (*cis*), it was observed that geraniol (*trans*) was obtained with enormous selectivity. The reason could be the nerol (*cis*) is thermodynamically unstable and prone to isomerize back to the thermodynamically stable geraniol (*trans*), which became the predominant product.[24]

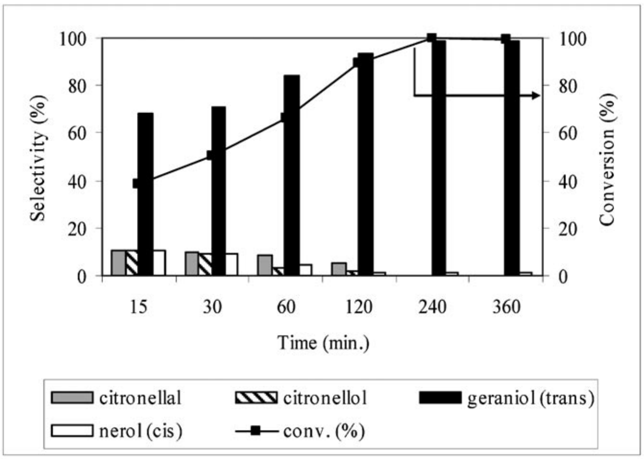


Figure 2. Effect of time variation on conversion and selectivity. *Reaction conditions:* $T=70\,°C$; $P_{CO_2}=14$ MPa; $P_{H_2}=4$ MPa; amount of catalyst = 0.1 g; reactant = 6.24 mmol.

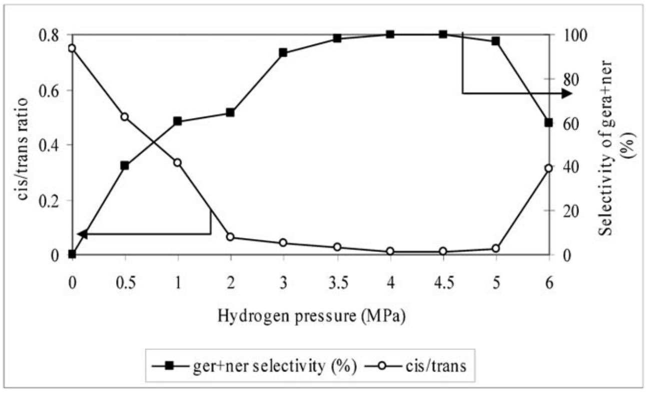


Figure 3. *cis/trans* Ratio and selectivity to geraniol (*trans*)+nerol (*cis*) as a function of H_2 pressure. *Reaction conditions:* $T=70\,°C$; $P_{CO_2}=14$ MPa; reaction time = 4 h; amount of catalyst = 0.1 g; reactant = 6.24 mmol.

Effect of H_2 Pressure

The effect of hydrogen pressure is an important parameter to describe the product distribution of citral hydrogenation in $scCO_2$. The reaction was carried out at different pressures of hydrogen keeping the other parameters constant. As the pressure changes from 2 to 4 MPa, the conversion of citral increases from 62.7% to 99.8% and maintains a first-order reaction rate. Since selectivity for the consecutive reaction depends on the conversion; the increase in conversion with hydrogen pressure might have some effect on the selectivity. A significant increase in the selectivity from 39.9% to 100% for geraniol (*trans*)+nerol (*cis*) was observed as the hydrogen pressure increased from 0.5 to 4 MPa and remained constant until 4.5 MPa but decreased when the pressure reached 6 MPa. Interestingly, the *cis:trans* ratio of the unsaturated alcohol [geraniol (*trans*)+nerol (*cis*)] was also changed along with the hydrogen pressure. Figure 3 shows the variation of *cis:trans* ratio and selectivity for geraniol (*trans*)+nerol (*cis*) as a function of hydrogen pressure. It has to be mentioned that the *cis:trans* ratio of the reactant was 1:1.3 but the ratio changes dramatically to 1:82.3 as the hydrogen pressure increased to 4 MPa. Hence, hydrogen pressure must be an important parameter obviously for hydrogenation as well as for isomerization to occur. To check the effect of hydrogen, we have carried out the reaction without hydrogen keeping the other parameters ($P_{CO_2}=14$ MPa; time = 4 h and temperature = 70 °C) constant (Figure 3). No isomerization (*cis* to *trans* of citral) took place. After the addition of 0.2 MPa of hydrogen, though, the conversion was substantially lower but isomerization of *cis*- to *trans*-unsaturated alcohol took place and the *cis*:*trans* ratio was changed to 1:1.8. An increase in hydrogen pressure to 1 MPa results in afurther increase in conversion and also favoured the *cis-trans* isomerization of the unsaturated alcohol (Figure 3), which confirmed that the isomerization was closely related to the hydrogenation. According to these results (Figure 3), hydrogen pressure of 2–4 MPa promoted hydrogenation and isomerization but at the 6 MPa of hydrogen the overall selectivity to geraniol (*trans*) + nerol (*cis*) decreases. The decrease in selectivity could be due to the transition of a single phase to a biphasic system. Addition of hydrogen in the citral + CO_2 binary system resulted in a shifting of the gas-liquid phase boundary to the higher pressure. Thus, an increase in pressure of hydrogen above 4.5 MPa is more likely to cause the phase separation and the system was unable to maintain its single phase status. Generally, it is accepted that the concentration of the hydrogen adsorbed on the catalyst is the factor that determines selectivity and isomer formation. If the coverage of hydrogen on the metal surface is high, the probability is higher that two atoms are in a position to react with any double bond on approach. This will nevertheless result in low selectivity, because saturation of any double bond approaching to hydrogen will occur promptly. However, if there are only a few hydrogen atoms adsorbed, it is more likely that only one hydrogen atom will react with the double bond, producing the half-hydrogenation-dehydrogenation sequence which increases the probability of isomerization. Hence, there must be an optimum hydrogen concentration (4–4.5 MPa) that governs the highest rate of hydrogenation and isomerization. Below that pressure (< 4 MPa) the conversion is low but selectivity to the *trans*-isomer of unsaturated alcohol was prominent. If the hydrogen pressure is higher than 4.5 MPa, hydrogenation dominates the reaction pathway.

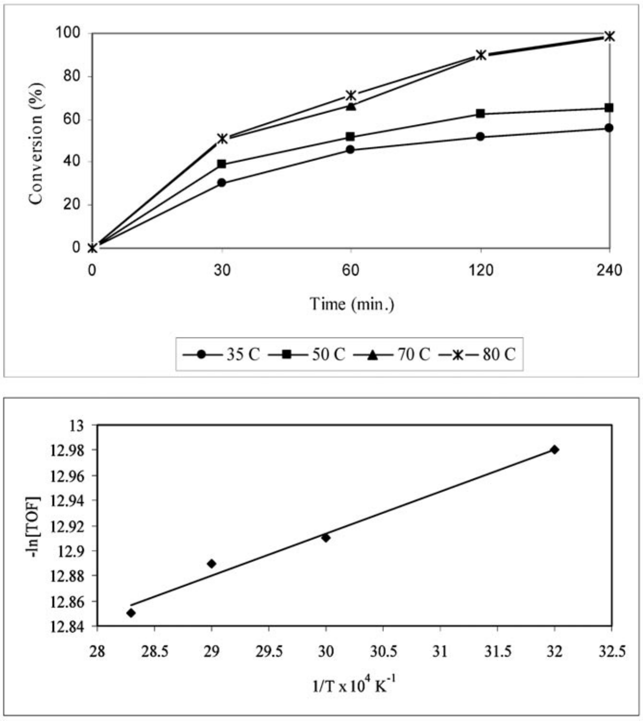


Figure 4. (*top*) Effect of temperature on citral conversion with time. (*bottom*) Arrhenius plot *Reaction conditions:* P_{CO_2} = 14 MPa; P_{H_2} = 4 MPa; amount of catalyst = 0.1 g; reactant = 6.24 mmol.

Effect of Temperature

To check the effect of temperature, citral hydrogenation was conducted at 35 °C, 50 °C, 70 °C and 80 °C at 14 MPa of CO_2 with the constant hydrogen partial pressure of 4 MPa (Figure 4, top). As expected the reaction was slow at 35 °C and a conversion of *ca.* 45% and the 57.5% selectivity for unsaturated alcohol [geraniol (*trans*) + nerol (*cis*)] were observed. When the reaction temperature was increased to 70 °C a considerable improvement in the conversion (99.8%) and the selectivity of 98.8% to geraniol (*trans*) was obtained. These results indicate that at the lower temperature the hydrogenation of C=C was favoured but at higher temperature C=O hydrogenation predominates as the gas phase bond dissociation energy of the C=O (174 kcal mol^{-1}) is higher than that of C=C (141 kcal mol^{-1}). Thus, higher temperature is necessary to enhance the activation of the C=O bond.[25] Accordingly, the increasing selectivity to geraniol (*trans*) + nerol (*cis*) changes the *cis*:*trans* ratio from 1:1.3 to 1:82.3. The product distribution does not change much as the temperature increased to 80 °C. From the above results, it could be suggested that an optimum temperature of 70 °C is necessary to achieve an excellent *trans* selectivity. Therefore, we have selected this temperature to study the other parameters affecting the conversion and selectivity. From the initial reaction rate an Arrhenius plot was obtained and the activation energy of 2.5 kJ mol^{-1} was calculated from the slope of the plot (Figure 4, bottom).

To summarize, the results of the reaction time, temperature and hydrogen pressure indicate that the high conversion leads to the high selectivty for geraniol (*trans*) + nerol (*cis*). A comparison was made between the selectivity (57.5% at 35 °C; 67.9% in 15 min and 39.9% at 0.5 MPa of hydrogen) obtained at the lowest conversion level to check the influence of the each of these individual parameters on the selectivity. These data indicates that the lowest selectivity was found at lower hydrogen pressure. Thus, hydrogen pressure is an important parameter, which strongly affects the selectivity for geraniol (*trans*).

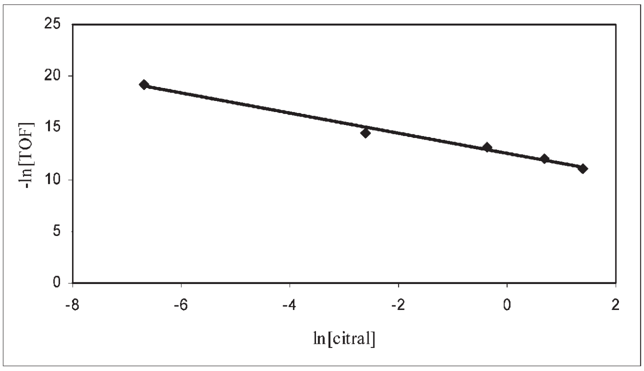


Figure 5. Reaction order with respect to the citral concentration. *Reaction conditions:* $T=70\,°C$; $P_{CO_2}=14$ MPa; $P_{H_2}=4$ MPa; amount of catalyst = 0.1 g.

Effect of Amount of Citral

Citral hydrogenation reactions were also conducted with varying amounts of citral (1.6, 3.12, 6.24 and 12.24 mmol) to examine the differences in the product distribution and to study the dependence of the initial TOF on reactant concentrations. Irrespective of the amount of the citral, geraniol (*trans*) + nerol (*cis*) was the main product. However, according to the conversion (99.8%) and selectivity (100%), 6.24 mmol of citral shows the best result. With 12.24 mmol of citral, the rate was slowest. To evaluate the reaction order with respect to citral, ln[TOF] was plotted against ln [*citral*], where [*citral*] is the initial citral amount and the slope of the plot gives the reaction order (Figure 5). Under the studied reaction conditions, the system exhibits the reaction order of 0.9715 ± 0.1, which is in contrast to the result of Singh et al.[26] They have reported a zero order reaction with respect to citral concentration for citral hydrogenation in hexane using Pt/SiO_2 catalyst. This result seems to show that, compared to the mesoporous catalyst in $scCO_2$, the deactivation process is faster for a conventional catalyst in an organic solvent medium.[27,28]

Effect of Catalyst Amount

To check the effect of the catalyst amount, on conversion and selectivity, citral hydrogenation was carried out for four different weights (0.025, 0.05, 0.1 and 0.2 g) of the catalyst. Figure 6 illustrates that the conversion and selectivity change with the amount of catalyst. For 0.025 g of catalyst *ca.* 15% conversion was obtained after 4 h of reaction suggesting that the rate of the reaction decreased and more time was necessary to reach complete conversion of citral. As the amount of catalyst was changed from 0.025 g to 0.1 g, the product distribution and the selectivity for geraniol (*trans*) + nerol (*cis*) changed from 48.8% to 100% as subsequently did the *cis/trans* ratio.

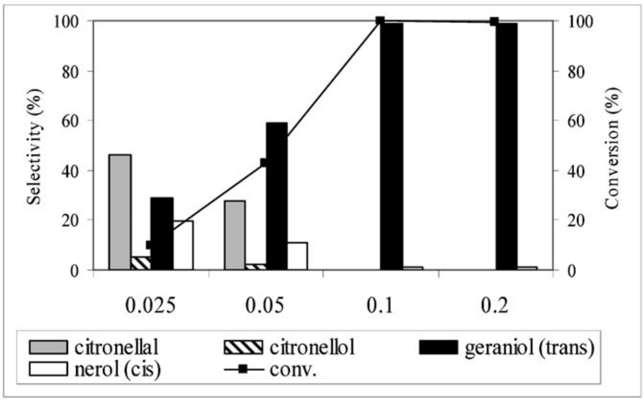


Figure 6. Effect of the catalyst amount on the hydrogenation of citral in $scCO_2$. *Reaction conditions:* $T=70\,°C$; $P_{CO_2}=14$ MPa; $P_{H_2}=4$ MPa; reaction time = 4 h; reactant = 6.24 mmol.

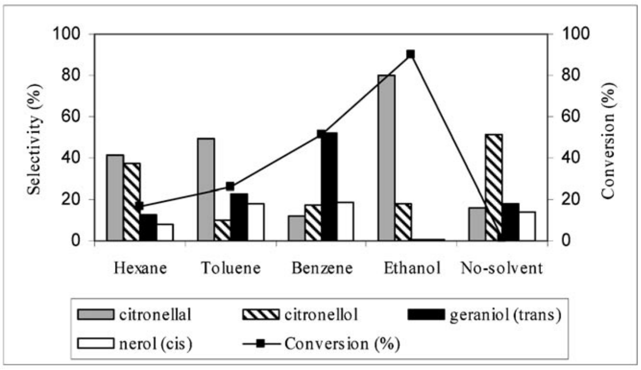


Figure 7. Effect of organic solvents and no solvent conditions on the conversion and selectivity of citral hydrogenation. *Reaction conditions:* $T=70\,°C$; $P_{CO_2}=14$ MPa; $P_{H_2}=4$ MPa; time = 4 h; organic solvent = 10 mL; amount of catalyst = 0.1 g; reactant = 6.24 mmol.

Supercritical Carbon Dioxide *vs.* Organic Solvent (h3)

Figure 7 represents the results of citral hydrogenation in different organic solvents and also in the solventless condition. Compared to $scCO_2$, conversion was lower in all organic solvents. Except benzene, mainly citronellal was obtained with high selectivity in each solvent. A maximum selectivity of 70% of the [geraniol (*trans*) + nerol (*cis*)] at *ca.* 50% conversion was achieved in benzene and the *cis:trans* ratio changed to 1:2.8. Considering the data obtained at 8 MPa of CO_2 (because of the same conversion of *ca.* 50%), it was observed that the rate of isomerization in $scCO_2$

(9.76×10^{-4} mmol s^{-1} g^{-1}) is greater than that in benzene (3.2×10^{-4} mmol s^{-1} g^{-1}). It might be suggested that, in the studied reaction conditions and al though this type of isomerization was also observed during hydrogenation in conventional organic solvents like benzene, the *cis:trans* ratio of the product (1:2.8) does not differ much from that of the reactant (*cis*:*trans* = 1:1.3). Hence, the formation of the unsaturated alcohol and consequently the pure *trans*-isomer is preferred in $scCO_2$ under the studied reaction system.

Effect of *cis:trans* Ratio

To check the effect of the *cis:trans* ratio of the substrate on the product distribution, a series of citral samples with different *cis:trans* compositions was hydrogenated in $scCO_2$ and the results are shown in Table 1. Independent of the *cis:trans* ratio of the substrate, geraniol (*trans*) was the main product. From the entry 1, where mainly *cis*-isomer was taken, a 70% selectivity for the *trans*-product was observed and the *cis:trans* ratio changes substantially. Similarly, the *cis:trans* ratio = 1:1 (entry 3) of citral also changes significantly to 1:49.1 in the product after the hydrogenation in $scCO_2$. Thus, *cis*- to *trans*-isomerization of the unsaturated alcohol occurred successfully during citral hydrogenation in $scCO_2$ using Pt-MCM-41 as catalyst.

The conversion profile of *cis*- and *trans*-isomers of citral during hydrogenation in $scCO_2$ medium shows that the concentrations of the *cis*- and *trans*-isomers decrease with time. The *cis*- and *trans*-isomers show first-order kinetics with respect to the citral concentration. A linear trend describes the monotonic decrease in the concentration (Figure 8). The decrease of selectivity for nerol (*cis*) selectivity and increase for geraniol (*trans*) was observed after the complete conversion of citral and attributes the high rate of conversion of the *cis*-isomer to the *trans*-isomer.

From the above discussion it was observed that the unsaturated alcohol, mainly geraniol (*trans*), was obtained with high selectivity from the hydrogenation of citral at optimum conditions of 4 MPa of hydrogen, 14 MPa of CO_2, 6.24 mmol of citral and the temperature of 70 °C in $scCO_2$ within the reaction time of 4–6 h using Pt-MCM-41 as catalyst.

Table 1. Effect of *cis:trans* ratio of the substrate on the product.[a]

Entry	*cis*:*trans* (Substrate)	*cis*:*trans* (Product)
1	1:0.07	1:0.65
2	1:10.9	No *cis* product
3	1:1	1:49.1

[a] *Reaction conditions:* reactant = 6.24 mmol; catalyst = 0.1 g; $T = 70\,°C$; $P_{CO_2} = 14$ MPa; $P_{H_2} = 4$ MPa; reaction time = 4 h.

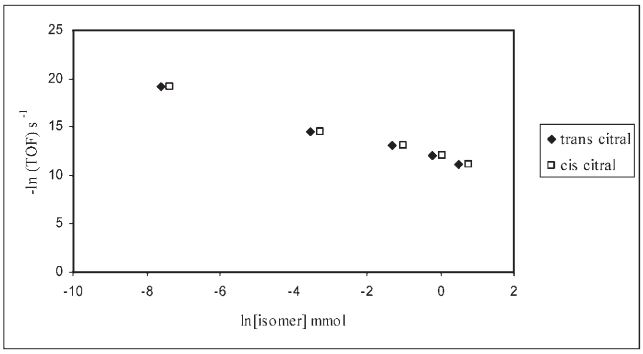
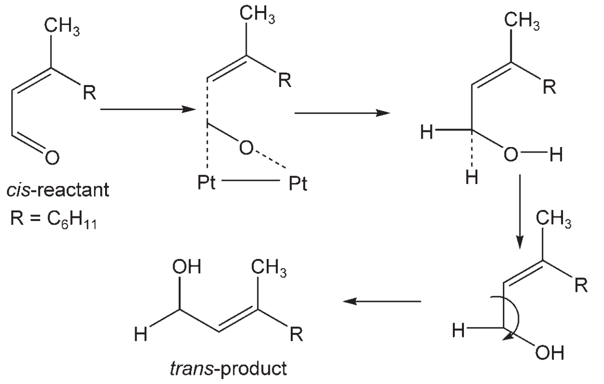


Figure 8. Dependence of hydrogenation rate with each isomer concentration. *Reaction conditions:* $T = 70\,°C$; $P_{CO_2} = 14$ MPa; $P_{H_2} = 4$ MPa; amount of catalyst = 0.1 g; reactant = 6.24 mmol.

Probable Reaction Path of Geraniol (*trans*-Isomer) Formation

It is well known that the product distribution pattern is associated with the stability of intermediate species on the catalyst surface at a particular pressure.[29] Figure 2 reveals that *ca.* 10–15% of citronellal and citronellol were obtained (the reaction was carried out at 14 MPa) in the beginning of the reaction and diminish at the end of the reaction. Hence, there might be the possibility of the dehydrogenation of citronellal or citronellol. To confirm this we have carried out the direct hydrogenation of citronellal and citronellol separately at the higher pressure (14 MPa) at 70 °C for 4 h. Interestingly, at higher pressure the direct hydrogenation of citronellal to citronellol was observed until 1 h and then it was dehydrogenated to citral. For citronellol also dehydrogenation to citronellal followed by citral was confirmed. Although we do not have any molecular level explanation at this stage, it might be suggested that the hydrogenation of citral to citronellal and citronellol is a reversible process and thermodynamically controlled. On the other hand, at short reaction time a higher selectivity for geraniol (*trans*) was observed [Figure 2; selectivity of geraniol (*trans*) is about 70% within 15 min]. It seems that the geraniol (*trans*) is formed from the direct hydrogenation of the reactant and the reaction path is kinetically controlled We hypothesize here that the *trans*-isomer could be formed from the (i) direct hydrogenation of the reactant and also (ii) as the time increases the probability of concentration of hydrogen increases in the medium and disturbed the equlibrium between citral, citronellal and citronellol, consequently the kinetically controlled path predominates.



Scheme 2. Probable reaction path of *cis* to *trans* isomerization during citral hydrogenation in $scCO_2$.

As the unsturated alcohol was the predominate product under the studied reaction conditions it could be suggested that the citral molecules adsorb strongly through the C=O using the most preferable adsorption geometry of di-$\sigma_{CO}\eta_2$ mode[30,31] at the expense of formation of a bond with surface Pt atoms. Adsorbed hydrogen occupied all the catalyst surface. Hence, the activated C=O penetrate along the Pt–H through the surface. Then an intermediate is formed between surface Pt and the citral molecule. Addition of a second hydrogen atom and subsequent desorption of product followed by the rotation of C–C bond results in isomerization[32] (Scheme 2).

Conclusions

In conclusion, we have demonstrated that $scCO_2$ is an attractive medium to carry out the selective hydrogenation of citral (*cis:trans* = 1:1.3) to produce only geraniol (*trans*) with remarkable selectivity of *ca.* 98.8% at a very high conversion of 99.8%. The selectivity for geraniol (*trans*) strongly depends on the several parameters such as CO_2 and hydrogen pressure, reaction time, citral concentration and the reaction temperature. To study the possible reaction path to the formation of geraniol (*trans*) a significant effect of CO_2 pressure (density) was observed. At higher density of CO_2, where the solubility of citral was high the hydrogenation of C=O occurred and the unsaturated alcohol was obtained with high selectivity. It has also been observed that hydrogen has an essential part in the isomerization. In $scCO_2$ the reaction kinetics exhibited a first-order reaction rate on citral concentration as well as hydrogen pressure suggesting that the catalyst is free from deactivation. Compared to other organic solvents the rate of isomerization was higher in $scCO_2$. The formation of several kinds of by-products that usually occur in organic solvents can be invalidated by using $scCO_2$ as reaction medium. This study demonstrates the versatility of the medium instead of being a simple “substitute solvent” to the conventional organic solvents.

Experimental Section

Materials

Citral (95% *cis:trans* = 1:1.3), citronellal (90%), citronellol (96%), geraniol (98%) and nerol (97%) were purchased from Aldrich and used as received. Citral samples containing a *cis:trans* ratio of 1:0.07, 1:10.9 and 1:1 were obtained from Kuraray Chemicals Co. Carbon dioxide (>99.99%) was supplied by Nippon Sanso Co. Ltd. Tetraethyl orthosilicate (TEOS) and chloroplatinic acid were obtained from Wako Japan and Aldrich, respectively. Cetyltrimethylammonium bromide (CTAB) from Aldrich, was used as template for the synthesis of the catalyst to obtain the mesoporous structure.

Catalyst Synthesis

Pt-MCM-41 catalyst was prepared by an *in situ* addition of 1 wt% solution of Pt salt ($H_2PtCl_6 \cdot xH_2O$) in a mixture of surfactant and silica precursor as described elsewhere.[33] Total amount of metal loading was *ca.* 1%.

Procedure for Citral Hydrogenation in $scCO_2$

The hydrogenation of citral was conducted in a stainless steel batch reactor (50 mL). The detailed method was described previously.[15] Briefly, 0.1 g of catalyst and 6.24 mmol of citral were loaded into the reactor and placed inside the oven at the desired reaction temperature. Hydrogen was first loaded into the reactor followed by the liquid CO_2 using a high-pressure liquid pump. Products were identified by GC/MS and analyzed quantitatively by GC (HP 6890) equipped with flame ionization detector (FID). The selectivity to each product was calculated by the following expression $S_i = Ci/\Sigma Cp$, where Ci is the concentration of the product ‘i’ and ΣCp is the total concentration of the product. Citral hydrogenation in an organic solvent was carried out under the same reaction conditions as of $scCO_2$ except that 10 mL of solvent were used instead of CO_2.

Separation of Geraniol (*trans*) from Nerol (*cis*)

As the separation of isomers was beyond the scope of this work, primarily, a very small-scale separation of geraniol (*trans*) from nerol (*cis*) was tried using the obtained product in ether + anhydrous $CaCl_2$. A white solid of the geraniol·$CaCl_2$ complex was formed at low temperature while nerol (*cis*) remained in solution. The resultant white solid was then washed with ether and decomposed in warm water followed by the formation of geraniol (*trans*) and $CaCl_2$. Although the result of separation was satisfactory, a lot of work is still necessary to optimize the separation conditions.

Phase Behaviour Studies

A 10-cm^3 high-pressure view cell equipped with sapphire window was used to determine the solubility of the reactant at 70 °C in $scCO_2$ at different pressures. The method is the same as that described previously.[15] This process was repeated at the intervals of 2 MPa of CO_2 pressure. The solubility of the substarte increased with increasing CO_2 pressure and a single phase was reached above 10 MPa of CO_2.

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References

[1] K. Bauer, D. Garbe, *Common Fragrances and Flavor Materials*, VCH, Weinheim, **1985**.
[2] M. Wink, *Biochemistry of Plant Secondary Metabolism Annual Plant Reviews*, Vol. 2, Sheffield, Academic Press, **1999**.
[3] S. Arctander, *Perfume and Flavor Chemicals*, Vols. 1 and 2, Allured Publishing, **2000**.
[4] P. J. Mohr, R. L. Halcomb, *J. Am. Chem. Soc.* **2003**, *125*, 1712.
[5] G. Lafaye, C. Micheaud-Especel, C. Montassier, P. Marecol, *Appl. Catal. A* **2002**, *230*, 19.
[6] A. M. Silva, O. A. A. Santos, M. J. Mendes, E. Joradao, M. A. Fraga, *Appl. Catal. A* **2003**, *241*, 155.
[7] J. C. Ruiz-Serrano, A. Sepulveda-Escaribino, A. Rodriguez-Reinoso, D. Durpez, *J. Mol. Catal. A: Chem.* **2007**, *268*, 227.
[8] M. A. Aramendia, V. Borau, C. Jiménez, J. M. Marinas, J. R. Ruiz, F. J. Urbano, *J. Mol. Catal. A:* **2001**, *171*, 153.
[9] a) P. Gallezot, D. Richard, *Catal. Rev.-Sci. Eng.* **1998**, *40*, 81; b) P. Mäki-Arvela, T. Hájek, T. Salami, D. Yu. Muzrin, *Appl. Catal. A: Gen.* **2005**, *292*, 1; c) R. Malathi, R. P. Viswanath, *Appl. Catal. A: Gen.* **2001**, *208*, 323; d) P. Reyes, H. Rojas, G. Pecchi, J. L. G. Fierro, *J. J. Mol. Catal. A: Chem.* **2002**, *179*, 293.
[10] P. G. Jessop, T. Ikariya, R. Noyori, *Nature* **1968**, *368*, 231; P. G. Jessop, Y. Hsiano, T. Ikariya, R. Noyori, *J. Am. Chem. Soc.* **1996**, *118*, 344.
[11] A. Fürstner, D. Koch, K. Langemann, W. Leitner, C. Six, *Angew. Chem.* **1997***, XXX,* XXX; *Angew. Chem. Intl. Ed.* **1997**, *36*, 2466.
[12] P. Meric, K. MK. Yu, A. T. S. Kong, S. C. Tsang, *J. Catal.* **2006**, *237*, 330.
[13] M. Chatterjee, A. Chatterjee, P. Raveendran, Y. Ikushima, *Green Chem.* **2006**, *8*, 445; R. Liu, F. Zhao, S. Fujita, M. Arai, *Appl. Catal. A: Gen.* **2007**, *316*, 127.
[14] M. Chatterjee, A. Chatterjee, Y. Ikushima *Green Chem.* **2004**, *6*, 114.
[15] a) M. Chatterjee, F. Y. Zhao, Y. Ikushima *Adv. Synth. Catal.* **2004**, *346*, 459; b) M. Chatterjee, F. Y. Zhao, Y. Ikushima, *New J. Chem.* **2002**, *##26##*27, 510.
[16] H. Tiltscher, H. Hofmann, *Chem. Eng. Sci.* **1987**, *42*, 959; H. Tiltscher, H. Wolf, J. Schelchshorn, *Ber. Bunsen-Ges. Phys. Chem.* **1984**, *88*, 897.
[17] P. Subra, A. Vega-Bancel, E. Reverchon, *J. Supercrit. Fluids* **1998**, *12*, 43.
[18] C. H. Giles, D. Smith, A. P. D. Silva, I. A. Easton, *J. Colloid Interface Sci.* **1974**, *47*, 755.
[19] R. D. Weinstein, A. R. Renslo, R. L. Danheiser, J. W. Tester, *J. Phys. Chem. B* **1999**, *103*, 2878.
[20] A. K. Dillow, J. S. Brown, C. L. Liotta, C. A. Eckert, *J. Phys. Chem. A*, **1998**, *102*, 7609.
[21] M. Burgener, R. Furrer, T. Mallat, A. Baiker, *Appl. Catal. A* **2004**, *268*, 1.
[22] P. Raveendran, S. L. Wallen, *J. Am. Chem. Soc.* **2002**, *124*, 12590.
[23] F. Zhou, S. Fujita, S. Akihara, M. Arai, *J. Phys. Chem. A* **2005**, *109*, 4419.
[24] J. M. Marinas, A. Porras, F. J. Urbano, *Appl. Catal. A Gen.* **1998**, *172*, 31.
[25] A. Patil, M. A. Banares, X. Lei, T. P. Fehlner, E. F. Wolf, *J. Catal.* **1996**, *159*, 458.
[26] U. K. Singh, M. A. Vannice, *J. Mol. Catal. A* **2000**, *163*, 233.
[27] A. F. Trasarti, A. J. Marchi, C. R. Apesteguia, *J. Catal.* **2007**, *247*, 155.
[28] S. C. Shen, S. Kawi, *Appl. Catal. B Environmental* **2003**, *45*, 63.
[29] M. Burgener, D. Ferri, J. D. Grunwaldt, T. Mallat, A. Baiker, *J. Phys. Chem. B* **2005**, *109*, 16794.
[30] F. Delbecq, P. Sautet, *J. Catal.* **2002**, *211*, 398.
[31] F. Delbecq, P. Sautet, *J. Catal.* **1995**, *152*, 217.
[32] A. Rossin, G. Kovacs, G. Ujaque, A. Lledos, F. Joo, *Organometallics* **2006**, *25*, 5010.
[33] M. Chatterjee, T. Iwasaki, Y. Onodera, T. Nagase, *Catal. Lett.* **1999**, *61*, 199.