Hydrogenation of Citral using Monometallic Pt and Bimetallic Pt-Ru Catalysts on a Mesoporous Support in Supercritical Carbon Dioxide Medium

M. Chatterjee,[a] F. Y. Zhao,[a] Y. Ikushima[a, b,*]

[a] Supercritical Fluid Research Center, National Institute of Advanced Industrial Science and Technology, 4-2-1 Nigatake, Miyagino-ku, Sendai 983–8551, Japan
Phone: (+81)-22-237-5211; fax: (+81)-22-237-5224, y-ikushima@aist.go.jp
[b] CREST, Japan Science and Technology Corporation (JST), Kawaguchi 332–0012, Japan

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Abstract: Supercritical carbon dioxide was shown to be a suitable reaction medium for the highly efficient hydrogenation of citral using monometallic Pt and bimetallic Pt-Ru supported on a mesoporous material, MCM-48, as catalyst. A remarkable change in the product distribution was observed after the addition of Ru to the monometallic Pt catalyst in supercritical carbon dioxide. The monometallic Pt catalyst was found to be highly selective to the unsaturated alcohol (geraniol + nerol) at a temperature of 323 K within 2 h whereas the bimetallic catalyst becomes selective to the partially saturated aldehyde (citronellal) under the same reaction conditions. Phase behavior plays an important role in the product distribution. Highest conversion and high selectivity to citronellal were achieved in the homogeneous phase for the Pt-Ru catalyst while on the other hand the unsaturated alcohol (geraniol + nerol) was produced in the heterogeneous phase for the monometallic Pt catalyst. An XPS study offers strong evidence of the electronic modification of Pt after the addition of Ru in the bimetallic catalyst. The change in product distribution on the Pt-Ru bimetallic catalyst may be explained by the appreciable interaction between the medium and the metal particles promoted by the presence of metallic Ru.

Keywords: citral; hydrogenation; monometallic Pt; phase behavior; selective bimetallic Pt-Ru catalysts; supercritical carbon dioxide

Introduction

Selective hydrogenation of α,β-unsaturated aldehydes is an important research area because of the relevance of these compounds in the pharmaceutical and fine chemical industries.[1] Citral is an unsaturated aldehyde, hydrogenated products of which have been widely used in the fragrance industry. It possesses an isolated C=C bond besides the conjugated C=O and C=C bonds, an interesting reactant from the scientific point of view. Scheme 1 displays the reaction network of citral hydrogenations. The hydrogenation of the conjugated C=O bond leads to *cis*- and *trans*-isomers of the unsaturated alcohol (geraniol and nerol), while hydrogenation of the conjugated C=C bond or the isolated C=C bond yields either the saturated aldehyde (citronellal). Moreover, the resulting unsaturated alcohol or partially saturated aldehyde can by hydrogenated at its remaining unsaturated bond to yield the partially saturated alcohol (citronellol). In addition, there are the possibilities of *cis-trans* isomerization or several types of side reactions such as cyclization, acetalization, etc. Thermodynamic calculations indicate that the isolated C=C bond is hydrogenated most easily followed by the conjugated C=C and C=O bonds. Several authors have reported the liquid-phase hydrogenation of citral over noble metals on different supports,[2] bimetallic catalysts such as Rh-Ge,[3] Ru-Sn,[4] and basic catalysts [5] in various organic solvents. The effectiveness of supported noble metals for the selective hydrogenation of citral can also be enhanced by the addition of promoters such as Sn, Ge, Fe, etc., whereas by altering the operating conditions such as temperature, pressure, and especially solvent, the product distribution can be varied significantly.[6] However, in hydrophobic solvents (such as cyclohexane, alcohols) and in the presence of quite acidic catalysts, different types of side reaction occur (acetal formation, cyclization etc), leading to a drop in selectivity for the desired product.[7]

Supercritical carbon dioxide ($scCO_2$) is receiving considerable and growing interest as an environmentally benign reaction medium for organic synthesis. The high miscibility of $scCO_2$ with many reactant gases can help to avoid mass-transfer limitations,[8] which are frequently encountered in gas-liquid phase reactions. The high compressibility of $scCO_2$,[9] especially in the

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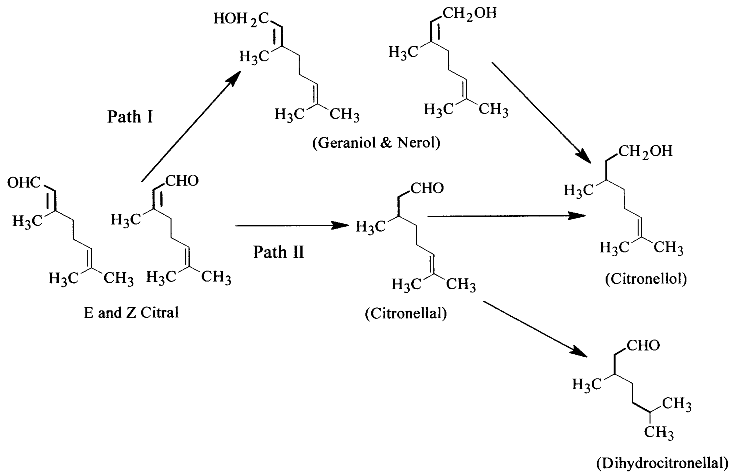

Scheme 1.

near critical region could result in a significant change in selectivity. Applications of $scCO_2$ to hydrogenation reactions involving heterogeneous catalysts[10–12] are particularly attractive. Furthermore, the careful design of solid catalysts to capitalize the unique solvent properties of $scCO_2$ may afford greater advantages, resulting in enhanced activity and selectivity. Considering our previous work[13] on the hydrogenation of cinnamaldehyde in $scCO_2$ using a Pt-Ru bimetallic catalyst, leading to the exclusive formation of unsaturated alcohol, we have now attempted to achieve the hydrogenation of citral using monometallic Pt and Pt-Ru bimetallic catalysts supported on MCM-48 in $scCO_2$.

Results and Discussions

Catalyst Characterization

The XRD patterns of the mesoporous silica support and the resulting materials either of the monometallic or the bimetallic type clearly implied the structural order for the cubic crystallographic space group *Ia3d* with distinct (2 1 1) and (2 2 0) reflections. The mesoporosity of the material was shown to remain unaltered after the *in situ* addition of Pt or Pt-Ru. For the monometallic and bimetallic catalysts, no line corresponding to Pt or the Pt-Ru alloy was observed.

TEM photographs also directly reveal the intact mesoporosity of the support after the encapsulation of Pt and Pt-Ru. For the monometallic Pt-MCM-48 catalyst, the images of the calcined material indicate a good Pt distribution represented by black dots and the particles were mainly spherical in shape. TEM images of Pt-Ru catalyst also show better visualization of the metal particle after long-term exposure. Massive agglomerations of smaller particles were observed on the surface of the mesoporous support. These agglomerates consisted of many small crystallites clustered together to form larger aggregates and were distributed randomly on the surface of the support. Mainly larger particles are seen on the surface of the bimetallic catalyst and they were in different shape.

To investigate the oxidation states of Pt and Ru, XPS analyses were performed. Table 1 shows the binding energies for the photoelectron peaks of Pt $4f_{7/2}$, $4f_{5/2}$, Ru$3d_{5/2}$, $3d_{3/2}$, C $1s$ and Si $2p$ peaks for Pt-Ru as well as Pt catalysts. As shown in Table 1 it can be observed that, for the monometallic catalyst, the binding energies of Pt $4f_{7/2}$ and $4f_{5/2}$ are 70.4 and 73.7, respectively, which are very close to the value of Pt foil[14] (Pt $4f_{7/2}$ and $4f_{5/2}$ 70.7 and 74.0 eV, respectively). Therefore, the presence of only metallic Pt in the monometallic Pt-MCM-48 catalyst has been suggested.

In the bimetallic catalyst, the spectrum can be fitted by two pairs of overlapping Lorentzian curves. The Pt $4f_{7/2}$ and $4f_{5/2}$ lines appearing at 71.0 and 74.3 eV are attributed to the metallic Pt. The second pair appearing as Pt $4f_{7/2}$ and $4f_{5/2}$ peaks with binding energies of 72.5 and 75.8, respectively, are very closely related to those of Pt^{2+}. So, regarding the state of Pt, it can be inferred that the bimetallic catalyst contains Pt^{2+} as well as metallic Pt. Analysis of Ru ($3d_{5/2}$ and $3d_{3/2}$) is less straightforward as peaks occur together with the carbon peak (Table 1); hence, much care has been taken to avoid misinterpreting the results. The Ru $3d$ spectra for Pt-Ru bimetallic catalyst exhibit a distinctive spin orbit doublet of metallic Ru (280.1 eV and 284.3 eV) along with the peak of oxidized Ru (282.5 eV and 286.6 eV, respectively, Table 1).

Table 1. XPS binding energies (B. E.) of monometallic Pt and bimetallic Ru-Pt catalysts.

Catalyst	Pt $4f_{7/2}$ B. E. (eV)	Pt $4f_{5/2}$ B. E. (eV)	Ru $3d_{5/2}$ B. E. (eV)	Ru $3d_{3/2}$ B. E. (eV)	Si $2p$	C $1s$
Pt-MCM-48	70.4	73.7	–	–	104.3	–
Pt-Foil[a]	70.7	74.0	–	–		–
Pt-Ru-MCM-48	70.8 (72.5)	74.3 (75.8)	280.1 (282.5)	284.3 (286.6)	104.3	284.4 and 285.7
Pt-Ru-MCM-48[b]	71.6	74.6	282.9	287.2	104.3	284.6 and 286.0

Data in the parenthesis indicate the higher valence state that was observed in the bimetallic catalysts

[a] Ref.: J. F. Moulder, W. F. Sticklle, P. E. Sobol, K. D. Bomben, *Handbook of X-ray Photoelectron Spectroscopy*, (Eds.: J. Chastain, R. C. King Jr.), Physical Electronics Inc., Minnesota, USA, **1995**.

[b] After on-stream operation.

Catalytic Activity

Monometallic Pt-MCM-48 Catalyst

Fig. 1a shows the influence of the CO_2 pressure on the performance of the monometallic Pt catalyst for the hydrogenation of citral at 323 K. Under the studied reaction conditions (reaction time: 2 h, P_{H_2}: 4 MPa) the hydrogenation reaction path from citral to unsaturated alcohol (path I) is more active than citral to citronellal (path II; Scheme 1). The selectivity to the unsaturated alcohol increases from ~15% to ~90% with an increase in pressure from 6 to 10 MPa, and then decreases. From the previous work[15] on the selective hydrogenation of cinnamaldehyde, it was found that Pt-supported catalysts are selective to the hydrogenation of C=O in $scCO_2$ medium. Citral also shows a similar trend in selectivity in the presence of the Pt catalyst. The selectivity to unsaturated alcohol (geraniol + nerol) changes with CO_2 pressure (or with CO_2 density). For instance, a change in pressure from 8 to 10 MPa corresponds to density changes from 520.8 to 708.3 kg m^{-3}.[16] Therefore, the CO_2-pessure-dependent selectivity to the C=O bond could be appropriately related to the density of the medium. The real reason for this effect may be a debatable issue but there is no doubt that the pressure effect has a strong influence on the selectivity. In addition, the presence of the metallic platinum, inferred from the XPS study (as the surface exposing metallic Pt is more favorable for C=O adsorption) favors the hydrogenation of C=O followed by the formation of unsaturated alcohol. No other by-product (isopulegol, cyclization product) has been found under the studied reaction conditions.

Bimetallic Pt-Ru Catalyst

Fig. 1b shows the results of the hydrogenation of citral using bimetallic Pt-Ru catalyst in $scCO_2$ medium at 323 K for 2 h. The addition of Ru significantly changed the product selectivity to the partially saturated aldehyde (citronellal). A selectivity of 80% to the citronellal has been achieved in 90% conversion at 12 MPa of CO_2 pressure (Fig. 1b). The addition of Ru to the Pt changes the reaction path from I to II (Scheme 1) and the conversion and selectivity increases with the Ru/Pt atomic ratio and reaches a maximum at ~30% Ru (Fig. 1c). Thus, it may be concluded that the Ru plays an important role in the formation of the partially saturated aldehyde. From the XPS study (Table 1), it was found that the Pt-Ru bimetallic catalyst contains metallic Ru along with Pt^{2+}. Furthermore, this result is in contrast to our earlier observation on the hydrogenation of cinnamaldehyde, [13], and so it can be suggested that citral may

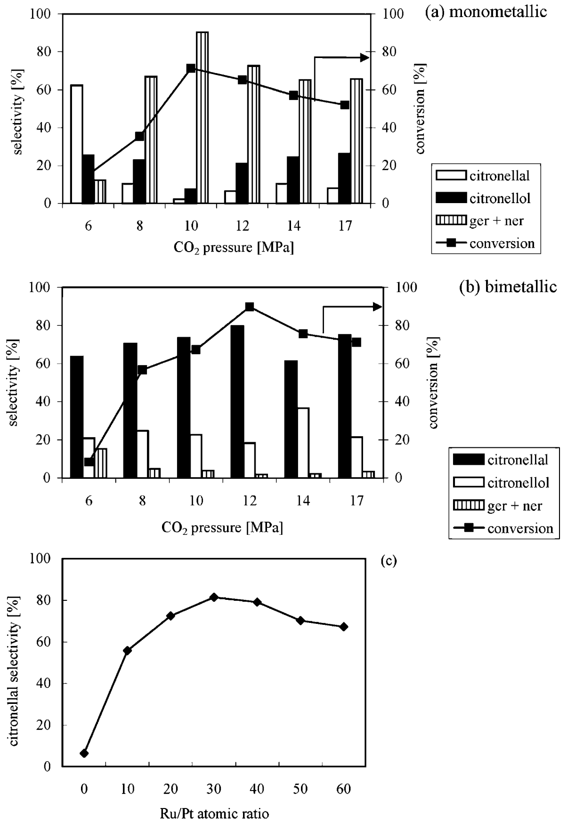

Figure 1. CO_2 pressure *vs.* conversion and selectivity for the hydrogenation of citral over (**a**) monometallic Pt-MCM-48 and (**b**) bimetallic Pt-Ru-MCM-48. Reaction conditions: T = 323 K; reaction time = 2 h; P_{H_2} = 4 MPa; amount of catalyst = 0.1 g. (**c**) Ru/Pt atomic ratio *vs.* selectivity to citronellal.

be adsorbed on the metal surface in such a manner that the hydrogenation of the C═C bond occurs smoothly since it is well known that hydrogenation of C═C is kinetically favored over C═O.

For the bimetallic Pt-Ru catalyst, the conversion and the selectivity to citronellal rises from ~8% to 80% and ~70% to ~90%, respectively, with an increase in CO_2 pressure from 6 to 12 MPa, reaching a maximum at 12 MPa (Fig. 1b). It should be mentioned that for both catalysts the corresponding product selectivity passes through a maximum. This phenomenon could be associated with tuning of the average distance between the solute molecules and the transition state, accompanied with the density, varies with pressure. That is, for a compressed liquid such as supercritical fluid, variation in density causes a change in chemical equilibrium and affects the activity and selectivity of a reaction.[17]

Figs. 2a and 2b, respectively, represent the variation of conversion and product distribution with time for the monometallic Pt and the bimetallic Pt-Ru catalysts at 323 K in the hydrogenation of citral. It can be seen that the rate of reaction is faster at short reaction times and almost a steady state has been reached within a period of 2 h of reaction. The conversion of citral is higher for the Pt-Ru catalyst compared to the monometallic Pt catalyst at the same reaction time. Fig. 2a also reveals that for the Pt catalyst the reaction proceeds through the reaction path I but for the bimetallic catalyst the path changes to II (Scheme 1). Hence, in $scCO_2$, the Pt catalyst favors the hydrogenation of the C═O bond instead of the C═C bond.

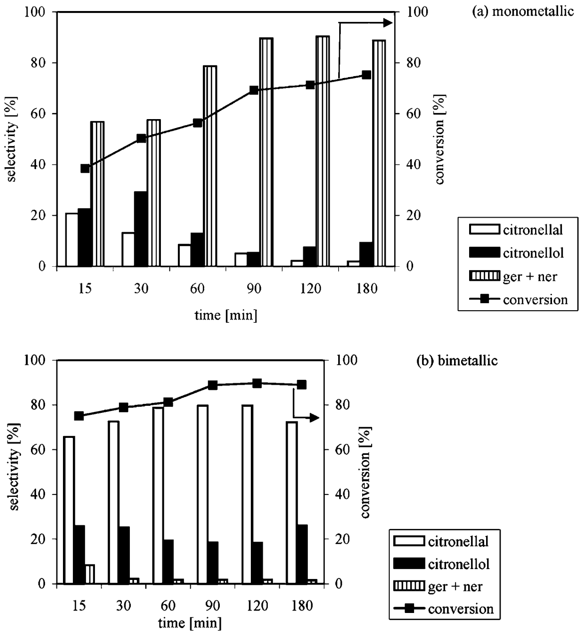

Figure 2. Variation of conversion and selectivity with time in the hydrogenation of citral over (**a**) monometallic Pt-MCM-48 and (**b**) bimetallic Pt-Ru-MCM-48. Reaction conditions: T = 323 K; P_{H_2} = 4 MPa; P_{CO_2} = 10 MPa for monometallic catalyst; P_{CO_2} = 12 MPa for bimetallic catalyst; amount of catalyst = 0.1 g in each case.

Phase Behavior Studies

The phase behavior of the reaction mixture is of major concern for the design and understanding of the catalytic systems operating in $scCO_2$. From naked eye observations, it has been found that the solubility of citral increases with increasing CO_2 pressure, and a homogeneous system was attained above 11 MPa of CO_2 and 4 MPa of hydrogen. A pronounced effect of phase behavior was observed on the catalytic performance during hydrogenation of citral. For both catalysts, at the lower CO_2 pressures below 7 MPa the conversion is lower due to the mass-transfer limitation in the liquid phase, but with increasing pressure the increase in the reactant concentration in $scCO_2$ results in higher conversion. Consequently, around 17 MPa of CO_2 pressure, additional amounts of CO_2 lower the reactant concentration and so reduce the conversion (Figs. 1a and 1b). Regarding the selectivity, for the bimetallic catalyst a maximum in the citronellal selectivity corresponds well to the appearance of the homogeneous phase around 12 MPa, whereas for the monometallic Pt catalyst a maximum in the selectivity to the unsaturated alcohol (geraniol + nerol) was observed around 10 MPa in the heterogeneous phase but not in the homogeneous phase above 12 MPa. Although the exact reason is not clear, the pressure-dependence of the appearance of the maximum peaks (Fig. 1a and Fig. 1b) may lead to some direct interaction between the metal particles and the medium; addition of Ru to Pt changes the nature of the metal and the types of interaction with the medium.[16] To get some primordial insight about the type of interaction between the medium and the metal, XPS and FTIR have been done after on-stream operation of the catalyst. A distinctive spin orbit doublet of oxidized Ru at 282.9 eV ($3d_{5/2}$) and 287.2 eV ($3d_{3/2}$), respectively (Table 1), indicates a significant change in the oxidation state of Ru. These binding energy values are in between those of the two oxidation states of RuO_3 (282.5) and RuO_4 (283.3). Hence it may be suggested that CO_2 could be dissociated on the metal particles and produces some oxygen fragments. The oxygen fragments may be partially replaced by surface hydrogen as observed in the primary data obtained from FTIR. This could be a reason but further studies are required to clarify the actual surface species during the reaction, which is beyond the scope of this article.

Effect of Hydrogen Pressure

We have further examined the effect of hydrogen pressure on the conversion and selectivity for the hydrogenation of citral. Figures 3a and 3b indicate an increase in conversion with the hydrogen pressure for the monometallic and bimetallic catalysts, respectively. The high solubility of hydrogen in $scCO_2$ compared to that in conventional organic solvents is responsible for the increase in conversion. On the other hand, Figure 3b indicates a change in selectivity of unsaturated alcohol (geraniol + nerol) from 5 to 33.4% with H_2 pressure from 2 to 6 MPa along with the increasing conversion. As the hydrogenation of citral consists of a series of reaction pathways, the change in hydrogen pressure could affect the individual rate constants due to the difference in activation volume, and hence the increased pressure may favor one reaction over others, resulting in an improved selectivity for the unsaturated alcohol (geraniol + nerol) in $scCO_2$.

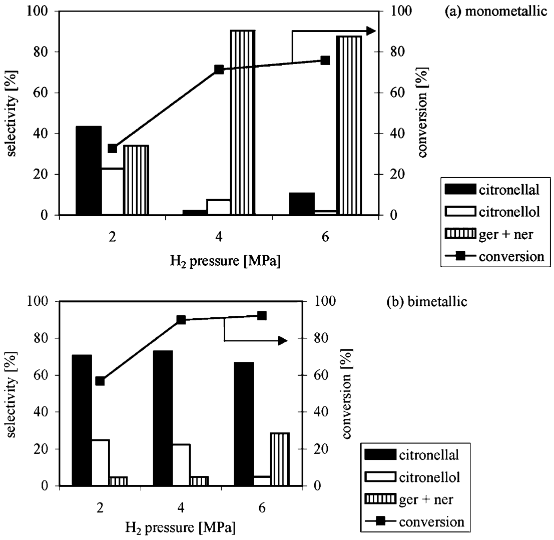

Figure 3. Influence of hydrogen pressure on conversion and selectivity in the hydrogenation of citral over (**a**) monometallic Pt-MCM-48 and (**b**) bimetallic Pt-Ru-MCM-48. Reaction conditions: T = 323 K; reaction time = 2 h; $P_{CO_2} = 10$ MPa for monometallic catalyst; $P_{CO_2} = 12$ MPa for bimetallic catalyst; amount of catalyst = 0.1 g in each case.

Effect of Temperature

Table 2 shows that the product distribution for the citral hydrogenation is strongly dependent on the reaction temperature for the Pt-Ru catalyst. The reactions were conducted at 308, 323 and 343 K at 10 and 12 MPa of CO_2 with the constant hydrogen partial pressure of 4 MPa using monometallic Pt (Entries 1–3) and bimetallic Pt-Ru catalysts (Entries 4–6). With an increase in temperature, the selectivity to the unsaturated alcohol (geraniol + nerol) was increased from 0 to 23.4% for the bimetallic catalysts; however, for the monometallic catalyst it remained constant (Table 2). Either the physical properties of $scCO_2$ such as density vary widely with change in temperature or the effect of temperature on the reaction network could change the product selectivity.

Comparison with Organic Solvents

The advantage of using $scCO_2$ as a reaction medium in the hydrogenation is further exemplified by comparing the conversion and selectivity in organic solvents and under solvent-less conditions. As shown in Figure 4, in the organic solvent, the monometallic Pt catalyst was found to be selective to citronellal, whereas unsaturated alcohol (geraniol + nerol) is the main product in $scCO_2$ (Figure 1a). This differentiated behavior of the monometallic catalyst in $scCO_2$ is due to the difference in the availability of hydrogen. In the liquid-phase hydrogenation the SiO_2-supported catalyst exhibits first-order dependences on hydrogen pressure.[18] In the $scCO_2$ medium the better availability of hydrogen leads to faster and more consecutive hydrogenation of the unsaturated aldehyde to the unsaturated alcohol.

For the bimetallic catalysts, although citronellal was the main product for $scCO_2$ and organic solvents, but when compared to $scCO_2$, the selectivity has been decreased significantly. Figure 4 also reveals that, in the solvent-less conditions, the conversion is 1.3% and 1.8%

Table 2. Effect of temperature on the hydrogenation of citral over Pt-MCM-48 and Pt-Ru-MCM-48 catalyst under $scCO_2$ medium.[a]

Entry	Catalyst	Temp. (K)	(%) Conv.	Selectivity (%)		
				Citronellal	Citronellol	Geraniol + Nerol
1	Pt/MCM-48[b]	308	32.7	23.2	22.8	54.0
2		323	71.3	2.1	7.5	90.4
3		343	75.8	1.4	10.1	88.5
4	Pt -Ru/MCM-48[c]	308	21.4	68.7	31.2	0.1
5		323	89.8	69.8	28.3	1.9
6		343	91.2	66.6	10.0	23.4

[a] Reaction conditions: citral, 6.5 mmol; catalyst, 0.1 g; $H_2 = 4$ MPa; reaction time = 2 h.
[b] CO_2: 10 MPa.
[c] CO_2: 12 MPa.

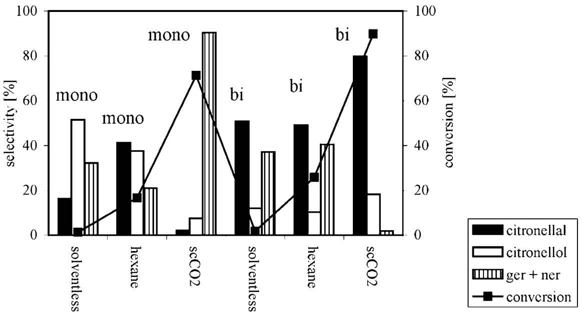

Figure 4. Effect of organic solvent in selectivity and conversion in the hydrogenation of citral. Reaction conditions: T = 323 K; reaction time = 2 h; amount of solvent = 10 mL; amount of catalyst = 0.1 g; P_{H_2} = 4 MPa.

Table 3. Catalyst deactivation studies during the hydrogenation of citral.[a]

	Conversion [%][b]	Conversion [%][c]
Fresh	89.8	71.3
Recycle 2	89.3	71.3
Recycle 3	89.3	71.0
Recycle 4	89.2	71.1

[a] Reaction conditions: citral, 6.5 mmol; catalyst, 0.1 g; H_2, 4 MPa; reaction time, 2 h.
[b] Monometallic, 10 MPa of CO_2.
[c] Bimetallic, 12 MPa of CO_2.

for the mono- and bimetallic catalysts, respectively. The remarkable reduction in conversion and selectivity can be attributed to the greater mass-transfer resistances existing in the liquid phase and solvent-less conditions relative to the $scCO_2$ medium. Therefore, the enhancement of conversion and selectivity for the above-mentioned reaction must be an advantage of $scCO_2$ medium.

Deactivation of Catalysts

Deactivation of the catalyst is a commonly occurring problem for the hydrogenation of citral in organic solvents, which is mainly associated with the decarbonylation reaction.[5,19–21] This is due to the accumulation of inhibiting carbonaceous species on the catalyst surface.[22,23] To check the probability of leaching of Ru, we used the liquid product as the catalyst but it was inactive. Moreover, in $scCO_2$ hydrogenation of citral can be carried out for a longer time and also for successive runs without facing any problems of deactivation such as a change in conversion and selectivity (Table 3). The reason could be a limitation of the inhibiting species in $scCO_2$ as an effect of the extraction power of $scCO_2$, which prevented the deposition of the inhibiting materials over the catalyst surface.[24] Therefore, this result highly implied the possible advantage of supercritical medium in heterogeneous catalysis over conventional processes for the hydrogenation of citral.

Conclusions

It was demonstrated that $scCO_2$ is an attractive medium to carry out the selective hydrogenation of citral. Simple tuning of the reaction condition leads to the formation of the desired product. The monometallic Pt catalyst was found to predominantly form the unsaturated alcohol (geraniol + nerol), whereas the addition of Ru to the Pt considerably changes the selectivity to the citronellal and a maximum in the selectivity was found at the homogeneous conditions. We speculate that this specific behavior could be due to the modification of the metal's surface upon interaction with the medium.[16] Further research should be required to elucidate the actual reason. The deactivation of catalyst as well as the formation of several kinds of by-products that usually occur in organic solvents can be avoided by using $scCO_2$ as reaction medium. Hence, from the practical viewpoint, $scCO_2$ as reaction medium can provide several advantages over organic solvents. In addition to that, the solubility of hydrogen also plays a key role in the rate enhancement (phase behavior). So, $scCO_2$ cannot be considered merely as a simple "substitute solvent" to the conventional organic solvents. The simple catalyst methodology presented here could be highly relevant for the further development of clean chemical processes based on heterogeneous catalysts in $scCO_2$ medium.

Experimental Section

Catalyst Synthesis

The bimetallic catalyst was prepared by an *in situ* addition of 1 wt % solution of Ru and Pt salt in a mixture of surfactant and silica precursor. The sources of silicon and Pt are tetraethyl orthosilicate (95%, TEOS) (Wako, Japan) and chloroplatinic acid (98.5%, Aldrich), respectively. As the Ru source, ruthenium acetylacetonate (97%, Aldrich) was chosen to prevent acetal formation.[25]. Cetyltrimethylammonium bromide (99%, Merck) was used as template to obtain the mesoporous structure. Under stirring conditions, the solutions of different Ru /Pt ratios followed by the TEOS (5.0 g) were added to the starting gel, containing template (2.39 g) and sodium hydroxide (0.33 g) in deionized water (27.0 g). The stirring was continued for 2 h. Finally, the resultant gel was autoclaved at 413 K for 48 h.0 The molar composition of the gel was: 1 TEOS: 0.27 CTABr: 0.34 Na_2O: 62.5 H_2O. The resultant material was filtered, dried and then calcined at 823 K for 10 h in air. The monometallic catalysts were also prepared in the same way as described above. The total amounts of metal loading were

~3.5% and 1% for bimetallic and monometallic catalysts, respectively.

Catalyst Characterization Techniques

All the catalysts were primarily characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The X-ray diffraction pattern was recorded on a Rigaku-RAD-X system using monochromatized Cu Kα radiation ($\lambda = 1.542$ Å). In general, the diffraction data were collected using the continuous scan mode with a scan speed of 2 deg/min over the scan range $2\theta = 2-15°$. Transmission electron microscopy (TEM) of the calcined material was performed on a JEOL JEM-2000 EX (II) operating at 200 kV. Calcined samples were deposited on a grid with a holey carbon copper film. The powder was suspended in ethanol by the ultrasonic method and a drop of this solution was placed on the support film. X-ray photoelectron spectra (XPS) were obtained with an Ulvac Phi 5601 spectrometer using Mg Kα (1253.6 eV) radiation of twin anodes in the constant analyzer mode with a pass energy of 50 eV. The X-ray power was limited to 14.0 kV and 400 W. The binding energy was determined by referencing to the Si 2*p* binding energy of 104.3 eV. The spectrum was fitted to the Gaussian spectra of Pt $4f_{7/2}$, Pt $4f_{5/2}$ and Ru$3d_{3/2}$, Ru $3d_{5/2}$ by optimizing the peak heights and positions assuming the fixed peak-to-peak difference at 3.30 eV.

General Procedure for the Hydrogenation of Citral in scCO$_2$

The hydrogenation of citral was carried out in a stainless steel batch reactor (50 mL). 0.1 g of catalyst and the reactant (6.5 mmol) were loaded into the reactor. Then the reactor was sealed and flushed two times with 2 MPa of CO_2 to remove the air. After flushing, the reactor was maintained at a reaction temperature of 323 K. A prescribed amount of hydrogen was first loaded into the reactor. Liquid CO_2 was charged into the reactor using a high-pressure liquid pump, and then compressed to the desired pressure. Pressure was kept constant by a back-pressure regulator. The hydrogen and the reaction mixture were stirred continuously with a Teflon-coated magnetic bar during the reaction. After the reaction, the reactor was cooled in ice/water and depressurized carefully by the backpressure regulator. The liquid mixture was identified by GC/MS and analyzed quantitatively by GC (HP 5890) equipped with a flame ionization detector. Quantification of the products was obtained by a multipoint calibration curve for each product. For recycle studies the catalyst was separated from the reactant and product then recharged with fresh reactant. The hydrogenation in organic solvents has also been performed by the above method using conventional organic solvents (10 mL) instead of CO_2. The selectivity to each product was calculated by the following expression $S_i = C_i/\Sigma Cp$, where C_i is the concentration of the product 'i' and ΣCp is the total concentration of the product.

Phase Behavior Studies

The phase behavior of the system under the reaction condition was observed at 323 K using a 10 mL high-pressure viewing cell containing citral, CO_2 and H_2. The same pressure controller as used for the hydrogenation experiment was used to regulate the pressure inside the viewing cell. Citral (0.2 g) was introduced into the viewing cell at a constant hydrogen pressure of 4 MPa and the CO_2 pressure was in the range of 7.0 to 17.0 MPa. A magnetic stirrer stirred the content inside the viewing cell.

References

[1] K. Bauer, D. Garbe, *Common Fragrances and Flavor Materials*, VCH, Weinheim, **1985**.

[2] a) U. K. Singh, M. A. Vannice, *J. Catal.* **2001**, *199*, 73–84; b) P. Reyes, H. Rojas, G. Pecchi, J. L. G. Fierro, *J. Mol. Catal. A* **2002**, *179*, 293–299; c) C. Milone, M. L. Tropeano, G. Gulino, G. Neri, R. Ingoglia, S. Galvagno, *Chem. Commun.* **2002**, 868–869.

[3] G. Lafaye, C. Micheaud-Especel, C. Montassier, P. Marecol, *Appl. Catal. A* **2002**, *230*, 19–30.

[4] A. M. Silva, O. A. A. Santos, M. J. Mendes, E. Joradao, M. A. Fraga, *Appl. Catal. A* **2003**, *241*, 155–164.

[5] M. A. Aramendia, V. Borau, C. Jiménez, J. M. Marinas, J. R. Ruiz, F. J. Urbano, *J. Mol. Catal. A* **2001**, *171*, 153–158.

[6] U. K. Singh, M. A. Vannice, *J. Catal.* **2000**, *191*, 165–180.

[7] A. Wismeijer, A. Kieboom, H. van Bekkum, *Appl. Catal.* **1986**, *25*, 181.

[8] a) P. G. Jessop, T. Ikariya, R. Noyori, *Nature* **1994**, *368*, 231–233; b) P. G. Jessop, Y. Hsiano, T. Ikariya, R. Noyori, *J. Am. Chem. Soc.* **1996**, *118*, 344–355.

[9] A. Fürstner, D. Koch, K. Langemann, W. Leitner, C. Six, *Angew. Chem. Int. Ed.* **1997**, *36*, 2466–2469.

[10] a) A. Baiker, *Chem. Rev.* **1999**, *99*, 453–473. b) M. G. Hitzler, F. R. Smail, S. K. Ross, M. Poliakoff, *Org. Process Res. Dev.* **1998**, *2*, 137–146.

[11] G. I. Childs, A. I. Cooper, T. F. Nolan, M. J. Carrott, M. W. George, M. Poliakoff, *J. Am. Chem. Soc.* **2001**, *123*, 6857–6866.

[12] U. R. Pillai, E. Sahle-Demessie, *Ind. Eng. Chem. Res.* **2003**, *42*, 6688–6696.

[13] M. Chatterjee, Y. Ikushima, FY. Zhao, *New Journal of Chemistry* **2003**, *27*, 510–513.

[14] a) J. F. Moulder, W. F. Sticklle, P. E. Sobol, K. D. Bomben, *Handbook of X-ray Photoelectron Spectroscopy*, (Eds.: J. Chastain, R. C. King Jr.), Physical Electronics Inc., Minnesota, USA, **1995**; b) K. S. Kim, N. Winograd, R. E. Davis, *J. Am. Chem. Soc.* **1971**, *93*, 6296–6297.

[15] a) M. Chatterjee, Y. Ikushima, FY. Zhao, *Catal. Lett.* **2002**, *82*, 141–144; b) B. M. Bhanage; Y. Ikushima; M. Shirai, M. Arai, *Catal. Lett.* **1999**, *62*, 175–177; c) F. Zhao, Y. Ikushima, M. Shirai, T. Ebina, M. Arai, *J. Mol. Catal.* **2002**, *180*, 259–265.

[16] M. Arai, Y. Nishiyama, Y. Ikushima, *J. Supercrit. Fluids* **1998**, *13*, 149–153.

[17] A. A. Clifford, K. Pople, W. J. Gaskill, K. D. Bartle, C. M. Rayner, *J. Chem. Soc. Faraday Trans.* **1998**, *94*, 1451 – 1456.

[18] U. K. Singh, M. A. Vannice, *J. Mol. Catal.* **2000**, *163*, 233 – 250.

[19] C. J. Houtman, M. A. Barteau, *J. Catal.* **1991**, *130*, 528 – 546.

[20] J. L. Davis, M. A. Barteau, *J. Am. Chem. Soc.* **1989**, *111*, 1782 – 1792.

[21] A. Wagray, D. G. Blackmond, *J. Phys. Chem.* **1993**, *97*, 6002 – 6006.

[22] R. Shekhar, M. A. Barteau, *Surf. Sci.* **1994**, *319*, 298 – 314.

[23] P. Gallezot, A. G. Fendler, D. Richard, *Chemical Industry* (Catalysis of Organic reactions), Vol. 47, **1992**.

[24] a) H. Tiltscher, H. Hofmann, *Chem. Eng. Sci.* **1987**, *42*, 959 – 977; b) S. Saim, D. M. Ginosur, B. Subramanium, *ACS Symp. Ser.* **1989**, *406*, 301.

[25] G. Neri, L. Mercadante, A. Donato, A. M. Visco, S. Galvagno, *Catal. Lett.* **1994**, *29*, 379 – 386.