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Pressure-dependent product distribution of citral hydrogenation over micelle-hosted Pd and Ru nanoparticles in supercritical carbon dioxide

Pascal Meric, Kai Man K. Yu, Adam T.S. Kong, Shik Chi Tsang *

Surface and Catalysis Research Centre, School of Chemistry, University of Reading, Whiteknights, Reading, Berkshire, RG6 6AD, UK

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Abstract

In situ synthesis and testing of Ru and Pd nanoparticles as catalysts in the presence of ammonium perfluorohydrocarbo-carboxylate surfactant in supercritical carbon dioxide were carried out in a stainless steel batch reactor at 40 °C over a pressure range of 80–150 bar CO_2/H_2. Direct visualization of the formation of a supercritical phase at above 80 bar, followed by the formation of homogeneous microemulsions containing dispersed Ru nanoparticles and Pd nanoparticles in $scCO_2$ at above 95–100 bar, were conducted through a sapphire window reactor using a W_0 (molar water to surfactant ratio) of 30. The synthesised Ru and Pd nanoparticles showed interesting product distributions in the selective hydrogenation of organic molecules, depending critically on the density and polarity of the fluid (which in turn depends on the pressure applied). Thus, selective hydrogenation of the citral molecule, which contains three reducible groups (aldehydes and double bonds at the 2,3 and 6,7 positions), is feasible as a chemical probe.

Keywords: Citral hydrogenation; Micelle-hosted Ru nanoparticle; Supercritical carbon dioxide; Citronellal selectivity

1. Introduction

Since the early 1990s, an increasing concern about discharge from chemical industries has led to the reassessment of various existing chemical processes. Particular attention has been paid on the use of supercritical carbon dioxide ($scCO_2$) to replace organic solvent because it is nontoxic, nonflammable, inexpensive, inert, and environmentally benign [1]. Pioneering researchers have focused on the advantages of using $scCO_2$ in polymer synthesis and processing and have achieved enormous success [2,3]. Encouraged by these promising results, $scCO_2$ is being explored as a new medium for catalytic hydrogenation of organic molecules. Higher reaction rates and excellent enantioselectivity have been claimed [4–8]. Catalytic fixation of CO_2 in its supercritical state, in which CO_2 is used as solvent and reactant, has also been reported [9,10]. Many enzymatic reactions taking place in this fluid are currently under investigation [11]. The medium is generally shown to be effective for a wide range of reactions, including hydroformylation [12,13] and oxidation [14–19], because of its intrinsically high miscibility with other gases, high diffusivity, and high mass transfer coefficient [1]. But little attention has been paid to the pressure effect on reaction selectivity, despite the fact that the fluid may offer some tunable properties leading to desirable products.

Consequently, we have investigated hydrogenation of the citral molecule, which contains three reducible groups (aldehydes and double bonds at the 2,3 and 6,7 positions) as a chemical probe for this new solvent medium. The economic importance of selective hydrogenation reactions of α,β-unsaturated aldehydes has been emphasized [20,21], because some partial hydrogenated products are widely used in the production of pharmaceuticals, fragrances, and perfumes [22]. In the literature, selective hydrogenation of these compounds has been studied extensively over a wide range of catalysts, including promoted and unpromoted metals/alloys [23–25], metal oxides [26,27], microporous supports [28], and polymer fibre catalysts [29] in both liquid [21,30–32] and vapour [33,34] phases. It has been empirically shown that the selectivity of the reaction can depend on some key parameters, including the nature of the metal and particle size [35], catalyst support [36–38], and

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* Corresponding author.
E-mail address: s.c.e.tsang@rdg.ac.uk (S.C. Tsang).

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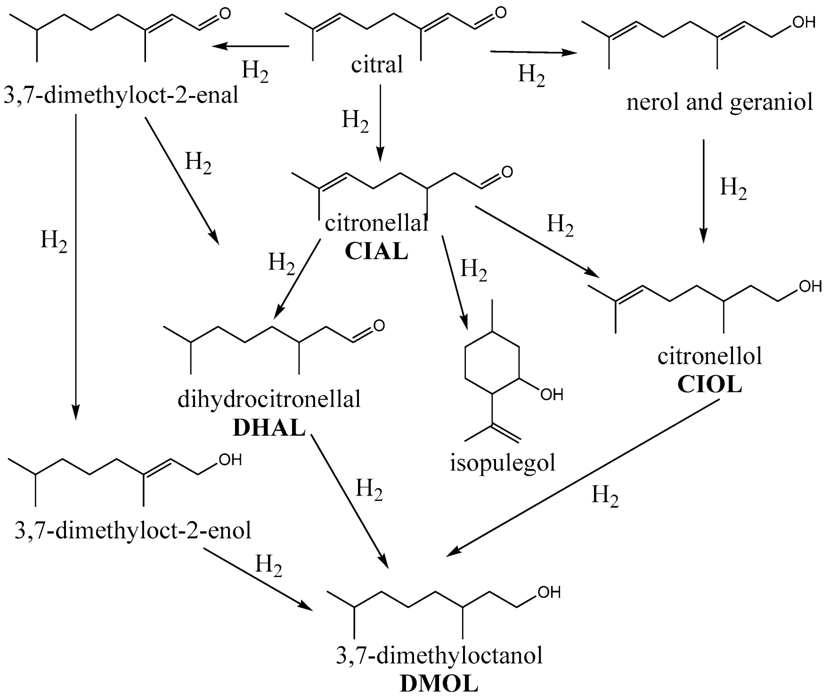


Scheme 1. Reaction pathways of citral hydrogenation.

type of promoters/additives [38–40] used; however, a systemic control in reaction selectivity by these parameters leading to tunable properties has not yet been achieved. Citral molecule is one interesting model compound for hydrogenation because it contains both conjugated and isolated double bonds as well as a carbonyl group; thus numerous partially hydrogenated products can be synthesised, depending on the selectivity of the hydrogenation reaction (see Scheme 1). Hydrogenation of the citral molecule over Pd nanoparticles with and without support materials [41,42] in $scCO_2$ has also been reported.

In the present paper we report a detailed study of pressure effect on citral hydrogenation by micelle-hosted Ru and Pd nanoparticles in supercritical carbon dioxide following our previous preliminary works on the Pd system [43,44]. Two fundamental issues are of particular importance in this paper: to carry out direct visualisation of surfactant/metal system in $scCO_2$ through a sapphire window reactor at different pressure ranges, and to investigate the pressure effect affecting product selectivity in hydrogenation. Both of these issues are fundamentally important in terms of the future development of this new type of catalysis.

2. Experimental

Citral, decane, perfluorotetradecanoic acid, and ammonia solution in methanol were supplied from Aldrich, and cyclohexane and methanol were supplied from Fischer Scientific. All of these reactants were used without any further purification. Palladium chloride, ruthenium chloride, unsupported (naked) palladium, and ruthenium nanoparticles were provided by Johnson Matthey.

2.1. Synthesis of the fluorinated ammonium surfactant

Perfluorotetradecanoic acid, $CF_3(CF_2)_{12}COOH$, was dissolved in methanol under stirring at the temperature of 40 °C. The synthesis, purification, and characterisation of Co(II) perfluorotetradecanoate salt were described previously [45]. Using a similar methodology, a five-fold excess of 2.0 M ammonia solution in methanol was added to the acid solution, and the mixture was maintained at 40 °C under vigorous stirring for 24 h. The generated $CF_3(CF_2)_{12}COO^-NH_4^+$ was collected as a dried powder by evaporating off the solvent and excess ammonia at 60 °C overnight. A slightly yellow-coloured solid was obtained. Purity of the synthesised material was confirmed by elemental analysis; the formation of ammonium salt could also be monitored by FTIR. A clear shift in wave number at the C=O stretching absorption region was observed when the ammonium salt was formed (from 1768 to 1683 cm^{-1}). To ensure that no acid was left over in the ammonium salt, the absence of an acid absorption peak was particularly noted.

2.2. Visualisation of the microemulsion through a sapphire window reactor

Experiments were carried out in a ca. 30-mL stainless steel Parr reactor equipped with two high-pressure transparent sapphire windows with the window separation of ca. 4.5 cm. Appropriate amount of reactants, palladium nitrate, surfactant, and water were introduced in the reactor to create the same conditions (40 °C and 150 bar overall pressure) as a 300-mL reactor in which catalysis was performed. The only difference between the two reactors was in the stirring; the small reactor was stirred using a magnetic stirrer at the bottom of the reactor.

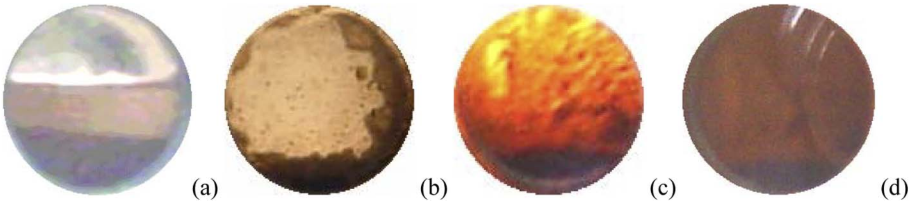


Fig. 1. Micro-emulsion visualisation through sapphire windows. (a) catalyst slurry at 25 °C and 67 bar (liquid CO_2); (b) the liquid meniscus disappeared at 40 °C with the pressure of above 80–85 bar suggesting that the fluid reached a supercritical state but most catalyst slurry remained insoluble in this pressure range; (c) a majority of slurry disappeared and the mixture reached a single transparent state at 40 °C when above 95–150 bar CO_2; (d) after addition of 10 bar H_2 a brown "solution" observed.

2.3. Catalytic tests

Hydrogenation reaction of citral was carried out in a 300-mL stainless steel reactor (Parr Instruments, model 4561), equipped with a heating jacket, an outlet for gas with needle valve, and an overhead stirrer. Typically, palladium nitrate (0.25 mmol), citral (0.5 mL), decane (internal standard, 0.1 mL), perfluorotetradecanoate ammonium surfactant (0.25 mmol), and an appropriate amount of water required to saturate the $scCO_2$ under the reaction conditions (i.e., 0.4768 mL for a 300 mL reactor, 140 bar $scCO_2$ at 40 °C), plus an extra amount of water to give a W_0 (molar water to surfactant) ratio of 30, were placed in the reactor. Dried CO_2 was then pumped into the autoclave reactor using a booster pump to reach the desired pressure (140 bar) at 40 °C. Stirring was done with an overhead magnetic stirrer, the motor of which was set at 3/4 of maximum speed (ca. 550 rpm). The mixture was stirred overnight to create the microemulsion system. Then the pressure was raised to 150 bar by adding 10 bar H_2, and the reaction was followed for 4 h. At the end of the reaction, the autoclave was allowed to cool to room temperature, at which time the reaction mixture was vented via double-liquid traps containing cyclohexane to remove soluble species in the carbon dioxide. Then the reactor was opened, and the remaining residue was extracted with another portion of the solvent. The resulting solutions were combined, and the solid containing metal particles was separated and collected from the solution by filtration. The filtrate was dried over sodium sulphate, then filtered before the cyclohexane was evaporated off. The leftover product was dissolved in another clean cyclohexane solvent and injected to both gas chromatography (using an HP 5890 gas chromatograph equipped with a flame ionisation detector and a 30 m × 0.22 mm ID-BPX5 0.25 capillary column) and gas chromatography–mass spectroscopy (using an Agilent Technologies 6890N gas chromatograph with the same column coupled to a 5973 mass selective detector) for product identification. Conversion and product selectivity were determined based on all detected products with reference to an internal standard.

The experiments carried out in nitrogen phase used the same experimental setup and the same experimental/work-up procedures with identical quantity of citral, decane (internal standard), water, fluorosurfactant, catalyst, and hydrogen. The only difference is that the $scCO_2$ was replaced by N_2.

For the experiments carried out using "naked" Pd and Ru nanoparticles, prereduction of the catalyst was performed at 100 °C under 40 bar of H_2 overnight before adding the reaction mixture (citral, decane, water) but no surfactant. This Pd and Ru had similar particle sizes (∼3–4 nm) as those nanoparticles obtained under micellar conditions [43,44].

Hydrogenation of citronellal (CIAL) was carried out under exactly the same conditions as for citral hydrogenation.

3. Results and discussion

Fig. 1 shows a direct visualisation of the fluid through sapphire windows under different conditions. As shown, separate phases of liquid CO_2 and insoluble surfactant/Pd nitrate/water mixture were clearly visible at below the supercritical temperature (room temperature; Fig. 1a). After the temperature was raised to 40 °C at about *80–85 bar*, the gas–liquid meniscus disappeared; however, the solid remained insoluble in the transparent fluid (Fig. 2b). The temperature and pressure values were above the theoretical critical points for pure CO_2, and the disappearance of the meniscus is consistent with the fact that the CO_2 fluid had reached a supercritical state [1]. (Our phase estimation based on Peng–Robinson calculation also suggested no significant modification of the critical points of the fluid by the small quantity of substrates used.) It is interesting to observe the dissolution of solid mixture at higher pressures starting from above 95 bar (with increasing fluid density). This fact agrees with our earlier finding that the density of the $scCO_2$ fluid allows establishment of a "microemulsion" state with surfactant and water at above *95 bar* (Fig. 1c). Fig. 1d shows the colour change of the "solution" upon the addition of H_2. Presumably, at this point the metal salt ingredients in the micelles are reduced to the micelle-hosted metal nanoparticles.

The sizes of typical micelle-hosted metal were carefully determined by X-ray diffraction (based on Debye–Scherrer equation, taking instrumental broadening into account) and transmission electron microscopy (TEM). As can be seen from Fig. 2a, the size of the typical Pd nanoparticle obtained under microemulsion conditions is ca. 3.65 ± 0.85 nm, with a sharp size distribution shown on TEM. In comparison, many poorly defined particles with a broader size distribution were obtained (Fig. 2b) under the same conditions when the Pd was not in microemulsion state (collected at below 90 bar). Occasionally, very large particle clusters were observed in this sample.

The influence of the overall pressure on both catalytic activity and product distribution was performed over Pd and Ru systems by varying the pressure of CO_2 while keeping the hydrogen pressure constant at 10 bar in all cases. It was found that virtually a complete conversion of citral (> 90%) was achieved

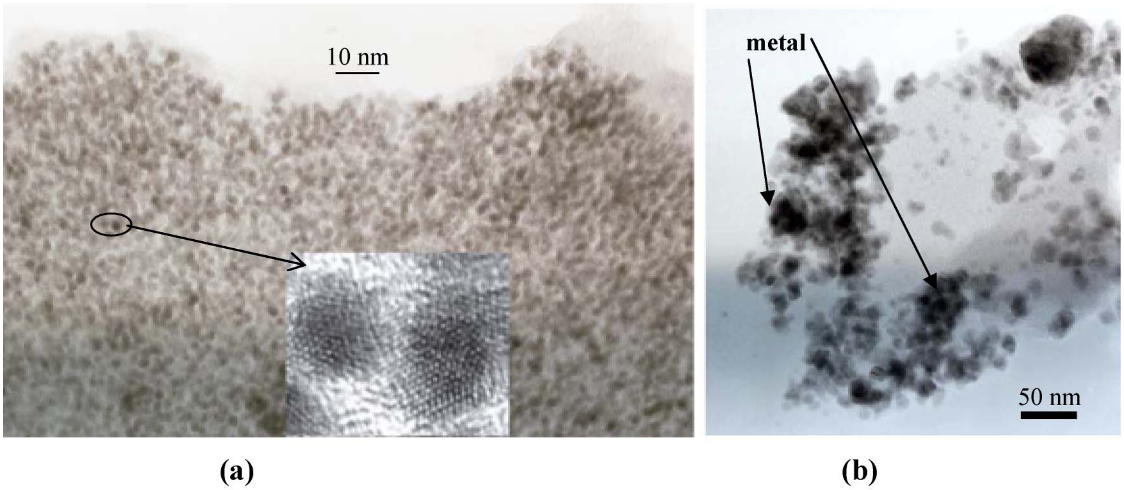
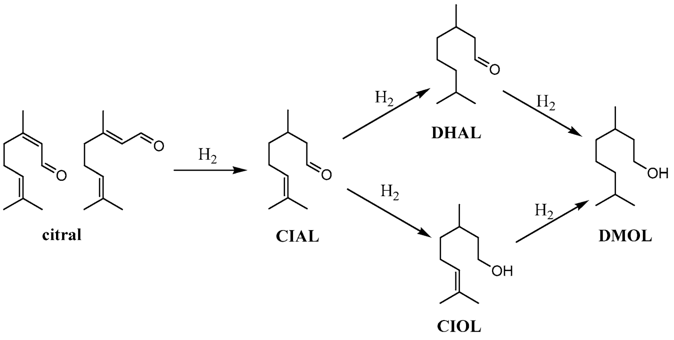


Fig. 2. (a) A typical TEM image of micelle hosted Pd nanoparticles in $scCO_2$ with size distribution of 3.65 ± 0.85 nm; (b) A typical TEM image of Pd nanoparticles in $scCO_2$ but with no micro-emulsion formation showing the much larger and broader particle sizes.



Scheme 2. Simplified reaction pathways of the citral hydrogenation.

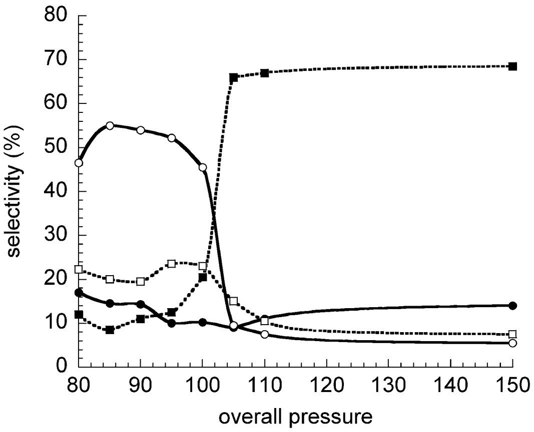


Fig. 3. Product distribution curve versus total overall pressure for citral hydrogenation over Ru system ((●) DHAL, (■) CIAL, (○) DMOL, (□) CIOL) comprised of $RuCl_2$ (0.25 mmol), citral (0.5 mL), decane (0.1 mL), water ($W_0 = 30$), surfactant (0.25 mmol), 40 °C, 10 bar H_2 topped up with 70–140 bar CO_2 for 4 h reaction time. Citral conversion was virtually at 100% hence the yield (%) of a product was equivalent to the selectivity (%).

shortly (< 1 h) after hydrogen addition in all cases with the reactions carried out under $scCO_2$ in a batch reactor. This clearly demonstrates the high activity of these noble metal catalysts in the fluid under such mild conditions. Unfortunately, kinetic measurements could not be determined because of technical difficulties in using the high-pressure batch reactor (i.e., the reaction rate could be misrepresented by the contributions of catalysis during the slow heating and cooling stages). Thus, comparison of product distribution at different conditions was made after 4 h reaction time at near-complete citral conversion.

It was found that for all of the reactions carried out in this study, the main products were the 2,3-conjugated C=C (citronellal, CIAL), the fully saturated aldehyde (dihydrocitronellal, DHAL), the unsaturated alcohol (citronellol, CIOL), and the fully saturated alcohol (3,7-dimethyloctanol, DMOL), altogether accounting for $> 90\%$ selectivity). Traces of isopulegol, geraniol, and 3,7-dimethyloct-2-enol were also observed. Thus, a much simplified reaction pathway of catalytic citral hydrogenation based on Scheme 1 in supercritical carbon dioxide is now presented in Scheme 2.

Plots of product distribution versus overall pressure ($CO_2 + H_2$) are presented in Fig. 3 for Ru and in Fig. 4 for Pd. It can be seen from Fig. 3 that increasing CO_2 pressure leads to a dramatic change in product distribution over the Ru. Between 80 and 95 bar (in a supercritical state but before the formation of microemulsion), the fully hydrogenated 3,7-dimethyloctanol (DMOL) was the major product of the reaction, which appeared to be stable at about 50–55%, whereas the other hydrogenated products accounted for only 10–20% each. At the pressure range of 95–105 bar corresponding to the regime of microemulsion (refer to Fig. 1), DMOL selectivity sharply decreased, settling at around 15%. At the same time, the selectivity toward CIAL increased markedly and became the dominant product (ca. 66%). A further increase in pressure over 105 bar did not cause any major change in product distribution. The DHAL selectivity remained constant throughout the whole range of pressure applied, and the CIOL selectivity decreased only slightly at high pressure.

It is interesting that for Pd, a very different profile in product distribution resulted from an increase in carbon dioxide pressure (Fig. 4). At low pressure (i.e., 80–85 bar), the fully hydrogenated DMOL was again the main product of the reaction (~85% selectivity), whereas DHAL was the only noticeable

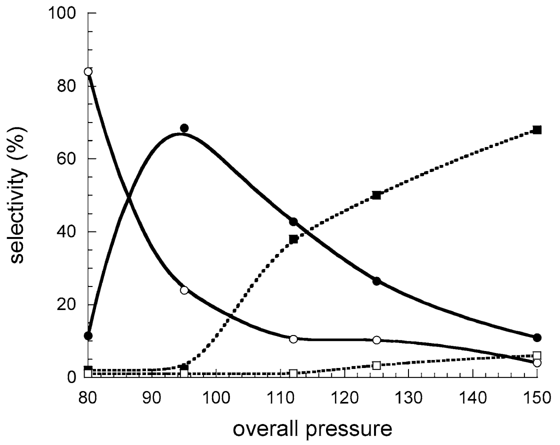


Fig. 4. Product distribution curve versus overall pressure for the citral hydrogenation over Pd system ((●) DHAL, (■) CIAL, (○) DMOL, (□) CIOL) comprised of Pd nitrate (0.25 mmol), citral (0.5 mL), decane (0.1 mL), water ($W_0 = 30$), surfactant (0.25 mmol), 40 °C, 10 bar H_2 topped with 70–140 bar CO_2 for 4 h reaction time. Citral conversion was virtually at 100% hence the yield (%) of a product was equivalent to the selectivity (%).

product (ca. 12%). CIAL and CIOL were detected as traces. However, an increase in pressure within this pressure range (increasing the density of the fluid but before the formation of microemulsion as according to Fig. 1) resulted in an increase in DHAL selectivity at the expense of DMOL selectivity. The DHAL selectivity reached the maximum at a total pressure of 95 bar. Fig. 4 shows that a similar switch in product distribution was also observed at above 95 bar along with the observation of microemulsion revealed earlier in Fig. 1. Note the marked enhancement in CIAL selectivity concomitant with the decrease in DHAL selectivity.

To rationalise these interesting results at this stage, keep in mind the evolution of the product distribution patterns is closely related to the working state of the catalytic systems and the stability of intermediate species on the catalyst surface(s) at a particular pressure. First, at the lowest pressure (i.e., 80–85 bar), carbon dioxide, although in a supercritical state, the density of the fluid is close to a gas-like phase [1]. Thus the volatile citral molecules can easily gain access to the metal surface (reduced metal nanoparticles without involving microemulsion; refer to Fig. 2b) and be exhaustively hydrogenated to DMOL (total reduction of the two C=C double bonds and C=O bonds before the desorption of the thermodynamically most stable DMOL to the mobile phase). But at higher pressure, the fluid becomes more liquid-like, enabling solubility of chemical species therein. This enhances desorption of partially hydrogenated intermediate species from the metal surface to the mobile phase. To verify the above postulation and further investigate the role of carbon dioxide, we tested the Pd and Ru systems at an overall pressure of 150 bar, using the same conditions but replacing CO_2 with N_2 gas (which cannot form a supercritical phase under the reaction conditions). In both cases, changing the medium (i.e., carbon dioxide or nitrogen) produced a significant difference in product distribution at virtually 100% citral conversion (see Table 1). It is clear from the Table 1 that the total hydrogenated product, DMOL instead of CIAL, indeed reverts as the main product in nitrogen at this high pressure, as also occurs when a low pressure of CO_2 (80–85 bar) is used.

As discussed, a further increase in fluid pressure from 80 to 95 bar (but before the formation of microemulsion at <95 bar), as shown in Fig. 1, resulted in a direct increase in fluid density, which began to provide solvency for the extraction of species from metal surface (enhanced desorption in liquid-like fluid). As a result, the nonpolar intermediate, DHAL, from the stepwise hydrogenation was gradually extracted by the increasingly dense fluid from Pd, reaching optimum concentration at 95 bar. However, Ru is well known to strongly bind oxygenates against desorption; hence virtually no intermediate was extracted. At pressure above 95–105 bar, the density of the fluid is sufficiently high to allow the onset of microemulsion with surfactant/water before reduction (as shown directly in Fig. 1c). CIAL is then the major product for both Pd and Ru. As reported pre-

Table 1
Influence of the medium on the product distribution

Entry	Solvent	CIAL (%)	DHAL (%)	DMOL (%)	CIOL (%)
Over Pd					
1	CO_2	72.0	18.0	4.0	6.0
2	N_2	12.0	20.5	62.0	5.5
Over Ru					
3	CO_2	75.5	13.5	5.5	6.5
4	N_2	10.0	8.5	73.5	8.0

Note. Pd nitrate (0.25 mmol) or $RuCl_2$ (0.25 mmol), citral (0.5 mL), decane (0.1 mL), water ($W_0 = 30$), surfactant (0.25 mmol), 40 °C, 10 bar H_2, 140 bar CO_2 or N_2. Citral conversion was virtually at 100% hence the yield (%) of a product was equivalent to product distribution (%).

Table 2
Influence of the Pd and Ru environment (micro-emulsion or naked) on the activity and product distribution

Entry	Catalyst	Conversion (%)	CIAL (%)	DHAL (%)	DMOL (%)	CIOL (%)
1	Naked Pd[a]	100	21.5	78.5	–	–
2	Pd in ME[b]	100	72.0	18.0	4.0	6.0
3	Naked Ru[a]	10	79.5	7.5	3.5	7.0
4	Ru in ME[b]	100	75.5	13.5	5.5	6.5

Note. Pd or Ru (0.25 mmol), citral (0.5 mL), decane (0.1 mL), 40 °C, 10 bar H_2, 140 bar CO_2.

[a] No water and fluorous surfactant.

[b] ($W_0 = 30$), surfactant (0.25 mmol).

Table 3
Conversion and product distribution for the citronellal hydrogenation over Pd and Ru

Entry	Catalyst	Pressure (bar)	Conversion (%)	CIOL (%)	DMOL (%)	DHAL (%)
1	Ru	95	93.5	–	81	19
2	Ru	150	0.4	–	–	–
3	Pd	95	100	–	21	79
4	Pd	150	0.5	–	–	–

Note. Pd or Ru nanoparticles (0.25 mmol), citronellal (0.5 mL), decane (0.1 mL), water ($W_0 = 30$), surfactant (0.25 mmol), 40 °C, 10 bar H_2, 85 or 140 bar CO_2.

viously [43], the high CIAL selectivity is attributed to the high kinetic reluctance for double-bond hydrogenation of citral at the hydrophobic end (6,7 position) and the terminal –C=O hydrogenation (desorption of hydrophilic alcohol in densely hydrophobic $scCO_2$ is not favourable) due to a *unique* micelle environment with a hydrophilic aqueous core hosting the metal particle in the hydrophobic carbon dioxide fluid. (The approach from the hydrophobic end of the molecule to the metal surface is unfavourable.) Thus, hydrogenation of the activated double-bond 2,3 position to CIAL is the only facilitated route.

To investigate the role of microemulsion during the hydrogenation reaction of citral molecule, nanoparticles hosted in micelles and "naked" nanoparticles (with no surfactant/water) of similar size were compared in terms of activity and product distribution. Table 2 reports that 78.5% selectivity to DHAL in citral hydrogenation in supercritical carbon dioxide is obtained over the naked Pd nanoparticles at the total pressure of 150 bar. This finding agrees very well with the recent work of Chatterjee et al., who clearly demonstrated that the solvency of the supercritical carbon dioxide fluid indeed favours the desorption of the relatively hydrophobic DHAL in citral hydrogenation over a range of supported Pd catalysts [41,42]. Note, however, that 72.0% selectivity to CIAL was achieved in the case of microemulsion. A very similar product distribution was also obtained over Ru when it was in the microemulsion state (entry 4). In a sharp contrast, the conversion for the Ru system was found to remain at only 10%. It is assigned to some kind of strongly adsorbed species, possibly the DHAL or related species, which deactivates the Ru.

A possibly key question is how the metal in microemulsion inhibits the further conversion of CIAL to further hydrogenated products. Table 3 reports the hydrogenation of CIAL instead of citral at two different pressures: at 95 bar, before the onset of microemulsion, and at 150 bar, at which the microemulsion working state is well established. It is interesting to note from Table 3 that a sharp decrease in the CIAL conversion is indeed observed for both catalysts from the transition of no microemulsion (fluid phase) to microemulsion. This clearly suggests that CIAL, the first intermediate produced from the citral hydrogenation in our microemulsion system, is kinetically stable against further hydrogenation. This finding also reinforces the observation of no change in CIAL selectivity over the prolonged reaction time. Thus, the low reactivity of CIAL can be clearly explained by the mismatch of this unsaturated molecule in hydrophilicity with the micelle-hosted metal catalyst system, resulting in a repelling phenomenon of the molecule being denied access to the enclosed metal.

Overall, our results clearly show that by controlling the quantity of surfactant and the water-to-surfactant ratio, unusually high selectivity toward citronellal (CIAL) can be achieved at high $scCO_2$ pressures (>105 bar) compared with other media. Indeed, it has long been known that inhibiting the subsequent hydrogenation to the unactivated double bond of the citral is difficult. Thus our results on obtaining the kinetically stable CIAL against further hydrogenation for a prolonged contact time with the Pd and Ru microemulsion catalysts are rather intriguing. The work of Aumo et al. [29] on citral hydrogenation using polymer-supported fiber Pd catalyst has clearly demonstrated that the initially high selectivity to CIAL (85% at 40% conversion) decreased rapidly with time at a gain in dihydrocitronellal selectivity, demonstrating the kinetically labile nature of this partially hydrogenated product. Work has been done on inhibiting total hydrogenation using transition metal ions, such as Fe or Sn, doped on a noble metal surface. It has been postulated that these promoters will form interaction(s) with the terminal aldehyde group, hence favouring the head-on attack of the molecule to the catalyst, and thereby reducing the likelihood of subsequent hydrogenation on the hydrophobic end. Placing noble metal clusters in rigid inorganic zeolitic pores to favour the head-on attack has also been reported [46].

We observed a high selectivity to citronellal, which remained a principal product at all times when using micelle-hosted Pd as a catalyst without promoting our Pd with transition metal ion or zeolitic material. Clearly, this interesting observation is related to the actual metal microemulsion working state. One possibility is that the metal nanoparticles synthesised inside the micelles in supercritical carbon dioxide may give higher selectivity to citronellal than those particles made in nitrogen, because of their particular particle size and structure. But we believe that the effect of particle structure on selectivity is minor, because naked particles can still be accessed freely by substrate molecules to different crystallographic planes, leading to poor control of regioselectivity.

On the other hand, on the basis of micelle molecular assembling, the microemulsion in $scCO_2$ is envisaged to consist of a water core containing Pd nanoparticles, surrounded by the oriented surfactant molecules as a shell. Depending on the fluxional behaviour of the individual surfactant molecules, the citral molecule must align itself to minimise repulsions due to sterical crowding in accessing the enclosed metal surface. Thus, we posit that the relatively hydrophilic carbonyl head group penetrates into the aqueous micelle aggregate (i.e., a head-on attack). Such molecular orientation of citral guided by the micelle assemblies allows highly selective hydrogenation of the α,β-conjugated double bond that lies close to the metal surface, and hence citronellal is formed. This partially hydrogenated product is immediately expelled from the aqueous reverse micelle because the spatial limitation and mismatched hydrophilicity reduce the likelihood of further hydrogenation of isolated double bonds at the hydrophobic end. Note that similar molecular guidance of a rod-shaped unsaturated molecule leading to unusual selectivity was reported by Toshima and Takahashi [47], who observed higher regioselectivity for the hydrogenation of 10-undecenoic acid than for hydrogenation of 2-undecenoic acid over colloidal dispersion of platinum and palladium hosted in a normal micelle in aqueous solution. (A hydrophobic end group containing a double bond is easily hydrogenated by the inner micelle-hosted metal in a hydrophobic environment.)

4. Conclusion

In this work we investigated the affect of CO_2 pressure on product distribution for the hydrogenation of citral over Pd and Ru nanoparticles hosted in a water in $scCO_2$ microemulsion.

We found that selective formation of a particular hydrogenated product can be made possible by carefully tuning the pressure of the fluid (density), which can alter the balance between solvation of the molecule into the fluid and its binding affinity to the metal surface.

References

[1] M. Poliakoff, S. Howdle, Chem. Ber. 31 (1995) 118.
[2] J.M. DeSimone, Z. Guan, C.S. Elsbernd, Science 257 (1992) 945.
[3] T.A. Davidson, J.M. DeSimone, in: P.G. Jessop, W. Leitner (Eds.), Chemical Synthesis Using Supercritical Fluids, Wiley–VCH, New York, 1999, p. 297.
[4] P.G. Jessop, T. Ikariya, R. Noyori, Science 269 (1995) 1065.
[5] P.G. Jessop, Top. Catal. 5 (1998) 95.
[6] T. Ikariya, Y. Kawaku, Catal. Surv. Jpn. 4 (2000) 39.
[7] W. Leitner, Appl. Organometal. Chem. 14 (2000) 809.
[8] W. Leitner, Acc. Chem. Res. 35 (2002) 746.
[9] M.T. Reetz, Chimia 47 (1993) 493.
[10] P.G. Jessop, T. Ikariya, R. Noyori, Nature 368 (1994) 231.
[11] O. Aaltonen, in: P.G. Jessop, W. Leitner (Eds.), Chemical Synthesis Using Supercritical Fluids, Wiley–VCH, New York, 1999, pp. 414–445, chap. 4.9.
[12] L. Schmid, M.S. Schneider, D. Engel, A. Baiker, Catal. Lett. 88 (2003) 105.
[13] T. Mallat, A. Baiker, J. Paschneider, Appl. Catal. A: Gen. 79 (1991) 59.
[14] T. Tsujino, S. Ohigashi, S. Sugayama, K. Kawashiro, H. Hayashi, J. Mol. Catal. 71 (1992) 25.
[15] H. Kimura, A. Kimura, I. Kokubo, T. Wakisaka, Y. Mitsuda, Appl. Catal. A: Gen. 95 (1993) 217.
[16] T. Mallat, A. Baiker, L. Botz, Appl. Catal. A: Gen. 86 (1992) 147.
[17] J.M. Nicolletti, G.M. Whitesides, J. Phys. Chem. 93 (1989) 759.
[18] H.M. van Dam, A.P.G. Kieboom, H. van Bekkum, Appl. Catal. 33 (1987) 361.
[19] T. Mallat, Z. Bodnar, A. Baiker, Stud. Surf. Sci. Catal. 78 (1993) 377.
[20] P. Gallezot, D. Richard, Catal. Rev.-Sci. Eng. 40 (1998) 81.
[21] P. Claus, Top. Catal. 5 (1998) 51.
[22] M. Ash, I. Ash, Specialty Chemical Source Book, first ed., Synapse Information Ressources Inc., New York, 1997.
[23] B. Coq, F. Figueras, P. Geneste, C. Moreau, P. Moreau, M.G. Warawdekar, J. Mol. Catal. 78 (1991) 211.
[24] D. Richard, J. Ockleford, A. Girior-Fendler, P. Gallezot, Catal. Lett. 3 (1989) 53.
[25] L. Sordelli, R. Psaro, G. Vlaic, A. Cepparo, S. Recchia, C. Dossi, A. Fusi, R. Zanoni, J. Catal. 182 (1999) 186.
[26] B. Coq, P.S. Kumbhar, C. Moreau, P. Moreau, M.G. Warawdekar, J. Mol. Catal. 85 (1993) 215.
[27] R. Hubaut, J.P. Bonnelle, M. Daage, J. Mol. Catal. 55 (1989) 170.
[28] P. Gallezot, A. Girior-Fendler, D. Richard, Catal. Lett. 5 (1990) 169.
[29] J. Aumo, J. Lijla, P. Maki-Arvela, T. Salmi, M. Sundell, H. Vainio, D.Y. Murzin, Catal. Lett. 83 (2002) 219.
[30] R. Touroude, J. Catal. 65 (1980) 110.
[31] B. Sen, M.A. Vannice, J. Catal. 115 (1989) 65.
[32] T.B.L.W. Marinelli, S. Nabuurs, V. Ponec, J. Catal. 151 (1995) 431.
[33] L. Mercadante, G. Neri, C. Milone, A. Donato, S. Galvagno, J. Mol. Catal. A 105 (1996) 93.
[34] G. Neri, L. Mercadante, C. Milone, R. Pietropaolo, S. Galvagno, J. Mol. Catal. A 108 (1996) 41.
[35] S. Galvagno, C. Milone, A. Donato, G. Neri, R. Pietropaolo, Catal. Lett. 18 (1993) 349.
[36] U.K. Singh, M.A. Vannice, J. Catal. 199 (2001) 73.
[37] R. Malathi, R.P. Viswanath, Appl. Catal. A 208 (2001) 323.
[38] M. Consonni, D. Jokic, D.Y. Murzin, R. Touroude, J. Catal. 188 (1999) 165.
[39] Z. Poltarzewski, S. Galvagno, R. Pietropaolo, P. Staiti, J. Catal. 102 (1986) 190.
[40] M.A. Aramendia, V. Borau, C. Jiménez, J.M. Marinas, A. Porras, F.J. Urbano, J. Catal. 172 (1997) 46.
[41] M. Chatterjee, F.Y. Zhao, Y. Ikushima, Adv. Synth. Catal. 346 (2004) 459.
[42] M. Chatterjee, A. Chatterjee, Y. Ikushima, Green Chem. 6 (2004) 114.
[43] P. Meric, K.M.K. Yu, S.C. Tsang, Catal. Lett. 95 (2004) 39.
[44] P. Meric, K.M.K. Yu, S.C. Tsang, Langmuir 20 (2004) 8537.
[45] J. Zhu, A. Robertson, S.C. Tsang, Chem. Commun. (2002) 2044.
[46] M.J. Clarke, K.L. Harrison, K.P. Johnston, S.M. Howdle, J. Am. Chem. Soc. 119 (1997) 6399.
[47] N. Toshima, T. Takahashi, Chem. Lett. (1988) 573.