Selective hydrogenation of citral catalyzed with palladium nanoparticles in CO_2-in-water emulsion

Ruixia Liu,[a,b] Chaoyong Wu,[a,b] Qiang Wang,[a,b] Jun Ming,[a,b] Yufen Hao,[a,b] Yancun Yu[a] and Fengyu Zhao*[a]

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CO_2-in-Water (C/W) emulsion was formed by using a nonionic surfactant of poly (ethylene oxide)-poly (propylene oxide)-poly (ethylene oxide) (P123), and palladium nanoparticles were synthesized *in situ* in the present work. The catalytic performance of Pd nanoparticles in the C/W emulsion has been discussed for a selective hydrogenation of citral. Much higher activity with a turnover frequency (TOF) of 6313 h^{-1} has been obtained in this unique C/W emulsion compared to that in the W/C microemulsion (TOF, 23 h^{-1}), since the reaction was taking place not only in the surfactant shell but also on the inner surface of the CO_2 core in the C/W emulsion. Moreover, citronellal was obtained with a higher selectivity for that it was extracted to a supercritical carbon dioxide ($scCO_2$) phase as formed and thus its further hydrogenation was prohibited. The Pd nanoparticles could be recycled several times and still retain the same selectivity, but it showed a little aggregation leading to a slight decrease in conversion.

Introduction

Emulsion systems have been an important research topic for years, and they are widely used in cleaning, materials science, chemical reactions, manufacturing, enhancing oil recovery and many other processes.[1–8] As is well known, emulsion is the heterogeneous system consisting of at least two immiscible liquids and amphiphile (surfactant). Water and carbon dioxide are the most abundant and green solvents on the earth, and the emulsions composed of water and carbon dioxide are nonflammable, essentially nontoxic and environmentally benign. However, the understanding of water–CO_2 emulsions is still in its infancy, relative to that of water–oil emulsions. Conventional surfactants used in water–oil emulsions often exhibit low solubilities in CO_2 due to the weak solvent strength of CO_2 limited by weak Van der Waals Forces.[9] To achieve satisfactory tail solvation in CO_2, fluorinated polymers such as polyfluoroethers, polyfluoroacrylates, and polyfluoromethacrylates are usually used to stabilize the CO_2–water emulsions.[10–12] However, these fluorinated compounds are more harmful and expensive compared with conventional surfactants. Therefore, much attention has been paid to the surfactants of CO_2-philic groups of branched hydrocarbons. Da Rocha *et al.* reported that carbon dioxide-in-water (C/W) macroemulsions stabilized with inexpensive hydrocarbon surfactants of poly(ethylene oxide)-*b*-poly(butylene oxide)(EO_{15}-*b*-BO_{12}) were stable over 48 h against both flocculation and coalescence.[13] In addition, water-in-carbon dioxide (W/C) microemulsions[14,15] and macroemulsions[16] have been prepared successfully with hydrocarbon surfactants.

The emulsion is the most often employed strategy to overcome the reagent incompatibility and increase the interfacial areas. It was reported that the organic reaction between a hydrophobe, benzyl chloride, and a hydrophile, KBr was performed smoothly in the CO_2–water emulsions and in which the rate of the reaction increased dramatically compared with that in water-in-octane emulsions.[17] And the reaction rates of styrene hydrogenation in the CO_2–water emulsions and/or microemulsions were reported to increase more than 38 and 5 times compared with those in toluene/water and CO_2/water systems, respectively.[18] These results suggested that the CO_2–water emulsions and microemulsions are efficient catalytic systems, especially for hydrogenation due to the improvements in hydrogen concentration, mass diffusion and interfacial area. Furthermore, the emulsions could be broken rapidly by decompressing.[17,18] Recently, the W/C microemulsion technology offers a new approach in the synthesis of metal nanoparticles such as Pd and Cu, and these nanoparticles formed *in situ* could catalyze chemical reactions efficiently.[19–21] Wai *et al.* have done thorough research into the preparation of metal nanoparticles in W/C microemulsions such as Pd nanoparticles, and these Pd nanoparticles presented high activity and stability in the hydrogenation of olefins in W/C microemulsions.[22–25]

In this work, Pd nanoparticles were prepared in the C/W emulsion through *in situ* reduction with H_2. The catalytic performance of the Pd nanoparticles in C/W emulsion was investigated for a selective hydrogenation of unsaturated aldehyde of citral. Several important factors which affect the emulsion environments such as the surfactant concentration, temperature and CO_2 pressure have been discussed. In comparison to the catalytic systems reported, the present C/W emulsion is more suitable for the 'CO_2-soluble reactants' reactions.

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[a] *State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, P. R. China. E-mail: zhaofy@ciac.jl.cn; Fax: +86 431-85262410; Tel: +86 431-85262410*
[b] *Graduate School of the Chinese Academy of Sciences, Beijing, 100049, P. R. China*

Results and discussion

Emulsion formation and stability

Emulsions are inherently thermodynamically unstable because of the large interfacial free energy compared with the microemulsions, but could be kinetically stable for long periods.[26] For the present C/W emulsion, block copolymer P123 was used as the surfactant to provide steric stabilization, the CO_2-philic blocks are of poly (propylene oxide), and the CO_2-phobic blocks are of poly (ethylene oxide), favored the formation of CO_2-in-water (C/W) emulsion.[27] The stability of the C/W emulsion is highly dependent on the phase behavior.[28] Thus, the phase behavior was investigated by varying the surfactant concentration, temperature and CO_2 pressure. The concentration of surfactant was ranged from 0.1 wt% to 1.1 wt%, which is far beyond the critical micelle concentration of P123 (CMC 0.052 mM at 25 °C).[29] And the surface tension of the P123 aqueous solution has a negligible effect as the surfactant concentration changed during this range.[30] The emulsions could be stable for more than 15 min after ceasing stirrer at the lower temperatures from 35 °C to 65 °C, while a distinct phase separation was observed above 65 °C. Higher temperature caused the EO head groups to dehydrate, therefore its emulsification capacity and solubility in water decreased causing the surfactant to partition further towards CO_2.[13,31] As the pressure increased, CO_2 was highly dispersed in water and the size of the foams became smaller. It was observed that the volume percentage of CO_2 is about 61% at 8.6 MPa and it increased to 72% when CO_2 pressure was increased up to 9.8 MPa under the ordinary conditions as illustrated in Fig. 1.

Hydrogenation of citral in C/W emulsion

Surfactant concentration. Fig. 2 shows the results of citral hydrogenation (Scheme 1) catalyzed by Pd nanoparticles formed *in situ* in C/W emulsion at the different surfactant

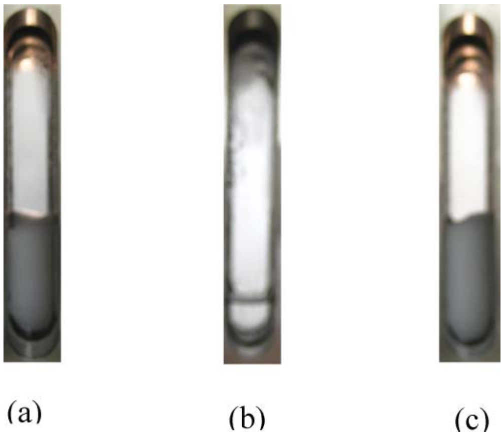


Fig. 1 Photographs of the phase behavior of the C/W emulsion at 0.5 wt% P123 concentration, 45 °C (a) C/W emulsion at 8.6 MPa (b) P123 aqueous solution without CO_2 (c) C/W emulsion at 9.8 MPa.

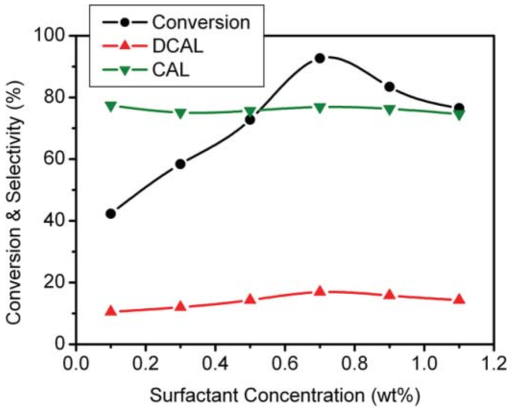
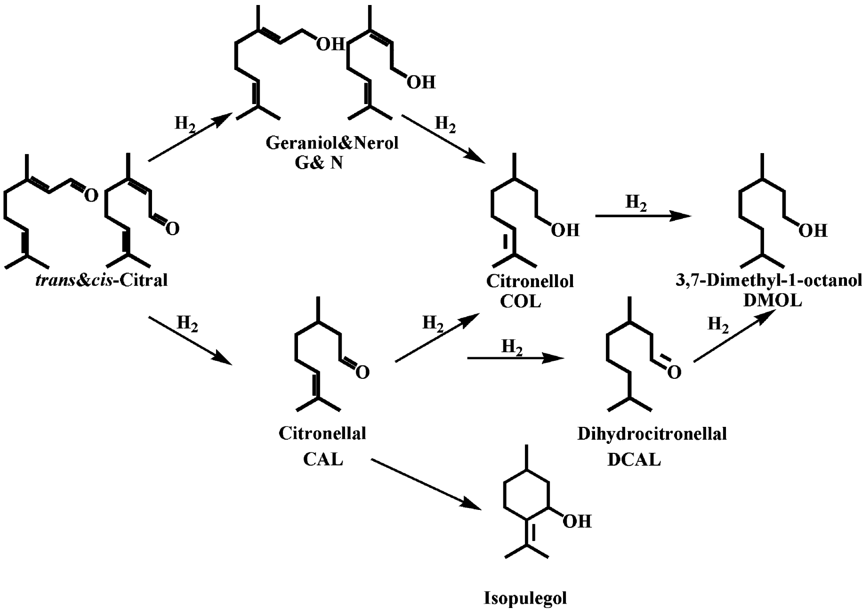


Fig. 2 Influence of surfactant concentration on citral hydrogenation with Pd nanoparticles in C/W emulsion. Reaction conditions: Citral 5 mmol, H_2 4 MPa, CO_2 10 MPa, DI-H_2O 5 ml, $Pd(CH_3COO)_2$ 0.001 mmol, 50 °C, 45 min, wt % relative to the total weight of both water and surfactant.



Scheme 1 Reaction pathways of citral hydrogenation.

concentrations. As seen, with the surfactant concentration increased from 0.1 wt% to 1.1 wt%, the conversion increased sharply from ~42% to the maximal value of 93% at the concentration of 0.7 wt%, and then decreased as the concentration further increased to 1.1 wt%. However, the selectivity of the main products changed slightly, citronellal was produced with a selectivity above 75% and dihydrocitronellal, its further hydrogenated product, was about 15%, besides trace amounts of geraniol, nerol, isopulegol, as well as 3,7-dimethyl-1-octanol were also detected. The block copolymer, protected and combined with Pd nanoparticles, assembled at the interface of water and CO_2, and so the emulsion droplets were formed, which act as microreactors (micelle aggregation) during the chemical reaction. And the increase in the surfactant concentration caused an increase of the microreactors, meanwhile the solubilization of the reactants in the micelle could increase, *i.e.* the concentration of citral was increased. Consequently, the conversion of citral increased sharply. But if the concentration of surfactant increases further after the reactants are solubilized almost completely in the micelle, the concentration of the reactants and the catalysts will decrease, causing the reaction rate decrease. Furthermore, as the surfactant concentration increases, the viscosity of the emulsion increases and thus the mass diffusion is hindered.

Reaction temperature. The conversion of citral increased linearly as temperature increased as shown in Fig. 3. While for the selectivity, dihydrocitronellal increased at the expense of citronellal. At a constant surfactant concentration of 0.5 wt%, as the temperature increased, the solubility of the surfactant in water decreased in that the EO–water interaction was weakened at a higher temperature causing the increase of microreactors,[13,31,32] which would condense the local concentration of the reactants, and accelerate the reaction rate, except for that the enhancement of temperature itself will accelerate the reaction rate.

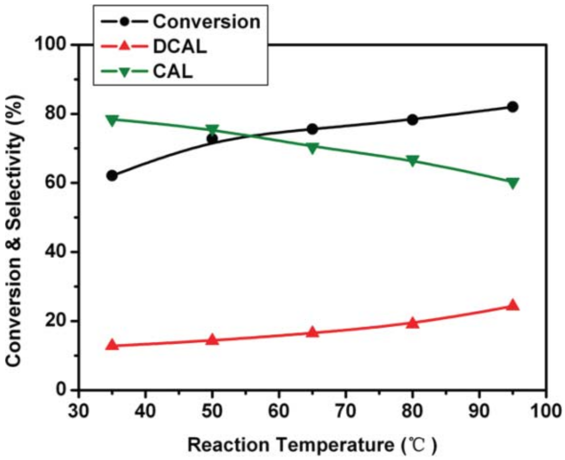


Fig. 3 Results for citral hydrogenation with Pd nanoparticles in C/W emulsion at different reaction temperatures. Reaction conditions: Citral 5 mmol, H_2 4 MPa, CO_2 10 MPa, 0.5 wt% P123 5 ml, $Pd(CH_3COO)_2$ 0.001 mmol, 45 min.

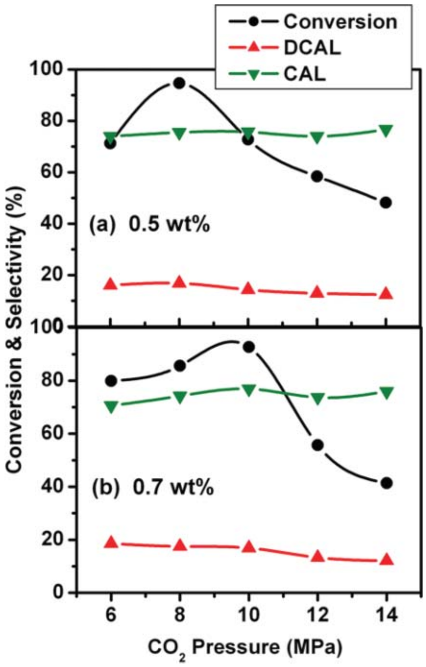
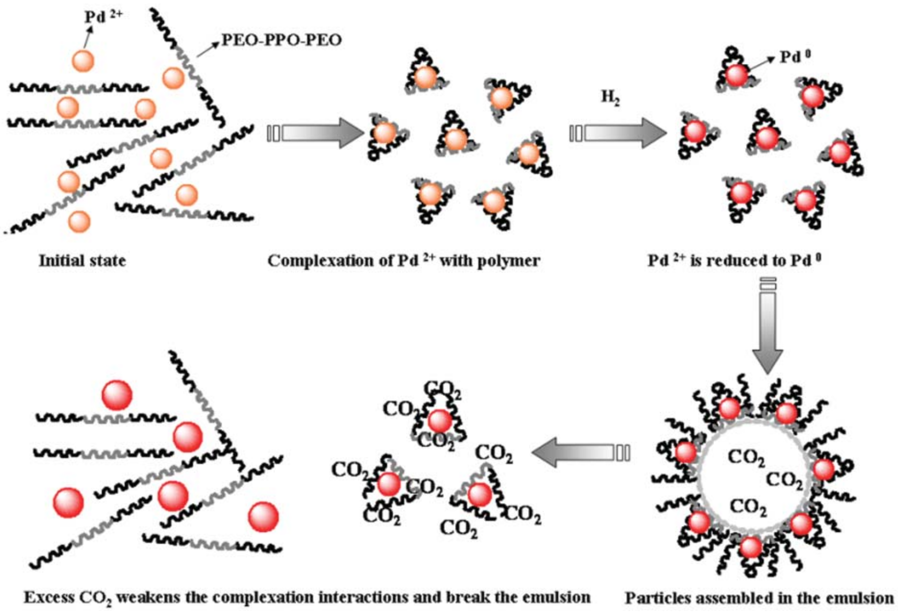


Fig. 4 Influence of CO_2 pressure on citral hydrogenation with Pd nanoparticles in C/W emulsion with surfactant P123 concentration of (a) 0.5 wt% and (b) 0.7 wt%. Reaction conditions: Citral 5 mmol, H_2 4 MPa, $Pd(CH_3COO)_2$ 0.001 mmol, 50 °C, 45 min.

CO_2 pressure. The influence of CO_2 pressure on catalytic activity and product distributions are presented in Fig. 4. The conversion showed a volcano-trend as CO_2 pressure increased and was irrespective to the concentration of surfactant. However, the maximum conversion was 94.7% at 8 MPa and 92.7% at 10 MPa with the surfactant concentration of 0.5 wt% and 0.7 wt%, respectively. While the product selectivity was almost independent of CO_2 pressure in the present C/W emulsions. But, it was reported that,[33] in W/C microemulsions, the product selectivity could be tuned by changing the pressure of CO_2, which altered the balance between solvation of the citral molecule into the $scCO_2$ and its binding affinity to the metal surface.

At a constant temperature, increasing CO_2 pressure, the solubility of CO_2 in the micelle as well as citral in CO_2 increases.[28] In the present C/W emulsion system, CO_2 expanded the micelles and took the reactants (citral and H_2) to approach the Pd nanoparticles in the micelles, accelerating the reaction rate. Most of the previous studies showed that excess CO_2 decreased the conversion due to the dilute effect.[34,35] It was reported that the stability of the C/W emulsions in the presence of the block copolymers depended strongly on CO_2 pressure.[28] First, the solvation of the stabilizing chains by CO_2 must be sufficient to mediate interactions between chain segments otherwise the solvent will expand away from the chains producing flocculation. Second, the surfactant chains must keep the particles far enough apart to prevent flocculation. So it was speculated that the block copolymer would be solvated properly at appropriate pressure, but at higher CO_2 pressure the emulsions might tend to break and become the solution of unimers of the block copolymer. Furthermore, excess CO_2 weakened the complex interaction between the polymer chains with the Pd nanoparticles. Consequently, the protecting capacity of block copolymer for the Pd nanoparticles would decrease and the schematic diagram was given in Scheme 2.



Scheme 2 Schematic diagram of the formations of Pd nanoparticles and C/W emulsion.

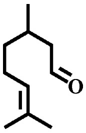
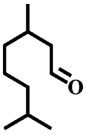
It is well known that water becomes acidic (pH ~ 3) in the presence of CO_2, due to the formation and dissociation of carbonic acid,[36] but the pH of the solution changed slightly with increasing the CO_2 pressure.[37,38] Acid can salt in non-ionic surfactants in aqueous solutions, because H^+ could form complexes with ether groups in the formation of oxonium compounds,[39] which disrupted the EO–water interactions and pushed the surfactant towards CO_2, and decreased the capacity to form C/W emulsions.[13] However, the effect of H^+ at these conditions was small,[13,40] and could be ignored.

Comparison with other catalytic systems

Table 1 gives the results of citral hydrogenation in different systems. When the hydrogenation was performed in neat water the conversion was 65%, while it increased sharply to 95% in the CO_2/H_2O system in the presence of 8.5 MPa CO_2. However, in the case of using N_2 to replace CO_2, the conversion decreased to 17%, and the lowest conversion was obtained in the hexane/H_2O system. With respect to the product selectivity, citronellal was the main product and higher selectivity was obtained in the CO_2/H_2O emulsion system.

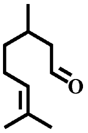
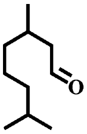
Furthermore, the hydrogenation of citral in the CO_2/H_2O system has been compared with literature as shown in Table 2. A high selectivity of 82% towards the fully hydrogenated aldehyde, dihydrocitronellal, was observed in the vapor phase, but it was 66% in the liquid phase. It was interesting to note that selectivity to dihydrocitronellal was very low (16%) in the present C/W emulsions, but citronellal, one of the most important products of hydrogenation of citral, was obtained as the main product with selectivity around 75% under complete conversion of citral. It was well documented that, for conventional metal catalysts,

Table 1 Results of hydrogenation of citral in different systems with Pd nanoparticles protected by P123

		Selectivity (%)		
System	Conversion (%)			TOF/h^{-1}
H_2O	65	65	22	4313
CO_2/H_2O	95	76	17	6333
N_2/H_2O	17	66	22	1147
Hexane/H_2O	6	62	22	387

Reaction conditions: Citral 5 mmol, H_2 4 MPa, CO_2 8.5 MPa, 2 ml hexane, N_2 9.4 MPa, DI-H_2O 5 ml, $Pd(CH_3COO)_2$ 0.001 mmol, 0.5 wt% P123 5 ml, 50 °C, 45 min. TOF (turnover frequency) was calculated as moles conversion of citral/moles of catalyst/time.

Table 2 Comparison with literature in other catalytic systems for hydrogenation of citral with Pd nanoparticles

		Yield (%)		
System	Surfactants			TOF/h^{-1}
[a]Vapor	—	1	82	—
[a]Cyclohexane	—	19	66	—
[a]W/C Micromulsion	$CF_3(CF_2)_{12}COO^-NH_4^+$	68	12	23.2
[b]C/W Emulsion	PEO-PPO-PEO	72	16	6313

TOF (turnover frequency) was calculated as moles conversion of citral/moles of catalyst/time under citral completely consumed. The product yield was calculated under 100% conversion of citral. [a] results in Ref. 42. [b] present work.

the subsequent hydrogenation of the unsaturated bonds of citral was very difficult to inhibit. Hence, a high selectivity to dihydrocitronellal was normally obtained over Pd catalysts, even for a short contact time.[41] It was reported that the micelle environment was responsible for the high selectivity to citronellal in the W/C microemulsions over Pd nanoparticles, and it was thought that the conjugated C=C bond preferred to be close to the metal particles in the W/C microemulsion.[42] In the present work, the higher selectivity of citronellal in C/W emulsions was also attributed to its higher solubility in $scCO_2$, besides the presence of water would facilitate the adsorption of the conjugated C=C bond on the surface of the catalyst. It was observed that citral (5 mmol) is completely soluble in $scCO_2$ at 8.6 MPa and citronellal (5 mmol) soluble in $scCO_2$ at 7.9 MPa, 50 °C, *i.e.* the solubility of citronellal is 1.91% (molar fraction), which is higher than that of citral (1.75%). In the present system, the C/W emulsion and $scCO_2$ phases were observed through the view cell. Citronellal could be extracted into the $scCO_2$ phase as it formed during the reaction, and isolated from the catalytic C/W emulsion phase so its further hydrogenation to dihydrocitronellal was prohibited. With respect to the reaction activity, the current C/W emulsion system gave a much higher turnover frequency (TOF) (6313 h^{-1}), which is 272 times higher than that in the W/C microemulsion (TOF, 23.2 h^{-1}), although the area/volume is higher for a microemulsion droplet compared to emulsion one. These results could be well explained by the reaction mechanism as illustrated in Scheme 3, in present C/W emulsion formed with the nonionic surfactant P123, the reactants of citral and H_2 were dissolved in both the inner CO_2 core and outer surfactant shell, so the reactant molecules could attack the Pd nanoparticles from both the inter and outer surfaces of emulsion. While in the W/C microemulsion formed with ionic surfactant $CF_3(CF_2)_{12}COO^-NH_4^+$, the reactants could only attack from the outer surfactant shell due to the reactants not being solubilized in the water core. So the present C/W emulsion is more efficient and suitable for the 'CO_2-soluble reactants' reactions compared with W/C microemulsions.

Separation and recycling of the catalysts

It was also suggested that the Pd nanoparticles were more stable in the C/W emulsion stabilized with P123, because the PEO-PPO-PEO block copolymer could stabilize the Pd nanoparticles through the formation of a complexation bond between PEO and PPO with the metal particles. Moreover, the block copolymer could prohibit the agglomeration of Pd nanoparticles *via* the coverage of the block copolymer on the surface of Pd nanoparticles as reported in the literature.[43] The stability of Pd nanoparticles has been examined in the present work, the hydrogenated products were separated from the emulsion successfully by extraction with $scCO_2$, and the Pd nanoparticles and surfactant left in the aqueous phase were reused several times. The recycling results are given in Fig. 5. The conversion decreased gradually in the recycling runs, but dropped to 86% from 99.9% after the fourth run due to the agglomeration of Pd nanoparticles. The TEM images of Pd nanoparticles in Fig. 6 show that the size of Pd nanoparticles was about 1 nm after the first run (Fig. 6a), but the size grew up to about 8 nm after the fourth runs (Fig. 6b). The agglomeration of Pd nanoparticles should be responsible for the activity decrease, which was also claimed in the hydrogenation of olefins in the W/C microemulsion stabilized with sodium bis(2-ethylexyl) sulfosuccinate (AOT).[25] In the recycling runs, the selectivity of the main products was almost unchanged,

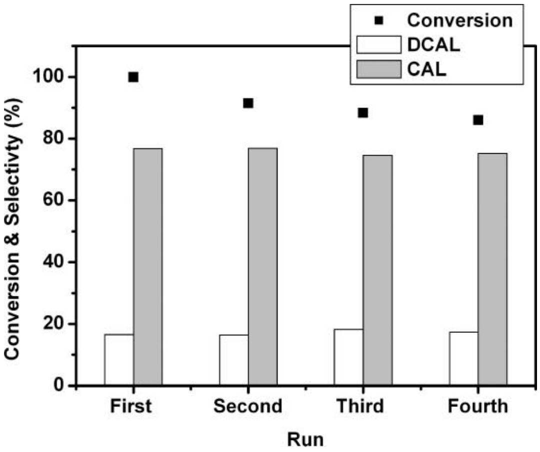
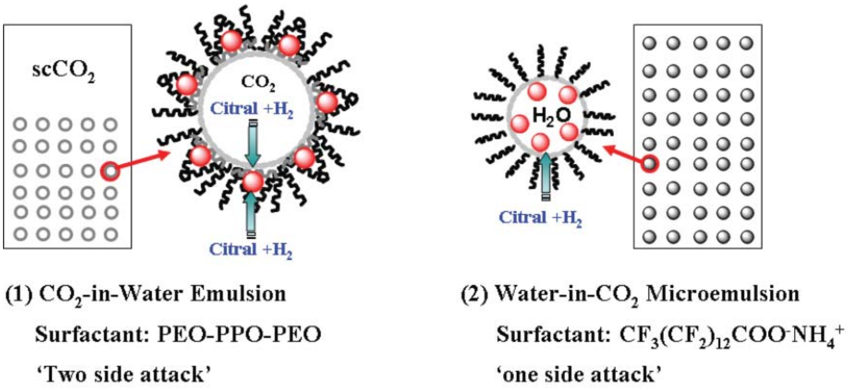


Fig. 5 Recycling results of Pd nanoparticles in citral hydrogenation in the C/W emulsion. Reaction conditions: Citral 5 mmol, H_2 4 MPa, 8 MPa CO_2, 0.5 wt% P123 5 ml, $Pd(CH_3COO)_2$ 0.001 mmol, 60 min, 50 °C.



Scheme 3 Diagram of citral hydrogenation with Pd nanoparticles in (1) C/W emulsions (2) W/C microemulsions.

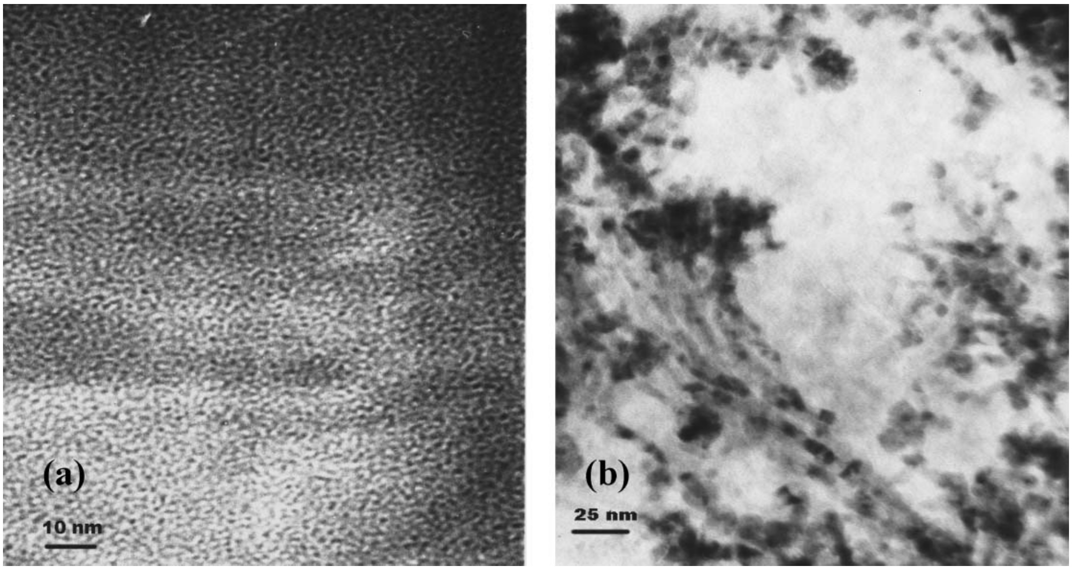


Fig. 6 TEM images of the Pd nanoparticles (a) After the first run; (b) After the fourth run.

suggesting that the product distribution does not depend on the Pd particle size under the conditions used, which is in agreement to the citral hydrogenation catalyzed with Ru catalyst.[44]

Conclusion

The environmental benign CO_2-in-water emulsion was formed by the assembly of the block copolymer P123 at the water–CO_2 interphase. Pd nanoparticles synthesized *in situ* by H_2 reduction was an efficient catalyst for citral hydrogenation in the emulsion. Higher TOF of 6313 h^{-1} and higher selectivity to citronellal (>75 %) were obtained compared to other catalytic systems. The excellent performance is ascribed to the unique emulsion environment. The C/W emulsion formed with block copolymer P123 could make reactants of citral existing in CO_2 core as well as in the surfactant shell, so that the 'two sides attack' model resulted in the higher reaction rate compared with the W/C microemulsion. And the higher selectivity of citronellal obtained in the present system is due to citronellal being extracted to the $scCO_2$ phase and its further hydrogenation was prohibited. In addition, the Pd nanoparticles in C/W emulsion could be recycled several times and still retain the same selectivity, while the Pd nanoparticles aggregated slightly during recycling and led to a decrease in conversion.

Experimental details

Materials

Citral (*trans* and *cis*), $Pd(CH_3COO)_2$, and poly(ethylene oxide)-poly(propylene oxide)-poly (ethylene oxide) $(EO)_{19}(PO)_{70}(EO)_{19}$ block copolymer (P123) were purchased from Aldrich. Gases of CO_2 (99.9 %) and H_2 (99.999 %) (Changchun Xinxing Gas Company) were used as delivered. Double distilled water was used.

Apparatus and phase behavior studies

The phase behavior of the CO_2-in-water emulsions was observed in 80 ml view cell. In a typical experiment, appropriate amounts of citral, P123, de-ionized water and $Pd(CH_3COO)_2$ were added into the reactor in order to create the same conditions as those in the 50 ml reactor, and then replaced the air in the view cell by CO_2. After that, the contents were heated up to the desired temperature. After thermal equilibrium had been reached, the stirrer was started. H_2 firstly and then CO_2 were charged into the cell slowly and the solution was hazy and milky.

Catalytic hydrogenation

The hydrogenation of citral was carried out in a stainless steel batch reactor (50 ml), and the Pd nanoparticles were synthesized *in situ* by H_2 reduction in the C/W emulsion. Typically, 5 ml of P123 aqueous solution, 0.001 mmol of $Pd(CH_3COO)_2$ and 5 mmol of Citral (with a mole ratio of citral/Pd of 5000) were added into the reactor. The reactor was then sealed and flushed with 2 MPa CO_2 more than three times. H_2 firstly and then CO_2 were introduced into the reactor to the desired pressure with a high-pressure liquid pump after the reactor was heated up to the desired temperature. The mixture was stirred continuously during the reaction, and the speed of stirring kept constant for all the reactions. At the end of the reaction, the reactor was cooled to room temperature and the gases (H_2 and CO_2) stream were vented to ambient pressure through the traps containing *n*-hexane. Then the reactor was opened, and the remaining residue was extracted with another portion of *n*-hexane. The resulting solutions were combined and analyzed with gas chromatography (GC-Shimadzu-14C, FID, Capillary column Rtx-Wax 30 m–0.53 mm–0.25 mm) and gas chromatography/mass spectrometry (GC/MS, Agilent 5890).

For the catalyst recycling, after one reaction was finished, the reaction mixture was extracted with 7.6 MPa CO_2 at a flowing rate of 2 ml min^{-1} at 35 °C until no effusion came out, and the reaction mixture were almost completely extracted within 30 min. Then the next run was carried out with recharging the fresh reactants.

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