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Molecular guided catalytic hydrogenation by micelle-hosted Pd nanoparticle in supercritical CO_2

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Homogeneous dispersion of microemulsion containing palladium nanoparticles in $scCO_2$ is, *for the first time*, observed *via* sapphire window reactor and these particles show an unusual reluctance for double bond hydrogenation of citral aldehyde at hydrophobic end rather than hydrophilic end (high regioselectivity) owing to the unique micelle environment in supercritical carbon dioxide that guide a head-on attack of the molecule.

KEY WORDS: supercritical carbon dioxide; Pd nanoparticle; micelle; hydrogenation; catalysis; selectivity.

1. Introduction

The use of molecular assemblies such as micelles in catalysis has long been receiving attention as it mimics enzyme, the biological catalyst, in organic synthesis [1]. Micellar catalysts contain microscopically solvent droplets carrying catalytic species, which are stabilised by self-organised surfactant molecules in an immiscible solvent. However, separation of them from product poses a major practical problem. The rate of catalytic reaction may also depend on the dynamic nature of surfactant molecules encapsulating catalyst species (could cap the active site) in a particular solvent. To one extreme, it can lead to substantial rate attenuation. On the other hand, micellar properties in supercritical carbon dioxide ($scCO_2$) as solvent may offer a new scenario in this area. Apart from being a green solvent, $scCO_2$ facilitates simple separation *via* altering the solvency through pressure and temperature control. It has been demonstrated that a simple but chemically inert perfluoro-hydrocarbon tail with a polar (or ionic) head group can act as surfactant to stabilise reversed micelle formation in $scCO_2$ [2]. Excellent micelle catalysis using water-soluble catalyst species has then been reported [3]. In some cases, catalytic rate measured is higher than in homogeneous medium, suggesting the intrinsic high mass transfer associated with this solvent and the extremely mobile nature of the surfactant assemblies [3]. Very recently, Ohde *et al.* [3c] have demonstrated that catalytic hydrogenation of unsaturated organic substrate can be achieved in $scCO_2$ using a mixture of water-soluble Rh species, the substrate and the micelle ingredients on the addition of hydrogen. This implies that catalysis occurs over the *in situ* synthesised Rh nanoparticle in the microemulsion (ME). If the formation of nanocatalysts in micelle is confirmed, it will be very interesting and important both academically and practically to investigate their unique catalytic properties in $scCO_2$ as compared with ordinally metal catalysts. In this short letter, we report a direct visualisation and post-mortem characterisation of ME in $scCO_2$ through a sapphire window reactor at different molar water to surfactant ratios (W_0). These experiments clearly indicate that a majority of the Pd nanoparticles is in the ME state. It is also interesting to note that the micelle-hosted Pd crystallite obtained under stable homogeneous ME conditions shows a high regioselectivity in citral hydrogenation. Indeed, partial hydrogenated citronellal is mainly formed, with a high kinetic barrier for further hydrogenation. In contrast, Pd crystallites obtained in vapour, conventional liquid phase, or in extremely high W_0 in $scCO_2$ (co-existence of phases with most Pd particles partition in large water paddles) lead to the fully hydrogenated aldehyde. This reveals that the unique micelle environment in $scCO_2$ can alter the catalytic selectivity of the hosted particles.

2. Experimental

Experiments were carried out in a 300 mL stainless steel and also in 25 mL sapphire windows autoclaves equipped with an overhead stirrer and a magnetic stirrer respectively. In a typical procedure, 500 μL of citral, 100 μL of decane (internal standard), 0.25 mmol of $CF_3(CF_2)_{12}COO^-NH_4^+$ fluorosurfactant, 0.25 mmol of $Pd(NO_3)_2$, water required to saturate the $scCO_2$ fluid 29 mmol. H_2O is required to saturate 5.30 mmol. CO_2 at 40 °C, 140 bars and the appropriate amount of H_2O required at different molar water to surfactant ratios (W_0) are mixed in the reactor. The autoclave is then heated up to 40 °C, and charged with 140 bar by

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pumping CO_2 until emulsion/ME is formed overnight. 10 bar of H_2 is then added to the mixture (in a great excess for both metal salt reduction and for catalytic hydrogenation). Conversion and product distribution are determined using GC analysis. It was found that straight after the hydrogen addition (< 1 h), a complete citral conversion (> 99%) is quickly achieved. This clearly demonstrates the high activity of the Pd catalyst. For comparative purpose, 4 h reaction time is used to ensure a complete reaction in other media.

3. Results

Stability of water-in-scCO_2 ME formation at different W_0 was investigated using a sapphire windows reactor. Figure 1 presents a direct visualisation of the fluid through the sapphire windows under different conditions. Below the supercritical temperature (rt), separate phases of liquid CO_2 and insoluble surfactant/Pd nitrate/water mixture are clearly visible (figure 1a). Upon raising the temperature to 40 °C at 140 bar, a single-phase transparent fluid is then observed for W_0 from 2 to 20, which is consistent with the reported water-in-scCO_2 ME state [3a]. Upon addition of H_2, the ME remains stable (single phase), but the colour of the fluid becomes gradually intensified to a brown ‘‘solution’’ (figure 1b). Similar observations are made when $W_0 = 30$. However, it takes a much longer time to break up the water droplets into the coloured fluid. Hence, it is attributed that this W_0 may be close to the maximum W_0 sustained under our conditions. In extreme cases, when W_0 was set at 100–200, a clear distinction of phases (water droplets and solid powder are dispersed in a clear scCO_2 phase) was evidenced. It is therefore believed that most soluble Pd precursor species would partition into these large water paddles hence depriving the Pd from the ME. The sizes of the micelle-hosted Pd under stable microemulsion regime were determined by TEM and XRD (based on Debye–Scherrer equation). They were of a very uniform size with a sharp distribution (ca. 4.01 nm from XRD; ca. 3.65 ± 0.85 nm from TEM), indeed many of them showed a well-defined cubo-octahedron in shape under a high magnification (figure 2). This is in sharp contrast to the poorly defined particles (8.22 ± 4.08 nm with occasionally a high large patch of metal) obtained under conditions where no MEs are formed.

It was anticipated that the new micelle-hosted noble metal particles in scCO_2 might show different catalytic

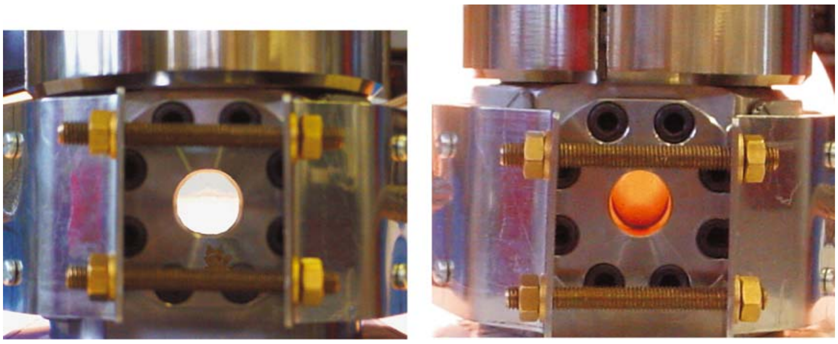


Figure 1. (a) Catalyst slurry at 25 °C, ~67 bar (liquid CO_2); (b) a homogeneous yellowish brown ‘‘solution’’ obtained after adding 10 bar H_2.

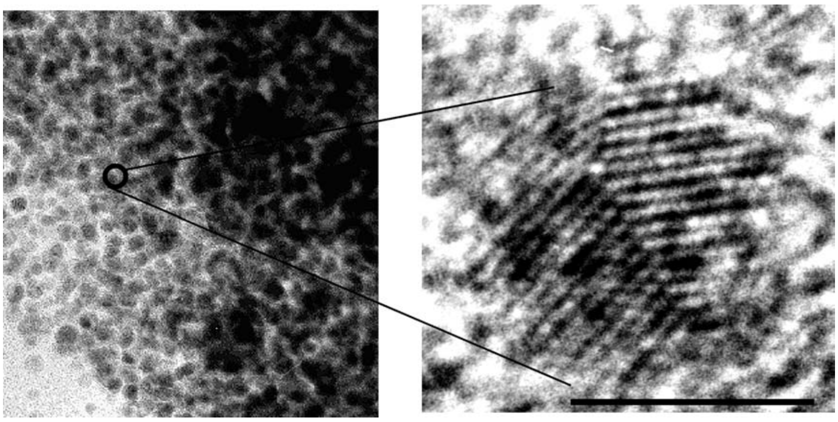


Figure 2. TEM image (left) of a typical micelle-hosted Pd particles (scale bar 20 nm) and the detailed high resolution TEM image of a selected Pd particle (right) showing most of them adopt as a defined cuboctahedral shape cluster (scale bar 3.5 nm).

properties as compared with conventional metal catalysts. As a result, hydrogenation of citral, a molecule that has three reducible locations (a carbonyl polar head group and two double bonds on this rod shape molecule, one at the 2,3-position near the polar head and the other at the 6,7-position on hydrophobic end) was selected as a probe molecule. Hydrogenation of citral over Pd was investigated under different conditions, namely: in conventional conditions, in $scCO_2$ using different W_0 ratios and with different pre-treatments (H_2). Pd is well known to favourably catalyse the hydrogenation of double bonds but is sluggish to hydrogenate the carbonyl group [4]. Thus, for all conditions, the main products are the partially hydrogenated product of the 2,3-conjugated C=C (citronellal, CIAL), the unactivated 6,7-isolated C=C (3,7 dimethyloct-2-enal) and the fully saturated aldehyde (dihydrocitronellal, DHAL), altogether accounting for $>83\%$ selectivity. A small degree of hydrogenation at the terminal carbonyl to corresponding unsaturated alcohols (citronellol, CIOL and traces of 3–7 dimethyloct-2-enol and geraniol), saturated alcohols (3,7 dimethyloctanol, DMOL) and a cyclic product (isopulegol) is observed. It is noted from table 1 where the presentation is focused on the major products and the complete product distribution in figure 3 that, using low W_0 ratios (2–20) of a stable and homogeneous ME, CIAL is the main product (~60%). A maximum CIAL selectivity (68%) is obtained for a W_0 ratio of 30, with a surprisingly low selectivity towards DHAL (11%). However, at high W_0 ratios (100, 200) where phase segregation was clearly evidenced, a dramatically lower selectivity to CIAL with a concomitantly higher selectivity to DHAL (maximum of 54% for $W_0 = 200$) is seen over the same prolonged period of time. From the alcohol product distribution although to a lesser degree, the same pattern is observed over the CIOL and DMOL distributions with an increase in W_0. These results strongly indicate the kinetic reluctance for the double bond hydrogenation at the hydrophobic end of the citral by the micelle-hosted Pd particles at low W_0 ratios, but no such observation at high W_0 ratios (Pd not in micelles) is noted. To illustrate that our results are related to the micelle host, H_2 is immediately added prior to the ME formation at $W_0 = 30$ (*in situ* UV–vis monitor of the surfactant concentration at 267 nm suggests a few hours to establish the ME state where the fluorinated species undergo self-assembling with the water/$scCO_2$ in order to override the strong electrostatic interactions

Table 1
Influence of experimental conditions on cital hydrogenation[a]

Solvent	Working state	W_0 ratio	Product distribution (%)	
			CIAL	DHAL
–	Vapour	–	1	82
Cyclohexane	Solution	–	19	66
CO_2	ME (H_2 after)	2, 5, 10	58–60	14–17
CO_2	ME (H_2 after)	30	68	11
CO_2	No ME	200	22	57
CO_2	H_2 before ME	30	30	54

[a] 500 μL Citral (all consumed), 0.25 mmol Pd nitrate, 0.25 mmol F-surfactant, 140 bar CO_2 or 40 mL cyclohexane, 10 bar H_2, 40 °C, 4 h.

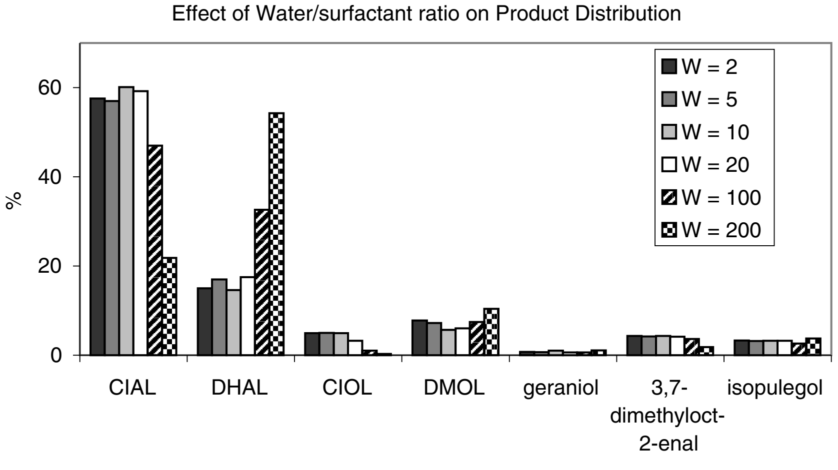
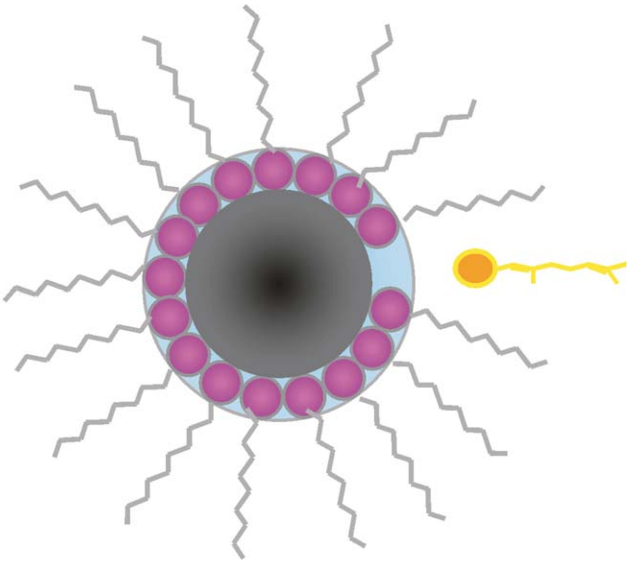


Figure 3. Product distribution depending on the W_0 ratio in the complete citral hydrogenation (500 μL citral, 0.25 mmol Pd nitrate, 0.25 mmol F-surfactant, 140 bar CO_2, 10 bar H_2, 40 °C, 4 h reaction time).



Scheme 1. Molecular guided catalytic hydrogenation by micelle-hosted Pd nanoparticle in supercritical CO_2.

within this particular ionic solid precursor. The activation time apparently depended on stirring and type of precursor used). A switch to the DHAL is detected (figure 3 and table 1). It is well documented that for conventional metal catalysts, the subsequent hydrogenation to the unactivated double bond of the citral is difficult to inhibit. Hence, a high selectivity to saturated aldehyde is obtained over Pd, even at short contact time [5]. This has been attributed to the strongly bound partial hydrogenated species on metal surface for subsequent attack by surface hydrogen (particularly the side-way attack of the molecule assessing both the double bonds by the surface). As a result, a number of ways for modifying noble metals (i.e. blending Fe) and placement of metal catalyst into zeolitic pores to guide the aldehyde to their surface have been studied [5]. In our case, when cyclohexane/vapour phase is substituted for $scCO_2$, a high DHAL selectivity is indeed observed over our unpromoted Pd (figure 3 and table 1). Thus, the key question is why the micelle-hosted Pd offers the high intrinsic kinetic barrier for the total hydrogenation of citral.

4. Discussion

On the basis of micelle molecular assembly (see scheme 1), the ME in $scCO_2$ is envisaged to consist of a water core containing Pd nanoparticles, which is surrounded by the oriented surfactant molecules as a shell. Depending on the fluxional behaviour of the individual surfactant molecules, we believe that the citral molecule must align itself in order to minimise repulsion due to the steric hindrance in accessing the enclosed metal surface. It is proposed that the relatively hydrophilic carbonyl head group will penetrate into the aqueous micelle aggregate (head-on attack). Such molecular orientation of citral guided by the micelle assemblies allow a highly selective hydrogenation of the α, β-conjugated double bond that is near to the Pd surface, hence citronellal, CIAL is formed. This partially hydrogenated product is immediately expelled from the aqueous micelle since both the spatial limitation and miss-match in hydrophilicity reduce the chance for the further hydrogenation of isolated double bond at the hydrophobic end. However, when citral molecules can freely access Pd nanoparticles (vapour, conventional solvents, and at high W_0 ratios), the described kinetic reluctance for subsequent hydrogenation is no longer imposed. As a result, DHAL is the main product as previously reported [6]. This postulation is also supported by our study of citronellal hydrogenation. When the W_0 ratio is decreased from 200 to 30, the DHAL yield is substantially reduced (from 70.5% to 46.2%) at prolonged hydrogenation. Thus, the presence of the ME encapsulating Pd nanoparticles clearly renders citronellal hydrogenation to DHAL much more difficult.

5. Conclusion

To conclude, a direct visualisation of the Pd crystallite of well-defined size in a homogeneous water-in-$scCO_2$ ME under various conditions is established. It is shown that micelle enclosed Pd displays excellent hydrogenation catalysis, which demonstrates the dynamic properties of surfactant molecules in $scCO_2$. Further, the aqueous micelle embracing metal particles makes the nanometals rather unusual in catalysis as compared to their naked counterparts. Isolation of the products from MEs is usually relatively difficult due to the high concentration of the surfactant, and part of the catalyst or the surfactant (or both) could be lost during workup. Work is in progress to address this aspect to investigate whether ME systems in supercritical carbon dioxide offers different scenario from the practical standpoint. However, this present work represents the first fundamental study on using soft molecular assemble as nano-catalyst vehicle to control reaction selectivity as akin to those of rigid zeolite catalysts, in supercritical carbon dioxide. Thus, a new but exciting avenue for a better control in tuning reaction selectivity using metal catalysts in *designed* micelle as a “soft” molecular scaffold could be developed.

Acknowledgments

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