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Solid supported micellar catalysis: some syntheses and characterisations

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Abstract

A synthetic method for chemically tethering organic based surfactant molecules and fluorous surfactant molecules onto a high surface and pore volume silica has been developed. It is shown that heterogenisation of a simple water-soluble ions (i.e. molybdate ion and Co^{2+}) can be accomplished onto these composite materials. They display an excellent activity and selectivity for oxidation of organic molecules in bulk organic solvent or in supercritical CO_2. Characterisations indicate that catalysis occurs within the surface supported surfactant assemblies (chemically tethered reversed micelles) in the porous silica structure.

Keywords: Supported micelles; Heterogenisation; Simple transition metal ions; Leaching

1. Introduction

In the area of partial oxidation of organic molecules (oxidation of fine chemicals at mild conditions) there is urgent need to replace stoichiometric reagents, for example, permanganate and dichromate ions with preferred technology based on catalytic oxygen transfer using clean oxygen donors [1]. Because of the remarkable success of solid titanium silicalite, TS-1 (developed by Enichem), extensive research is now centred on the exploration of heterogeneous catalysts containing other redox transition metal ions for oxidation. Although recent work reveals that some heterogeneous catalysts show a high activity and selectivity for a wide variety of oxidations, one aspect, which is generally overlooked, is their stability and hence, the true heterogeneity of these materials under typical oxidising conditions. For example, VAPO-5 catalysed olefin epoxidation and benzylic oxidation with tertiarybutylhydrogenperoxide (TBHP), which were originally believed to occur solely inside the micropores [2]. However, a recent and more careful study of this material under liquid phase showed the vanadium is leached and the presence of soluble metal ions accounted for observed catalysis [3]. Lempers and Sheldon [4] have also shown that an extremely low concentration of soluble Cr ions (<2 ppm) leached from their Cr containing microporous catalysts was actually responsible for most of their observed oxidation catalysis which was originally attributed to the catalytic activity of the anchored chromium species. These examples undoubtedly suggest that much work reported in the literature on the use of transition metal ions on solid surfaces may need to be repeated and subjected to rigorous proof of heterogeneity.

Despite continued search for other active but non-leachable heterogeneous catalysts, the direct use of inexpensive metal ions remains promising [5] should their separation problems from product mixture

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be solved. Thus, there is an alternative approach of using a biphasic system that is recently being industrially recognised. The concept depends on the use of two immiscible liquid phases, such that the homogeneous soluble species in one phase (e.g. water) and the product in the other (organic phase). The product can then be obtained by a simple phase separation. In particular, the use of a simple, inexpensive, water-soluble salt as a catalyst (e.g. ammonium molybdate) in the biphasic medium is worth noting since if some metal ion leaching occur this will not be too expensive and may not create insurmountable problems. However, the major problems of this present technology which limit wider applications are the intrinsic low solubility of organic reactants in water in which the catalyst resides, a limited interface between the reactants and some catalyst loss between the immiscible liquids [6].

We have recently reported the use of *free reversed micelles* using fluorous surfactant molecules in supercritical CO_2 ($scCO_2$), which carry simple water-soluble ionic catalysts (Co^{2+}) in $scCO_2$ (carry organic molecules and oxidant) for partial oxidation [7]. We demonstrate that this system provides a means to bring species of a very different polarity into contact within the small micelle as a *nano-reactor* with excellent mass and heat transfers, which sustains an extremely fast catalytic oxidation reaction [7]. In general, the main practical problem of micellar catalysis is the difficulty in separation of catalyst from product mixture. However, due to the unique properties of $scCO_2$ as a solvent separation of catalyst components together with the unbound micelles can easily be facilitated and be reused in a batch reactor with simple adjustments of temperature and pressure.

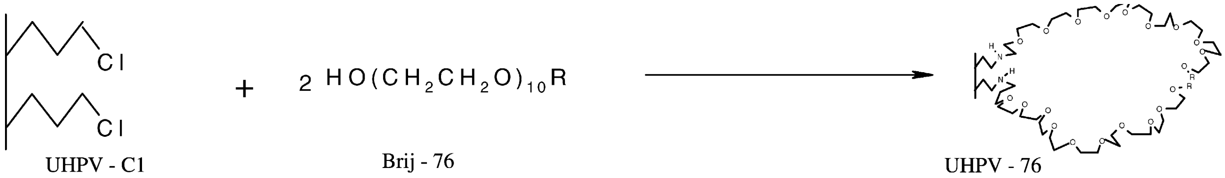
In order to appreciate the advantages of using small micelles as nano-reactors and facilitate separation in conventional organic solvent(s), we have proposed a new generic idea of developing chemically supported surfactant molecules on porous solid surface [8]. It has been envisaged that the anchored long surfactant molecules could form *supported micellar aggregates* on the surface (although their aggregate structure may be dissimilar to the corresponding free forms), which could support small water droplets that in turn contain a simple water-soluble catalyst. Evidence indicates that the supported surfactant assemblies are able to improve the interactions between hydrophilic and hydrophobic species due to the particular microenvironment and also serve to separate the reaction components [8].

This paper has been focused on some syntheses and more characterisations of new silica supported fluorous surfactant (hosting water-soluble Co^{2+} species in $scCO_2$ at a continuous flow [9]) and non-fluorous surfactant molecules (hosting water-soluble molybdate species in conventional organic solvents [8]). At present, we encounter difficulties to directly characterise the size and distribution 'micellar assemblies' within the porous solid structure. As a result, templated deposition of Pd nano-particles over the supported surfactant assemblies via reduction of its soluble precursor therein has been primarily developed as a *new chemical probe* for the material characterisation. Thus, it is hoped that the size and distribution of the Pd nano-particles (give a good contrast in electron microscopy) could reflect the actual distribution of these micellar assemblies within the porous solid structure. In addition, the tethered surfactant stabilised Pd nano-particles may find catalytic applications in fine chemical areas.

2. Experimental

2.1. Preparation of porous silica tethered with surfactant molecules

Functionalisation of surface hydroxyl groups on silica with linker molecule was achieved according to the literature [10]. In this study, ultra high pore volume (UHPV) silica (Aldrich) was used. Acid activated, washed UHPV silica (4.0 g) was mixed with the linker, 3-chloropropyltriethyoxysilane (CPTES, 4 ml) (Aldrich, purity $> 99\%$) in refluxing dry toluene (50 cm^3) under a nitrogen atmosphere for 12 h. After reaction, the mixture was filtered, washed with dichloromethane (DCM), transferred to a Soxhlet thimble for further exhaustively wash to remove any of the excess linker molecules. This wash was carried out by 1:1 solution of DCM and diethyl ether under refluxing condition in argon gas for 12 h. After the mixture was filtered and dried, solid product abbreviated as UHPV-Cl was collected. The dried UHPV-Cl sample was then allowed to react with excess polyoxyethylene stearyl ether surfactant molecule ($C_{18}H_{37}(OCH_2CH_2)_{10}OH$), Brij 76 (Aldrich) in



Scheme 1.

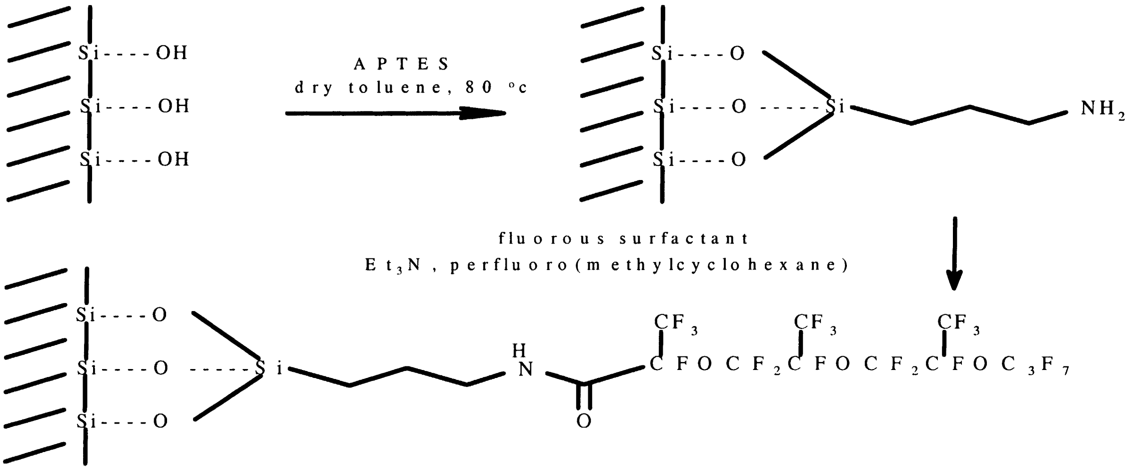
refluxing DCM (200 cm^3) for 12 h under a nitrogen atmosphere. The residue was collected from filtration, exhaustively washed with DCM and Soxhlet washed with DCM–ether mixture and air-dried at 90 °C. This yielded the product abbreviated as UHPV-76. The attachment reactions and tentative molecular aggregation on surface was expected in Scheme 1. Synthesis of silica tethered with fluorous surfactant molecules is shown in Scheme 2.

2.2. Preparation of porous silica tethered with fluorous surfactant molecules

For synthesis of silica supported fluorous surfactant molecules, nitric acid treated silica (4.0 g, acid treatment could maximise the surface silanol groups) was first mixed with other linker, 3-aminopropyltriethoxysilane (APTES, 4 ml) (Aldrich, purity > 99%) in refluxing dry toluene (50 cm^3) under a nitrogen atmosphere for 12 h. This was followed by the washing step as described above (giving UHPV-NH$_2$). In this case, perfluoro-(2,5,8-trimethyl-3,6,9-trioxadodecanoyl) fluoride (60% fluorine content by weight) (9 g) was used as the surfactant to react with the NH$_2$ functionalised silica (2 g) with the elimination of HF gas under refluxing toluene. This gave an orange fluorinated surfactant modified-silica material followed the extensive washing steps as described above. This material is abbreviated as UHPV-F.

2.3. Preparation of nano-particles on surfactant-tethered silica for characterisations: wet impregnation of Pd precursor salt onto silica

A soluble Pd precursor was initially prepared by adding 0.9 g aqueous palladium (II) nitrate solution (Pd assay 13.17%, Johnson Matthey) in 10.0 ml ethanol. Modified or unmodified silica (0.8 g) (UHPV, UHPV-76 or UHPV-F) was added to the Pd precursor with a vigorous stirring. Then, the mixture was stirred,



Scheme 2.

aged, and the slurry was allowed to dry under ambient conditions. The formation of Pd nano-particles was obtained by the reduction of these silicas wet impregnated with the Pd precursor in a 300 ml autoclave reactor using 5% H_2/Ar at 2 bar at 25 °C for 5 h. This yielded three different products abbreviated as Pd@UHPV, Pd@UHPV-76 and Pd@UHPV-F.

2.4. *Wet impregnation of Pd precursor onto modified silica with $scCO_2$ treatment*

Pd precursor was wet impregnated onto the modified silicas as described above. Prior to the H_2 reduction, the wet impregnated silica materials with five drops of ethanol (ca. 0.075 g) and 90 bar carbon dioxide (supercritical carbon dioxide is somewhat akin to hexane as a solvent property) were added into a 160 ml stainless steel Parr autoclave reactor equipped with Teflon linings, which was kept at 40 °C. The mixture was constantly stirred at 7000 rpm overnight using a magnetic driven stirrer. The H_2 reduction process was performed straight after the release of CO_2 followed by purging and kept the mixture in 5% H_2/Ar at 2 bar at 25 °C for 5 h without exposure to air.

This yielded three different products after the supercritical carbon dioxide treatment and they are abbreviated as Pd@UHPV-SC, Pd@UHPV-76-SC and Pd@UHPV-F-SC.

3. Results and discussion

3.1. *Catalytic testing*

Table 1 summarises our previous investigation, which clearly demonstrates that a water film containing a simple molybdate ions on silica surface can be used to catalyse epoxidation of cyclohexene with *t*-BuOOH in bulk DCM [8]. A high selectivity for the cyclohexene oxide (>90%) at good *t*-BuOOH conversions (around 45–50%) could be reached under mild conditions in the presence of small amounts of water (11–26%) as thin films on the silica surface. The dry supported molybdate catalyst in DCM is inactive indicating a minimum amount of water is necessary to observe dissent catalytic activity, a phenomenon that is attributed to a certain mobility of the molybdate species on the surface of the silica. It is noted that a significantly higher activity (92.17% vs. 44.32%) is obtained using surfactant modified-silica (UHPV-76) than unmodified silica of comparable water content. These results agree with our hypothesis that the attachment of surfactant molecules could form surface micellar aggregates that would increase the mass transfer across the aqueous–organic interface. A brief study on the stability of these anchored catalyst aggregates and the leaching of active molybdate species have also been reported previously [8].

Table 1
Catalytic activities in terms of *t*-BuOOH (TBHP) consumptions over different catalysts[a]

Catalyst system	Conversion (%) of TBHP (in DCM)
Two bulk biphasic layers (15 ml water carrying $(NH_4)_6Mo_7O_{24}$ and 15 ml DCM carrying TBHP, cyclohexene)	2.48
$(NH_4)_6Mo_7O_{24}$ on silica (dried by evaporation)	1.54
A thin water film carrying $(NH_4)_6Mo_7O_{24}$ on silica (14.1% H_2O)	44.32
$(NH_4)_6Mo_7O_{24}$ on UHPV-76 assemblies (11.1% H_2O)	92.17

[a] Hydrated ammonium molybdate (0.618 g) ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) was allowed to mix with 3.0 ml DI water and 0.5 g of unmodified silica or the surfactant-tethered silica. Excess water was pumped off under a dynamic vacuum (1×10^{-2} Torr) at RT for 1 h and then at 60 °C for another 1 h before test. Dried composite catalyst (0.2 g) prepared as above was mixed with the required small amount of water, followed by adding 10.0 ml DCM, 1.26 ml pure cyclohexene, 1.0 ml TBHP (5.5 M in decane) where 2:1 molar ratio of cyclohexene to TBHP is maintained. The mixture was then refluxed with continual stirring at about 45 °C for 24 h. The supernatant was collected, centrifuged and analysed.

3.2. *Characterisations of UHPV-76 and UHPV-F silica supported surfactant assemblies*

The initial methodology of APTES and CPTES linker molecules immobilisation onto silica surface was achieved according to a modified method published by Sutra and Brunel [10]. These surface reactions are akin to the general capping reactions with surface –OH groups that are known to readily take place at mild conditions. It is important to reduce/minimise any free organic molecules trapped within the porous silica. Thus, excessive washing/reflux were carried out to remove any physisorbed species. Evidence for the successful covalent

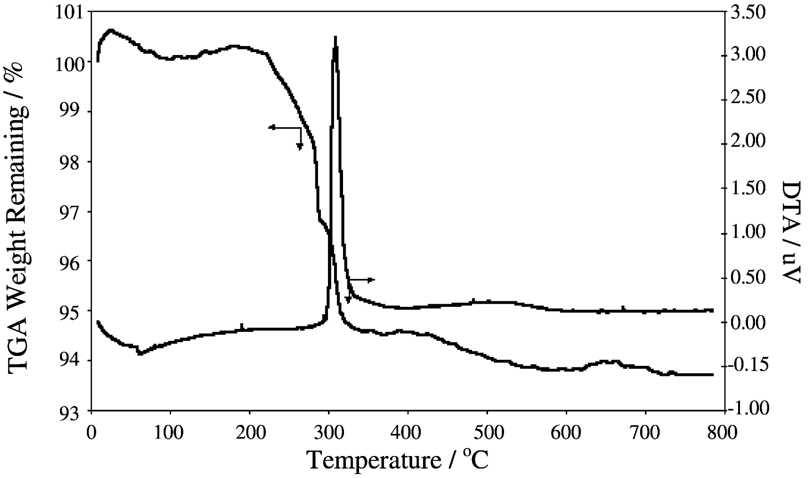


Fig. 1. TGA/DTA signals as a function of temperature for UHPV-Cl.

attachment of organic molecules onto the silica support comes from a range of analytical techniques. Typically, FT-IR new absorption peaks (2922.5, 860.0 and 698.6 cm^{-1}) attributed to the C–H stretching and bending modes associated with organic molecules were clearly observed. No peaks were detected when the silica was immersed initially with either the linkers or surfactants at room temperature, filtered and Soxhlet washed with DCM–ether mixture under identical treatments. This clearly suggests that the silica surface had been chemically tethered with organic groups rather than the physical retention of the organic compounds inside the porous structures.

For pure UHPV silica, an endothermic weight loss (5%) at around 100 °C and a gradual weight loss (further 2.3%) from 100 to 800 °C attributed to the removal of physisorbed water and surface dehydroxylation, respectively (not shown). In the case of all the organic modified silicas (Figs. 1–3) two extra exothermic events were observed with associated greater weight loss from 100 to 800 °C. These were assigned to the combustion of surface organic groups when the

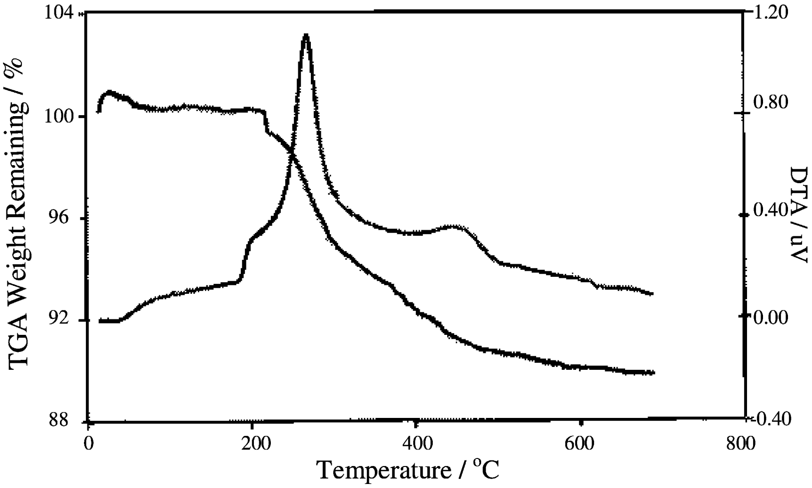


Fig. 2. TGA/DTA signals as a function of temperature for UHPV-76.

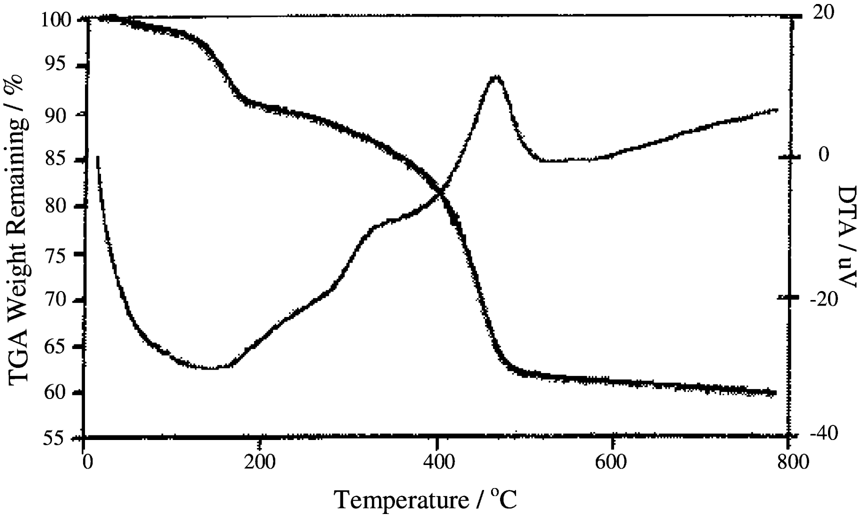


Fig. 3. TGA/DTA signals as a function of temperature for UHPV-F.

sample was heated in air. However, no further analysis was attempted to differentiate the two exothermic peaks. Fig. 1 shows about 5% weight loss from the TG analysis of the UHPV-Cl sample, associated with the combustion of silica anchored organic groups while UHPV-NH_2 gave about 3% (not shown) in the temperature range from 100 to 800 °C. There were 8 and >30% weight loses in the surfactant attached silica, UHPV-76 (Fig. 2) and fluorous surfactant attached silica, UHPV-F (Fig. 3), respectively. These values are substantially higher than their precursors with the only linker molecules attached suggesting that the subsequent attachments had been achieved. Our estimation suggests that almost all the surface Si–OH groups ($\sim 1 \times 10^{19}\,m^{-2}$) were covered with these surfactant molecules (approaching monolayer coverage). The highest weight loss in the case of UHPV-F was attributed to the bulkier group with the fluorine (EDX analysis shows the presence of the fluorine). The BET surface area and the pore size analysis were also consistent with the chemical modification of the porous silica surface with bulky organic groups. Typically, the surface area decreased from 304 to 223 $m^2\,g^{-1}$ with a significant decrease in pore volume at 20 nm and the appearance of a shoulder at smaller pore size of 16 nm when compared with unmodified silica with the UHPV-76 sample. Existence of free linker or surfactant molecules in these samples is not evident since the control experiments suggest the free organic molecules should have been totally removed. (Note that FT-IR, TG and BET characterisations showed no difference of the silica sample physically pre-mixed with the organic molecules as compared to pure silica under identical treatments.)

No direct morphological or structural characterisation is yet obtained, at this stage, on the solid supported reversed aqueous micellar cores as nanoreactors. However, we envisage that the nano-particles synthesised within the supported aqueous micellar cores may reflect the homogeneity of the size of the tethered micelles. As a result, Pd metal nanoparticle is synthesised (based of the H_2 reduction of water-soluble Pd ions) over our different silica samples. XRD was used to characterise the Pd@UHPV, Pd@UHPV-SC, Pd@UHPV-76, Pd@UHPV-76-SC and Pd@UHPV-F-SC samples. In general, no peak was assigned to the porous silica because of its amorphous nature, however, board peaks attributed to nano-size Pd were clearly visible. By applying the Scherrer analysis on the Pd (1 1 1) peak at $\sim 40^\circ$ 2θ, the average of Pd particle sizes (d_{XRD}) in these samples were determined. A standard technique of CO chemisorption was also applied to verify the sizes. The results are now summarised in Table 2.

According to the calculated Pd particle size summarised in Table 2, Pd nano-particles supported

Table 2
The calculated average particle sizes of Pd deposited on the unmodified and modified silicas

Sample	d_{XRD} (nm)[a]	$d_{\mathrm{CO\text{-}chem}}$ (nm)
Pd@UHPV-SC	23.1	57.7
Pd@UHPV-76	13.7	16.3
Pd@UHPV-76-SC	11.7	14.1
Pd@UHPV-F-SC	10.1	nd

[a] Pd (1 1 1) band was used to calculate the particle size where instrumental angular broadening had been corrected.

on both surfactant-modified silicas (Pd@UHPV-76, Pd@UHPV-F) are significantly smaller than the Pd nano-particles on the Pd@UHPV sample with and without $scCO_2$ treatment (no significant difference was found when compared Pd@UHPV to the Pd@UHPV-SC). When $scCO_2$ treatment was applied on the sample, there was a further reduction of 2–11.7 nm in the average size of the Pd nano-particles (Pd@UHPV-76-SC). It is noted that fluorinated surfactant-tethered silica (Pd@UHPV-F-SC) with $scCO_2$/ethanol treatment produced the smallest average Pd particle size of 10.1 nm and with an excellent dispersion (see TEM micrograph below).

Carbon monoxide chemisorption measurements were attempted to determine the average Pd particle size in order to ascertain the XRD results with another independent technique. The measurements were conducted at room temperature by using a pulse flow technique with a CO loop volume of ca. 0.25 ml. Prior to the measurement each sample (about 0.15 g) was pre-treated by 33% hydrogen in helium at 50 °C for 30 min. With a thermal conductivity detector (TCD) as the detector, the measurements were preformed with an injection of 0.25 ml CO after the samples were cooled down to the room temperature under the flow of hydrogen/helium. The metal dispersion was calculated by assuming a stoichiometry CO:Pd = 1, which also assumes a linear mode of adsorbed CO is formed on Pd [11,12]. Pd particles in three of the Pd/silica materials (Pd@UHPV-SC, Pd@UHPV-76 and Pd@UHPV-76-SC) were determined.

It is generally accepted that small noble metal particle size evaluated by CO chemisorption and XRD is comparable as also reflected from our results of different silica samples (Table 2) if the 1:1 Pd:CO stoichiometry remains valid. Larger particle size can be erroneously derived if some surface metal sites are inaccessible or the CO chemisorption mode on the metal site deviates from linear to bridging mode [13]. We note that there is a significant deviation in the particle size of Pd@UHPV-SC. It is believed that such larger Pd particles of >23 nm with the dominant high coordination metal sites on flat surface favours CO bridging mode hence with the consequence of inflating the Pd

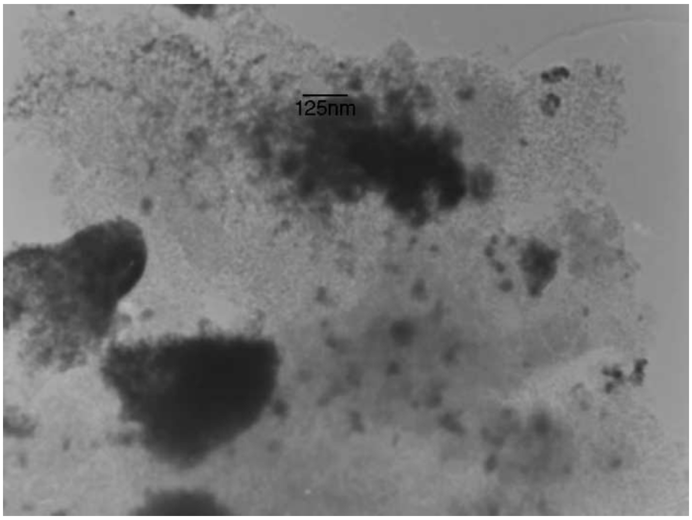


Fig. 4. A TEM image from Pd@UHPV-SC (80,000×).

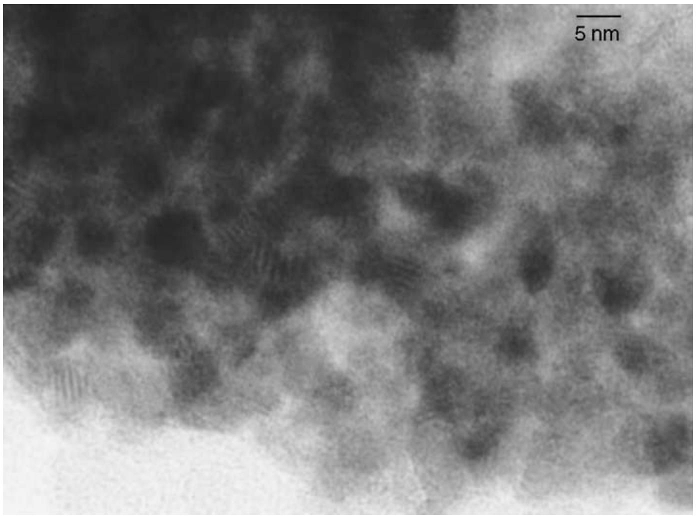


Fig. 5. An HRTEM image from Pd@UHPV-F-SC (2,000,000×).

particle size. This result is consistent with the interpretation of Sheu et al. [13] who showed that the linear CO is preferentially formed on low-coordinated (corner or edge) Pd atoms of small particles and bridging CO mode on large particles. Nevertheless, the significantly smaller particle synthesised by both surfactant modified UHPV silicas supports the fact that smaller supported aqueous micellar assemblies are indeed created within the porous silicas.

TEM images show that the dispersion of Pd metal particles on unmodified silica with and without $scCO_2$/ethanol treatment is virtually the same (Fig. 4) as large particles and aggregations of microparticles (much larger than the average particle size obtained from XRD and CO chemisorption) and some clean areas with no metal particle were clearly observed. Presumably, the particle size and distribution have reflected the uneven distribution of water paddles on the amorphous silica internal surfaces. In contrast, typical surfactant modified-silicas such as Pd@UHPV-F-SC clearly show a much smaller particle dimension with an excellent particle dispersion within all the modified silica matrices (particles are homogeneously dispersed through all areas investigated). From the typical HRTEM image (Fig. 5) 10 ± 2 nm well-defined Pd particles (the fringe separation of 2.3 Å corresponding to the Pd $\langle 1\,1\,1 \rangle$ inter-planar distance) are clearly visible in all areas. It is interesting to find that most of Pd particles found are indeed small but as regular shaped crystallites. Thus, it is clearly evident that the sizes of our supported micellar assemblies are much more uniformly distributed within the internal porous structures of the two surfactant-modified silicas.

4. Conclusion

Catalytic applications of using unbound micelles carrying catalyst components in conventional solvents have in general not been widely explored because of the separation problems. It is shown that a simple water-soluble metal salt can be carried by silica-tethered surfactant molecules, which catalyse oxidation of organic molecules in external bulk organic solvent with a pronounced high rate. This clearly suggests anchored surfactant molecules play an active role in enhancing the catalytic activity. Characterisations indicate that the surface anchored surfactant molecules can aggregate in a similar manner akin to free form micelles (though the precise morphology and structure is not yet known) but with themselves evenly dispersed within a solid matrix giving small aqueous paddles (reflected by the uniform nano-crystallites synthesised therein). Our results clearly imply that oxidation catalysis can be beneficially occurred within these small supported surfactant assemblies as nano-reactors which facilities separation.

Acknowledgements

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