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Micelle-hosted bimetallic Pd–Ru nanoparticle for in situ catalytic hydrogenation in supercritical CO_2

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Abstract

Bimetallic Pd–Ru nanoparticles of different elemental ratios are prepared *via* in situ reduction of their simple salts in reverse micelles in supercritical carbon dioxide ($scCO_2$). The optimised Pd:Ru (1:1) nanoparticle shows the highest activity for hydrogenation of functionalised alkene under mild conditions, which can be easily recycled under the reaction conditions without use of organic solvent.

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Keywords: Hydrogenation; Micelle-hosted nanoparticle; Bimetallic; Supercritical carbon dioxide; Nitrile

1. Introduction

There has been much recent interest in synthesising uniform bimetallic nanoparticles as new catalysts for organic reactions. The suitable geometric and/or electronic effects of blending foreign metal atoms into metal structure allow the bimetallic metal nanoparticles with tunable catalytic properties. This is especially important to any new catalytic process where high activity and ultra-selectivity to product in environmental conscious manner are urgently required. However, traditional methods for the bimetallic catalyst synthesis on support surface give a broad particle distribution [1] and often tend to suffer from phase segregation of metal components [2]. Recent report of using a single source of organometallic cluster with two metal centres as a precursor in mesoporous host represents a smart approach but the specific nature of the cluster reduces versatility of this methodology [3,4]. Also, there are some specific ways to synthesize bimetallic nano-particles with small particle size distribution including the reduction of metal ions using ultrasonic technique [5], thermal reduction [6] and microemulsion method [7]. The use of reverse micelle in supercritical carbon dioxide for making silver [8] and copper [9] nanoparticles has been attracting a lot of attention since supercrtical carbon dioxide as a green solvent can also allow in situ evaluation of catalytic properties of the metal particles. A number of other potential applications of using this new solvent is also noted [10,11]. It is interesting to point out that no synthesis nor testing of bimetallic nanoparticle in supercritical carbon dioxide is yet disclosed in the open literature.

In this work we show that reverse micelle in $scCO_2$ can be employed as a ‘nano-reactor’ for in situ synthesis of bimetallic Pd–Ru nanoparticles of a narrow size distribution *via* reduction of their readily available salts. Hydrogenation of *cis*-2-pentenenitrile containing both alkene and cyanide groups were selected as a chemical reaction probe. The optimised Pd:Ru (1:1) nanocatalyst was found to function much more effectively than individual metals by combining the strong binding ability of Ru for nitrile with facilitated hydrogen activation and transfer ability of Pd previously known in the literature [12,13]. Thus, this method allows rational optimisation of nano-bimetallic composition for hydrogenation of functionalised alkene without interference from support and phase segregation. In addition, it is demonstrated, *for the first time*, that the micelle-hosted bimetallic catalyst in $scCO_2$ can be reused with a simple workup for batchwise hydrogenation without the need of organic solvent.

2. Experimental

2.1. Materials

Palladium(II) nitrate solution (Pd assay 8%) and ruthenium(III) chloride (anhydrous, Ru assay 49%) were both obtained

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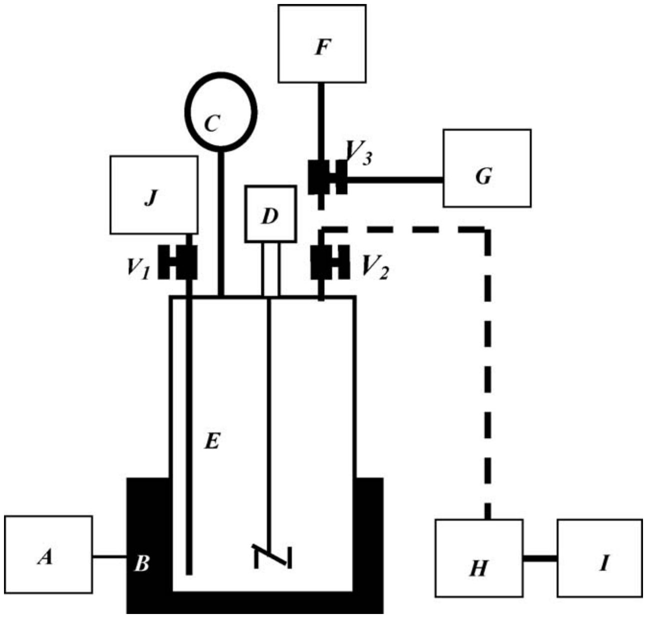

Fig. 1. A schematic diagram showing the setup for in situ synthesis of metal nanoparticles and their hydrogenation reactions in $scCO_2$. (A) Temperature and stirrer controller; (B) heater; (C) pressure gauge; (D): overhead stirrer; (E) autoclave reactor; (F) flow-meter (exit to atmosphere); (G) nitrogen inlet; (H) GC/FID equipped with a gas injection valve; (I) flow-meter (exit to atmosphere); (J) gas inlet (for the admission of carbon dioxide or methane via a three-way valve, not shown); V_1 and V_2: High-pressure two-way valve; V_3: high-pressure three-way valve; heated transfer line from V_2 to H.).

from Alfa Aesar. *cis*-2-Pentenenitrile and perfluorotetradecanoic acid were both obtained from Aldrich and used as received. Carbon dioxide, hydrogen and methane gas cylinders were all obtained from BOC. The synthesis of ammonium perfluorotetradecanoate surfactant was reported in our previous publication [14].

2.2. In situ synthesis and testing of micelle-hosted metal/bimetallic nanoparticles in supercritical carbon dioxide

Table 1
The quantity of water, Pd and Ru precursors (at defined by atomic ratios) used for the *cis*-2-pentenenitrile hydrogenation

Samples[a]	Pd precursor (μL)	Ru precursor (μL)	Water added (μL[b])
Pd	67.0	0	89.5
Pd:Ru (3:1)	47.5	31.5	77.5
Pd:Ru (1:1)	31.5	63.0	62.0
Pd:Ru (1:3)	16	92.0	48.5
Ru	0	123.0	33.5

[a] Total metal content set at 0.05 mmol.

[b] Total volume of water added: 156.5 μL (sufficient to saturate the carbon dioxide [14] as well as producing a molar water-to-surfactant ratio, W_o, of 30).

The in situ synthesis of the metal nanoparticles and their hydrogenation reaction of the α,β-unsaturated nitrile, *cis*-2-pentenenitrile were carried out in a 100 mL stainless steel reactor (Parr Instrument, Model number 4561 reactor) as shown in Fig. 1. It was reported earlier that aqueous microemulsion could be established in $scCO_2$ fluid using ammonium perfluorotetradecanoate surfactant and water [14,15]. Thus, 0.08 mmol of the surfactant and 156.5 μL of water were used to pre-saturate the $scCO_2$ and to give a W_o (water to surfactant molar ratio) of 30 in our 100 mL stainless steel reactor under 120 bar $scCO_2$ at 313 K. As a result, this amount of surfactant was mixed with appropiate extracts from palladium(II) nitrate aqueous solution (0.757 M, Pd assay 8%) and ruthenium(III) chloride aqueous solution (0.399 M, Ru assay 4%) together with corresponding DI water according to the designated Pd:Ru atomic ratios (Table 1) in order to keep the same metal content and W_o ratio in the microemulsion system. Twenty millimolar *cis*-2-pentenenitrile (2 mL) was also added into the same autoclave giving the molar substrate to catalyst ratio of 400. The reactor was then flushed with pure methane at 60 mL min^{-1} for 3 min, this gas was used as the internal standard for GC analysis. Carbon dioxide was then pumped into the autoclave reactor using a booster pump to reach the desired pressure (120 bar) at 313 K. The mixture was then stirred overnight (approximately 720 rpm) in order to create a stable microemulsion system. Then, the pressure was topped up to 140 bar by adding 20 bar H_2 (excess for hydrogenation) to the autoclave. The metal precursor salt(s) in the water-in-$scCO_2$ microemulsion was quickly reduced once the hydrogen was injected giving a homogeneous 'brown' solution in the reactor (visualisation of the reaction mixture through saphhire windows as shown in Fig. 2). Gaseous content of the autoclave

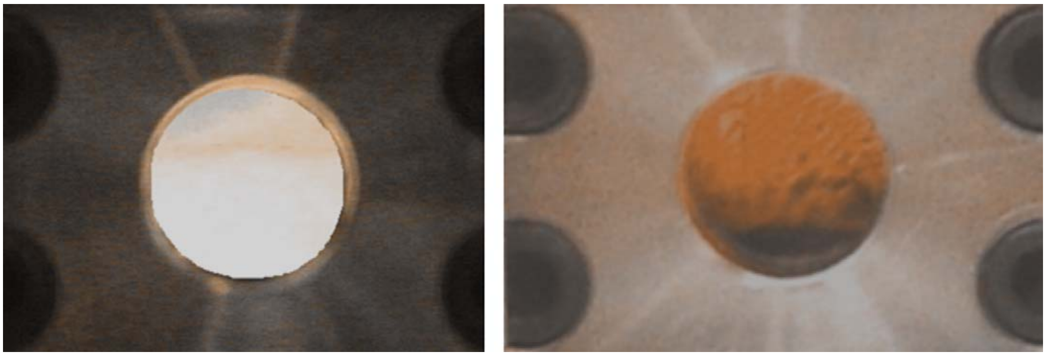

Fig. 2. (Left) the slurry containing *cis*-2-pentenenitrile, surfactant, Pd and Ru precursor solution at 298 K in liquid CO_2; (right) most slurry disappeared with formation of a brown 'solution' containing noble metal(s) nanoparticles in supercritical CO_2 (~140 bar), 20 bar H_2 at 313 K.

was carefully released and transferred to an on-line GC-FID equipped with a heated gas injection valve and gas transfer line (413 K) intermittently. Thus, the extent of in situ hydrogenation reaction according to time was followed.

Fig. 1 shows the schematic diagram of the reactor. The detailed procedure for chemical analysis of the fluid in autoclave by the on-line GC was as follows. While V_2 was closed, nitrogen was first allowed from G to flush though the heated transfer line (∼ 413 K) at about 60 mL min^{-1} to the sample loop of GC (H) via the flow-meter I. Then the sample loop of the GC was charged by the content of the autoclave (E) by switching the three-way valve, V_3 to the flow-meter F and opening the V_2 carefully. Thus, the fluid from the autoclave can then be forced to the on-line GC for analysis. To ensure the content of the autoclave free from contaimination the transfer line was flushed by the fluid from the autoclave several times before making an injection to the GC. After the injection was conducted, V_2 was closed again and nitrogen was allowed to flush the transfer line for next sample injection. Product identifications and conversions of the substrate to specific products at different times can therefore be worked out based on observed products (mainly pentanenitrile) and the unreacted *cis*-2-pentenenitrile detected by the on-line GC with reference to the internal standard (methane) added.

At the end of the reaction, the autoclave was allowed to cool down to room temperature and the reaction mixture in the fluid from the autoclave was then vented *via* double liquid traps containing dichloromethane cooled in propyl-alcohol/dry ice bath in order to trap volatile organic species from the carbon dioxide. Thereafter the reactor was opened and the remaining residue was extracted with another portion of dichloromethane. The resulting solutions were combined and the solid containing the metal particles was separated and collected from the solution by filtration. Here, all of the filtrate was collected in a 100 mL volumetric flask blended with 600 μL *n*-dodecane as an external standard for product identifications by the HP GC/MS.

2.3. Characterization of micelle-hosted metal/bimetallic nanoparticles

Finely ground samples were dispersed in isopropanol. A few drops of this suspension were deposited onto a lacey carbon film supported by a 300 mesh copper grid (obtained from AGAR) and air-dried at room temperature. The samples were then loaded into a chamber in the microscope, which was than evacuated. A Philips CM20 TEM and JEM JEOL 2010 high-resolution transmission electronic microscopes (HRTEM) were used for the microscopy study.

3. Results and discussion

Fig. 3 shows typical surfactant stabilised Pd:Ru (1:1) bimetallic particle of uniform size connected with each other to give a filamentary pattern. HRTEM clearly shows a homogeneous phase of each particle. The lattice fringe separation was found to be 2.18 Å by HRTEM (Fig. 3), which is different from those values of pure Pd or Ru obtained from our measurements. Phase segregation with an inner nucleus of one metal covered by a layer of second metal as previously observed using other preparation methods was not observed by this present study [16]. With taking the ZAF correction into account the observed composition of Pd and Ru in this sample by the EDX (Table 2) for six randomly chosen areas of examination matches well with the added ingredients (close to 1:1) within experimental errors. Also, these analyses clearly indicated that the sample contains a constant atomic ratio of Pd and Ru (and distribution) over the randomly selected areas. Fig. 3 also shows the particle size histogram. The result suggests that the size distribution of these bimetallic nanoparticles is unimodal giving an average particle size of 3.95 nm with a small deviation of 0.46 nm. This particle size agrees well with the size of Pd nanoparticles reported in our earlier work using the same W_o ratio [14]. In addition, our XRD (not shown) indicated that the sample gives a very broad peak (3.82 nm according to Scherrer equation with taking the instrumental broadening into account) located at 41.2° (2 theta, equivalent 2.19 Å) which clearly lies between the most intense Pd ⟨1 1 1⟩ at 40.1° and the Ru ⟨1 0 1⟩ at 44.0°. This observed XRD peak position also matches closely with the observed XRD peak of Pt:Ru (1:1) of 40.4° (2 theta) by Liu and co-workers clearly inferring the bimetallic nature of the nanoparticle [17]. However, according to the binary phase diagram in bulk phase [18], ruthenium and palladium are generally known to be non-miscible on most of the compositional range, thus the result suggests that the use of micelle as a nano-reactor might have forced the metal precursors to form true bimetallic particles at the nanoscale. This is obviously of great importance for potential applications of these materials.

Table 2
A table shows the EDX analyses of sample using 1:1 M Pd and Ru precursors

EDX analysis for Ru and Pd	Pd (at.%)	Ru (at.%)
Site of interest 1	54.5	45.6
Site of interest 2	53.3	46.7
Site of interest 3	53.7	46.3
Site of interest 4	51.4	48.6
Site of interest 5	54.6	45.4
Site of interest 6	54.9	45.6
Average	53.7	46.4
Standard deviation	1.3	1.2

Hydrogenation of *cis*-2-pentenenitrile in $scCO_2$ over the five different metal nanoparticles of different compositions was then studied. All the nanoparticles of different compositions converted *cis*-2-pentenenitrile to saturated nitrile:pentanenitrile was the sole product in $H_2/scCO_2$ mixture. Thus, the turnover frequency, TOF for each type of nanoparticle was calculated within the first 8 min where a low product conversion was ensured (<20%) and these results are plotted in Fig. 4. It is very interesting to observe that all of the metal nanoparticles of a wide range of composition synthesised in micelles in $scCO_2$ fluid were active for the hydrogenation of the unsaturated nitrile to the corresponding saturated product under mild conditions. No hydrogenation of the terminal nitrile of the molecule to the

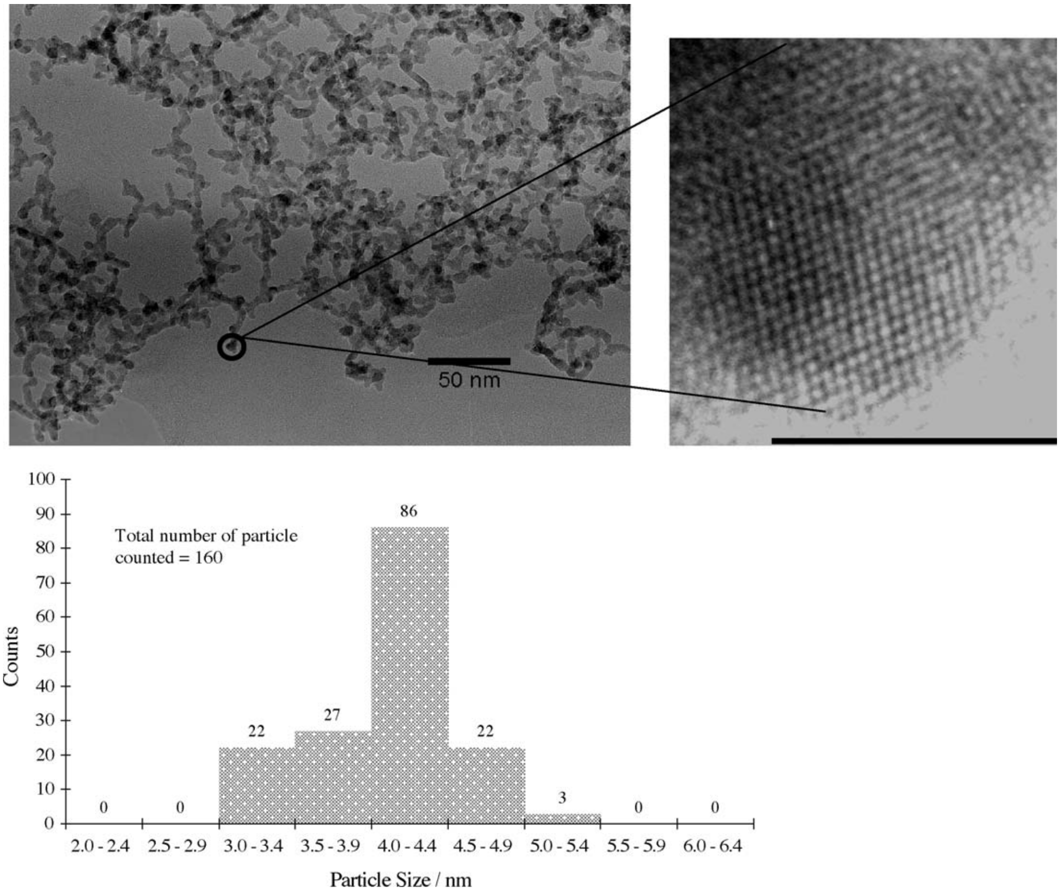

Fig. 3. TEM images (upper left) of a typical micelle-hosted Pd:Ru (1:1) particles and the high resolution TEM image (upper right) of a selected particle (scale bar 5 nm) with a lattice fringe separation of 2.18 ± 0.02 Å corresponding to (1 1 1) Pd:Ru (1:1) [17]. (Below) A narrow particle size distribution of 3.95 ± 0.46 nm is observed.

amine was found. The preferential hydrogenation of the double bond instead of the terminal cyanide group of the substrate may reflect the kinetic stability of the product under our reaction temperature (313 K) since the reduction of cyanide group over noble metal(s) catalysts normally requires a higher reaction temperature (>373 K).

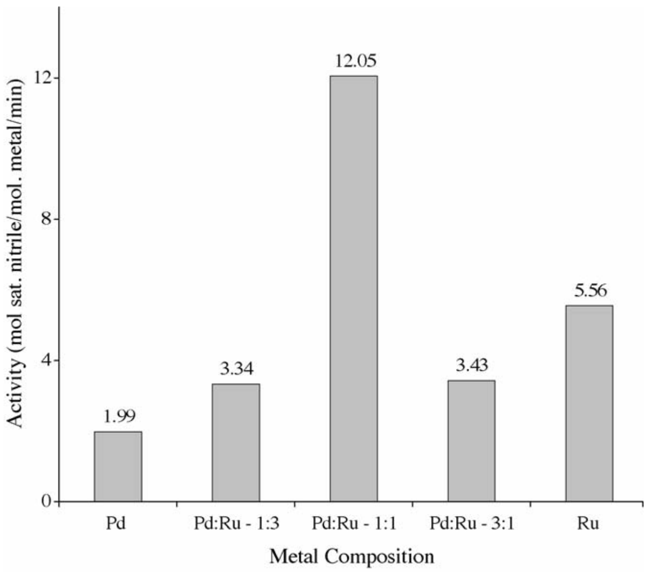

Fig. 4. Initial rate (evaluated within $t = 8$ min) of *cis*-2-pentenenitrile hydrogenation over micelle-hosted nanoparticles of different metal compositions at 313 K.

It is interesting to note from Fig. 4 that there is a ‘volcano’ relationship between activity and metal composition. The 1:1 mixture of the Pd–Ru bi-metallic nano-catalyst displayed the highest initial TOF value compared with other compositions. It has been reported in the literature [3] that Pd metal is the best metal to provide active site for hydrogen activation with a good degree of hydrogen spillover to environment. It is also well known that Ru metal facilitates adsorption of nitrile species onto its surface [12]. Thus, for the hydrogenation of this particular substrate with both nitrile and alkene groups, one would expect that a proper balance must be struck in hydrogen activation/spillover and substrate adsorption on the catalyst surface in order to obtain a maximum rate of hydrogenation in liquid phase (Langmuir–Hinshelwood mechanism). Our result seems to agree with this preposition. To ascertain whether the adsorption of nitrile group plays an important role in hydrogenation activity, the same quantity of 1-hexene (no nitrile group) and 3-pentenenitrile (no conjugation between the double bond and nitrile group) over the Pd:Ru (1:1) nanoparticle under identical conditions were hydrogenated, respectively. The measured TOFs of 3-pentenenitrile ($15.77\ \text{min}^{-1}$), 2-pentenenitrile ($12.05\ \text{min}^{-1}$) and 1-hexene ($5.09\ \text{min}^{-1}$) were obtained. The presence of nitrile group

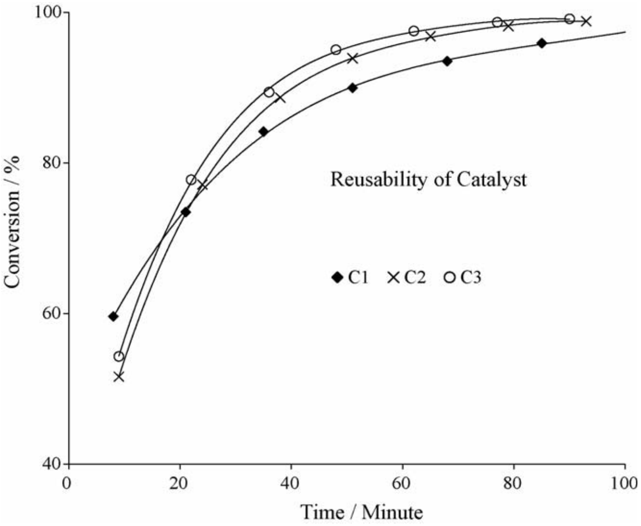

Fig. 5. A plot of activity for Pd:Ru (1:1) catalyst at 348 K against time. C1, C2 and C3 represent the first, second and the third catalytic cycles.

indeed significantly enhances the hydrogenation rate. Thus, this finding agrees with reports in the literature [3,19], which demonstrated that bimetallic catalysts are regarded as better hydrogenation catalysts for many hydrogenation reactions. Of prime importance of this work is that one can now rationally design a bimetallic nanocatalyst of optimum composition using simple metal salts without interferences from metal segregation and support interaction(s) for effective hydrogenation by using this microemulsion method in supercritical carbon dioxide where mass transfer limitations are generally insignificant. For practical use tailored bimetallic nanoparticle for a particular reaction from water-in-scCO$_2$ microemulsion could therefore be deposited on solid supports as catalysts as demonstrated in the case of nanoparticles stabilised in water-in-oil [20]. However, the deposited nanoparticles do not have the dynamic reaction environment inherent in microemulsion system in the environmentally friendly sovlent.

As a result, we have preliminary investigated the direct reusability of the micelle-hosted bimetallic nanoparticle in supercritical carbon dioxide. In this set of experiments, the first cycle was initiated by starting with a clean reactor, catalyst and ingredients. After testing as previously described, the catalyst was collected by first cooling the reactor to room temperature, depressurisation of the carbon dioxide/hydrogen (it was earlier shown by UV–vis experiment that dried liquid carbon dioxide does not dissolve our surfactant molecules), then heated up to 323 K in a stream of nitrogen at 60 mL min^{-1} at 1 atm for 2 h in order to recover the volatile pentanenitrile product (>95% collected). Then, the content of the reactor was dried in an oven kept at 373 K for half hour. Cycle 2 was conducted simply by recharging 2 mL of *cis*-2-pentenenitrile and 156.5 μL of water and repeated the testing. The third cycle was conducted in the same manner as the second cycle.

The time–activity curves of the micelle host Pd:Ru (1:1) nanoparticle are shown in Fig. 5. The first cycle shows only a slightly lower initial rate compared with subsequent two runs. (A complete reduction of metal precursor salt was probably not yet achieved in the first run.) But after the first run it is noted that this bimetallic nanocatalyst displays no noticeable catalyst deactivation for the subsequent two runs. This would indicate that the post-treatments of the nano-metal catalyst over the three cycles (depressurization, drying, re-hydration, cooling and reheating, etc.) did not seem to cause any irreversible changes to the nano-catalyst. It should be borne in mind that particle agglomerization (leading to deactivation of nanocatalyst) in solution depends on temperature, pH, nature of the stabiliser and nanoparticle (i.e. their surface electrostatic charge) and particularly on the solvent system used (these effects have been extensively studied in conventional aqueous or organic solvents but not in supercritical carbon dioxide). The precise roles of the fluorinated surfactant molecule in stabilising nano-metallic particle in supercritical carbon dioxide are not yet known. In this work, it was clearly shown that under the same scCO$_2$–H$_2$O mixture this new fluorinated surfactant stabilized nanocatalyst was able to undergo self-assembly and likely to revert to a similar structure over the repeated testings. However, from a practical standpoint, a larger number of catalytic cycles at a high substrate to catalyst ratio should be tested in order to evaluate the economic viability of the microemulsion nanocatalyst in superciritcal carbon dioxide since noble metal nanoparticles such as Pd and Pt are expensive. Nevertheless, the present work clearly demonstrates that the fluorinated micelle-hosted metal nanoparticle in supercritical carbon dioxide shows a degree of direct reusability without involving any complex separation methodology as previously adopted in the literature [21].

4. Conclusion

It is demonstrated that fluorinated micelle-hosted PdRu bimetallic nanoparticle is highly active for *cis*-2-pentenenitrile hydrogenation in supercirtical carbon dioxide fluid under mild conditions. We also show that it is possible to optimise its catalytic activity for the hydrogenation reaction by tuning the metal composition of the nanoparticle without interference from support and phase segregation through its in situ synthesis inside the micelle. Thus, the elementary surface-catalysis steps involving molecule adsorption and hydrogen activation/transfer for optimum hydrogenation activity can be manipulated. It is also interesting to observe that the fluorinated micelle-hosted bimetallic catalyst works effectively in the supercritical fluid without any observable deactivation for at least three catalytic cycles.

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