

# Triphasic liquid systems: generation and segregation of catalytically active Pd nanoparticles in an ammonium-based catalyst-philic phase

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A triphasic liquid system fabricated from isooctane, aqueous base, and trioctylmethylammonium chloride/decanol promoted the formation of Pd-nanoparticles in the size range of 2–4 nm which remained immobilised in the onium phase, catalysed organic reactions, and could be recycled.

Onium salts, that are phase transfer agents, can be used to produce and stabilize metal nanoparticles (NPs) *in situ*,<sup>1,2</sup> and to control their size,<sup>3</sup> starting from appropriate precursors. Reetz and co-workers<sup>2</sup> have amply demonstrated that nanostructured  $R_4N^+X^-$ -stabilized metal clusters can be prepared by a variety of methods. Recently, peculiar liquid systems formed by three separate liquid phases have attracted our attention, in particular with a view towards the possible effects on catalysis.<sup>4</sup> The interest was stimulated by knowledge of the formation of triphasic liquid systems made by mixtures of an organic solvent such as isooctane, water, and an onium salt (ammonium or phosphonium), and their use in heterogeneously catalysed organic reactions.<sup>5</sup> Increases in rates and selectivities could be achieved for a number of reactions catalysed, for example, by supported metals such as Pd, Pt, and by Raney-Ni. The onium salt was preferably liquid at the reaction temperature (20–50 °C), had a strong affinity for the catalyst, and formed a separate phase. The interaction between the liquid onium salt, and the catalyst was shown to be the factor controlling the improved catalytic effect.<sup>6</sup> In addition, the strong affinity of the onium salt for the catalyst made it a catalyst-philic phase, that simplified the separation of products from catalysts and from by-products once the reaction was complete.<sup>4</sup>

We reasoned that it would be interesting to take advantage of triphasic liquid systems, to generate, immobilise, and stabilise catalytically active metal NPs, starting from precursor metal complexes. The outcome was envisaged as shown in Fig. 1.

This system offers a number of potential advantages in view of process intensification: (i) the active catalytic NPs can be prepared directly in the reactor, (ii) it is easy to separate the organic products from the catalyst by decanting, (iii) the catalyst morphology can be tuned, (iv) the metal NPs are stabilized by the third phase, and (v) inorganic reagents (*i.e.* base) and by-products remain in the aqueous phase, not to mention that the amount of catalyst-philic phase can be as small as convenient. All these issues are the basis for cleaner, cheaper catalytic systems,<sup>7</sup> and characterize some of the principles of green chemistry.

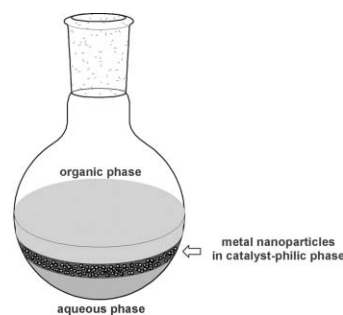


Fig. 1 Envisaged triphasic system.

This communication describes how a ternary system of this kind can be constructed, and used for catalytic reactions, through five subsequent steps: the preparation of a suitable ternary liquid system, formation of the active catalytic species, screening on a model organic reaction, catalyst recovery and recycle tests, and finally the characterisation of the active catalytic species by TEM.

At first, the conditions for the reproducible formation of a model triphasic system were determined starting from previous experience.<sup>5</sup> The aim was to generate a stable and reproducible ternary system. Aliquat 336<sup>®</sup> (tricaprylmethylammonium chloride, A336)—a well known industrially produced phase transfer agent used in previous studies—was chosen as the third liquid catalyst-philic phase. Commercial A336, however is a technical grade compound: the alkyl chains of are a mixture of C<sub>8</sub> and C<sub>10</sub>, and it contains varying amounts of water (up to 5%), and of long chain alcohols (1-decanol and 1-octanol, 5–10%), as well. It was soon apparent that different A336 batches showed a large degree of variability in their composition, and on their ability to form a third phase in the presence of isooctane, and of aqueous base (KOH). To eliminate this variable, trioctylmethylammonium chloride (TOMAC) was synthesised from trioctylamine and dimethylsulfate by adapting a reported procedure.<sup>8</sup> The appearance of TOMAC was that of a light amber coloured viscous liquid at room temperature, effectively an ionic liquid. It was immiscible in isooctane and in water, of intermediate density with respect to these two solvents, with which it therefore formed a triphasic system, placing itself between the other two.

With the aim to generate and immobilize Pd-black in the third TOMAC phase, a suitable palladium precursor was sought, by testing PdCl<sub>2</sub>, Pd(OAc)<sub>2</sub>, Pd(PPh<sub>3</sub>)<sub>4</sub>, and PdCl<sub>2</sub>(BzCN)<sub>2</sub>. Preliminary screening tests carried out with commercial A336 had indicated that Pd(PPh<sub>3</sub>)<sub>4</sub> was the best precursor: it formed Pd-black which resided in the A336 phase. The other complexes also formed Pd metal, in these cases however the particles were dispersed in more than one phase.

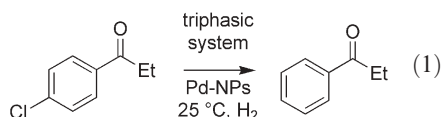
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The same tests were therefore carried out with the triphasic system made using TOMAC prepared in-house.† Unlike the screening tests done with commercial A336, these yielded Pd-black very slowly. Only by adding 0.1 ml of 1-decanol to the standard triphasic mixture—thereby reproducing a standard commercial A336 composition—was a rapid formation of Pd-black in the intermediate TOMAC/decanol phase observed. The effect of decanol is presently beyond the scope of this work, but it may indicate the formation of a water-in-oil microemulsion promoted by the addition of the alcohol that may act as co-surfactant,<sup>9</sup> and intervenes in the precipitation of metallic palladium.<sup>10</sup>

While a relatively large amount (1.0 mL) of TOMAC was used throughout this study in order to visually monitor the phase separation, the amount of catalyst-philic phase can be smaller.

The system was tested for catalysis by using as the model reaction the hydrodehalogenation (HDX) of 4-chloro-propiofenone (0.50 mmol) with hydrogen at atmospheric pressure to yield propiofenone (eqn (1)).<sup>5b</sup>



At room temperature, the hydrodehalogenation reaction was sluggish for the first 80 min, this induction period lasted until Pd-black started to precipitate. After that, quantitative and selective removal of chlorine was observed in two hours (Fig. 2). No competitive carbonyl reduction was observed, consistent with the results obtained in the presence of Pd supported on charcoal as catalyst, reported in earlier papers.<sup>5</sup>

When stirring was interrupted, the triphasic system settled and the Pd-black catalyst remained segregated in the middle TOMAC/decanol phase (Fig. 3a).

The reaction product (PhCOEt) was removed along with the isooctane top layer, and the remaining phases (TOMAC/decanol and aqueous base) were recycled by adding additional reagent and organic solvent. The recycle procedure was repeated four times (Fig. 4). No induction period was observed in run 2, and the reaction was complete after 80 min, still maintaining complete (>99%) selectivity for HDX.

Run 2 was faster than run 1, likely due to a higher concentration of Pd-black that had finished forming during run 1. This was substantiated by the fact that after run 2, the triphasic system showed a clearer phase separation than after run 1, and both the

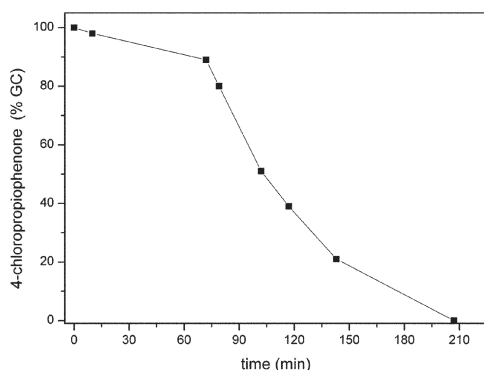


Fig. 2 Plot of the hydrodehalogenation reaction of eqn (1).



Fig. 3 Appearance of the triphasic system: (a) after run 1, (b) after run 2.

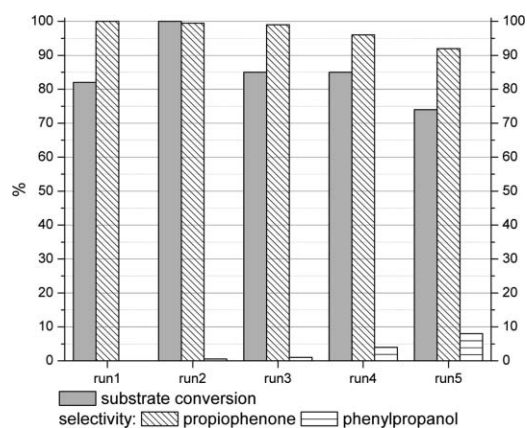


Fig. 4 Recycling tests (conversion and selectivity after 2 h).

upper organic and lower aqueous layers appeared perfectly clear, with the catalyst segregated in between (Fig. 3b).

The TOMAC–Pd catalytic ensemble could be used repeatedly without significant loss of activity, and without the induction period of the first run. After 2 h, conversion of the reagent reached 85, 85, and 74%, in runs 3, 4, and 5 respectively (Fig. 4). However, the Pd particles tended to aggregate, to become visibly larger and less dispersed than in the beginning, and to slowly precipitate at the TOMAC/water interface. This phenomenon was accompanied by a slight decrease in selectivity in runs 3–5 where up to 8% of phenylpropanol—deriving from concurrent carbonyl reduction—was observed. The diminished selectivity was accounted for by the structure sensitivity of the substrate towards the metal particles. In fact, palladium particles with sizes in the 2–4 nm range are composed predominantly of corner atoms, while larger particles have a higher proportion of their surface composed of face atoms.<sup>11</sup> For the former, used in the first runs, the hydrodechlorination occurred selectively, since the substrate approached only single-atom active sites. For the larger particles, approach to the

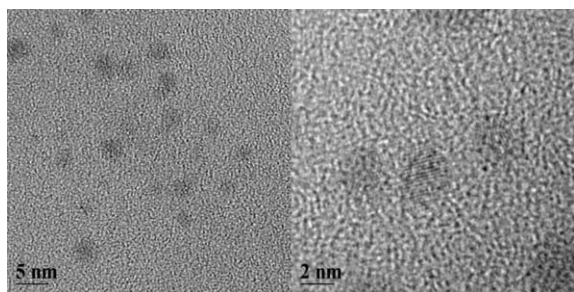
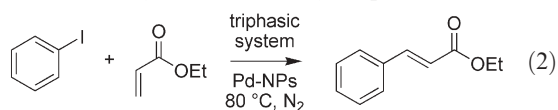


Fig. 5 HREM of the specimen after the first run.

face atoms on the flat surface promoted concurrent reduction of both functional groups.<sup>5b,12</sup>

In view of efficiently segregating the Pd in the catalyst-philic phase, it was important to determine whether any metal leaching to the organic phase was occurring. Leaching was monitored after run 2 and run 4, by filtering the organic phase, adding 4-chloroacetophenone as reagent, and stirring the organic phase under hydrogen.<sup>13</sup> No traces of acetophenone, the hydrodehalogenation product, were observed in either case. This indicated that none of the hydrodehalogenation-catalysing Pd nanoparticles leached to isooctane. Any leaching of Pd in the inorganic phase was not monitored since it did not affect the outcome of the reactions, the aqueous phase was in fact always retained in the recycling experiments.

The scope of the same triphasic catalytic system was then extended by testing its activity for the Pd-catalysed Heck coupling reaction of phenyl iodide with ethyl acrylate in the presence of NaHCO<sub>3</sub> as the base (eqn (2)).<sup>14</sup> At 80 °C after 1 h, 95% conversion to the coupling product ethyl cinnamate was observed. In this case the system showed a clear separation of the phases at the end, and no leaching of Pd into the organic phase was detected.



The size of the Pd particles was then determined by TEM measurements. Fig. 5 shows two HREM images of the catalyst-philic phase from the HDX reaction (after run 1), taken at different magnification (400 k and 1 M). Rounded crystalline Pd particles, with no defects, are present with size ranging from 2 to 4 nm. The particles are well dispersed, isolated, and with no formation of agglomerates. Some of the particles show lattice fringes corresponding to Pd–Pd distances; in some case the lattice fringes are not visible due to the covering by TOMAC.

This communication shows that it is possible to use multiphase solvent systems to generate highly dispersed Pd nanoparticles that are active, and selective, for catalysis. Since separation of catalytic particles from a reaction mixture is a practical problem, the system was designed to segregate these particles in a catalyst-philic phase—thus allowing reuse of the catalyst. It represents an approach towards the development of catalytic systems that are in a different phase from the reaction species, thereby simplifying purification of the product, catalyst re-use, and reducing the amount of energy used and of waste produced. Caution should of course be used in this respect since the number of variables affecting the formation of the third catalyst-philic phase (e.g. the

polarity and molar fraction of all the components) imply that these systems must be constructed and fine-tuned for each particular case.

Issues still open include whether the nanoparticles, or rather a soluble form of palladium in equilibrium with them, are the active catalytic species.<sup>2</sup> We feel this may not be a problem since we have demonstrated that Pd is not present in catalytically significant amounts in the organic phase. Another issue is the tendency of the Pd particles to aggregate. Although the catalytic efficiency is only slightly reduced with each recycling sequence, it is probable that this aggregation is responsible for the progressive deactivation. This aggregation is likely due to the observed progressive loss of decanol—i.e. of its nanoparticle stabilising effect—that slowly leaches to the organic phase.<sup>5g,15</sup>

## Notes and references

† **Experimental note.** The standard triphasic catalytic system was made by loading 1.0 ml of TOMAC, 9.0 ml isooctane, 0.10 ml 1-decanol and 2.0 ml KOH(aq) (20%) (for the Heck reaction the latter was substituted by 5.0 ml of 6% NaHCO<sub>3</sub>(aq)) in a three necked flask. To this were added 0.025 mmol of Pd(PPh<sub>3</sub>)<sub>4</sub>, and the reaction stirred under air for 1 h until the middle phase turned completely black. The substrate was added (1.0 mmol 4-chloropropiophenone for HDX, or 1.0 mmol PhI and 1.5 mmol ethyl acrylate for the Heck reaction) and the reaction products monitored by GC-MS.

TEM measurements were performed using a JEM 3010 (JEOL) electron microscope operating at 300 kV; the lens parameters were Cs = 0.6 mm, Cc = 1.3 mm, giving a point resolution of 0.17 nm at Scherzer defocus. A few milligrams of the specimen were sonicated for 5 min in order to disrupt possible agglomerates. A 5 μL droplet of suspension was transferred onto an amorphous carbon film, coating a 200 mesh copper grid, dried at room temperature, and then put into the microscope.

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