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Encapsulation of palladium in polyurea microcapsules

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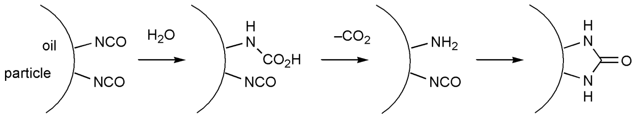
An interfacial polymerisation approach is adopted to encapsulate palladium(II) acetate and palladium nanoparticles in polyurea microcapsules for use in catalysis.

Catalytic transition metal species are essential tools for the assembly of bioactive molecules. The need for practical and economic translation of these laboratory methods to large-scale operations coupled with the trend for clean manufacturing processes has led to the development of new strategies for reagent immobilisation which may allow for the recovery and reuse of catalysts.[1] In typical supported transition-metal catalysts,[2] the metal is coordinated to a ligand which is covalently bound to a polymer backbone, or it is adsorbed on an inert surface such as silica or carbon. In this approach, synthesis of the polymer-bound ligand can be lengthy and expensive and there can be problems associated with leaching and the reactivity of the catalyst.

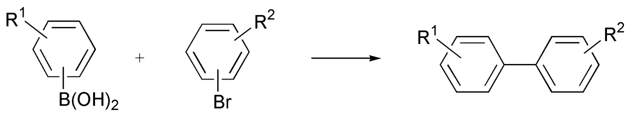
Microencapsulation, a process of entrapping materials in a polymeric coating, may offer a solution to these problematic limitations.[3] This approach has found application in drug delivery systems,[4] radiation therapies,[5] cell entrapment[6] and controlled release of pesticides.[7] Microcapsules can be prepared by an *in situ* interfacial polymerisation approach[8] which involves dispersing an organic phase containing polyfunctional monomers and/or oligomers (along with the material to be encapsulated) into an aqueous phase containing a mixture of emulsifiers and protective colloid stabilisers. This resulting oil-in-water emulsion undergoes *in situ* interfacial polymerisation, with the monomers/oligomers reacting spontaneously at the phase interface to form microcapsule walls. The permeability and size of these microcapsules and the coordinating properties of the polymer matrix may be tuned by varying the nature of monomers/oligomers, other reagents and conditions used in the encapsulation procedure. Efficient entrapment of transition-metal based catalysts requires the design of systems possessing ligating functionality in order to retain the metal species. These systems should be physically robust and chemically inert to reaction conditions whilst also being cost effective. Polyurea microcapsules[9] were found to be suitable by virtue of their chemical structure — a backbone of urea functionality — that could ligate and thus retain metal species such as $Pd(OAc)_2$.

The microencapsulation process is very straightforward. Using a laboratory overhead stirrer fitted with a 50 mm rotary blade, a solution containing polymethylene polyphenylene di-isocyanate (SUPRASEC 5025, average functionality of 2.7)[10] and $Pd(OAc)_2$ in dichloroethane was dispersed at 800 rpm for 1 min into an aqueous solution of sodium lignosulfonate (Reax 100M),[10] polyvinyl alcohol (Goshenol GL03)[10] and the poly-oxypropylene polyoxyethylene ether of butyl alcohol (Tergitol XD).[10] This resulted in an oil-in-water microemulsion with a particle size range of 20–250 microns which was gently shaken for 16 h. The wall-forming reaction (Scheme 1) is initiated when some of the peripheral isocyanate groups are hydrolysed at the oil–water interface to form amines which in turn react with other unhydrolysed isocyanates to form a urea-linked polymeric coating resulting in insoluble and permeable polyurea microcapsules with a particle size ranging between 20–250 microns (average size 150 microns).† The microcapsules were filtered and washed several times with deionised water and a range of organic solvents and dried. According to X-ray fluorescence (XRF) and Inductively Coupled Plasma (ICP) analysis the average palladium content in these polyurea microcapsules (MC-[Pd]) was found to be 0.4 mmol g^{-1}. These microcapsules were tested for catalytic activity in Suzuki-type reactions involving the cross-coupling of aryl boronic acids with aryl bromides.[11] Reactions were carried out in a toluene–ethanol–water solvent system (4 : 2 : 1) on a 1 mmol scale using 5 mol% of the catalyst (with respect to palladium content). At 80 °C, the reactions proceeded smoothly to give the required biaryl products in good yields (Scheme 2 and Table 1).

The microcapsules were recovered by a simple filtration and reused four times without significant loss in activity, and subsequent ICP analysis of the crude product (obtained by filtration, concentration and drying) detected palladium levels (wt/wt) at 13 ppm corresponding to 0.2% leaching of the original Pd content of the capsules. This suggests that the extent of leaching of the palladium species is extremely low. It is not clear if the polyurea microcapsules are functioning as a reservoir of homogeneous catalytic metal species whilst efficiently scavenging the metal species after each catalytic cycle.[12] To ascertain the morphology and metal distribution within the polymer matrix, extensive electron microscopy studies were carried out. Scanning electron microscopy (SEM) showed the interior of the spheroid microcapsules to be made up of uniform porous microstructure [Fig. 1(a)]. These studies



Scheme 1 Schematic representation of the polyurea wall-forming reaction occurring at the oil–water interface.



Scheme 2 *Reagents and conditions*: MC-[Pd], 5 mol%, toluene–H_2O–EtOH (4 : 2 : 1), K_2CO_3, 80 °C, 6–12 h.

Table 1 Cross-coupling reactions‡

Entry	R¹	R²	Yield (%)[a]
1	*p*-OMe	*p*-OMe	87
2	*p*-OMe	*p*-F	89
3	*p*-OMe	*p*-NO_2	91
4	*o*-OMe	*o*-OMe	71
5	*p*-Ac	*p*-OMe	84
6	*p*-Ac	*p*-F	90
7	*p*-Ac	*p*-NO2	97
8	H	*p*-OMe	94
9	H	*p*-F	93
10	H	*p*-NO_2	97

[a] Based on isolated yields.

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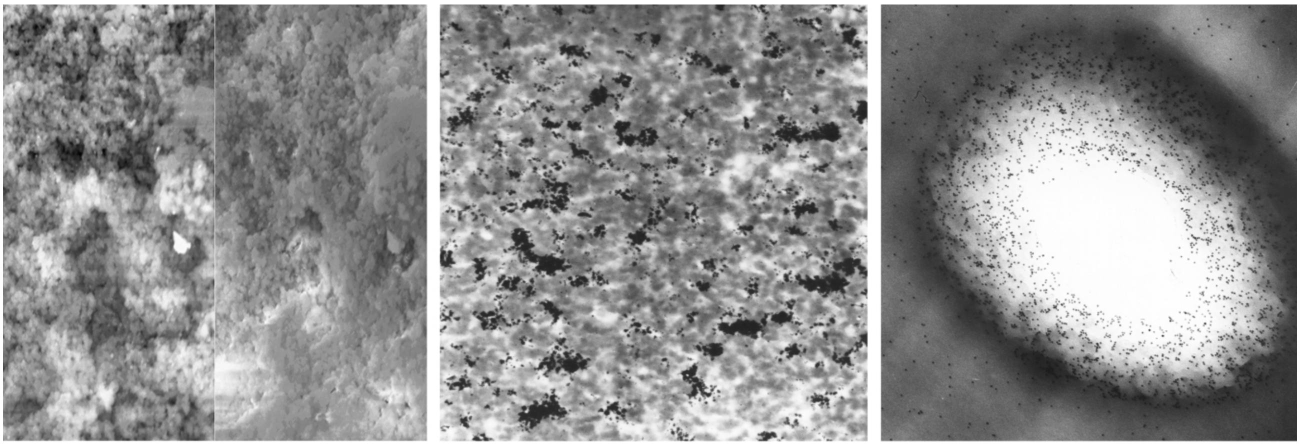

(a) (b) (c)

Fig. 1 (a) Scanning electron micrograph (SEM) showing the interior of a Pd(OAc)$_2$ containing polyurea microcapsule (magnification × 2500); (b) TEM of a sliced Pd(OAc)$_2$ microcapsule after chemical reaction (magnification × 14000); (c) TEM of a sliced microcapsule showing the distribution of palladium nanoparticles (dark spots) along a channel formed within the polyurea matrix (magnification × 46000).

carried out on polyurea microcapsules (before use in chemical reaction) revealed that the metal was not bound on the surface and contained within the polymeric matrix and core. The Energy Dispersive X-Ray (EDX) pattern along the cross section of a sliced microcapsule showed an even distribution of palladium. Similarly, the transmission electron micrograph (TEM) of a sliced microcapsule recovered after a chemical reaction shows an even distribution of palladium [Fig. 1(b)].

In an attempt to extend the scope of this encapsulation approach, palladium nanoparticles stabilised by tetraoctylammonium bromide were prepared[13] and microencapsulated in polyurea. These nanoparticulate palladium(0) microcapsules proved just as effective in similar Suzuki-type cross-coupling reactions as encapsulated Pd(OAc)$_2$. The presence of the palladium nanoparticles (average size of 5 nm) [Fig. 1(c)] was detected by TEM; this showed a higher metal concentration along the channels formed within the polyurea matrix. This suggested that the palladium nanoparticles were being stabilised and contained by the urea-linked polymer as the washing procedure adopted should remove all traces of the tetraoctylammonium bromide stabiliser.

In summary, palladium species in the form of palladium(II) acetate and nanoparticulate palladium have been effectively entrapped in a polyurea matrix. These microcapsules have proven to be effective as recyclable catalysts for use in Suzuki type cross-coupling reactions and do not require expensive phosphines as co-ligands. The flexibility of this system should allow the co-encapsulation of specific reaction-enhancing materials and monomers leading to the generation of bespoke polymer matrices. The following paper highlights the applications of these versatile microcap catalysts in chemical synthesis.

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Notes and references

† Representative procedure for the preparation of polyurea microcapsules containing Pd(OAc)$_2$: a mixture of Pd(OAc)$_2$ (5 g) and polymethylene polyphenylene isocyanate (PMPPI, average functionality 2.7, 50 g) in dichloroethane (70 cm^3) was stirred for 1 h at rt. The resulting dark solution was added at a steady rate to an aqueous mixture containing Reax 100 M (10 g), Tergitol XD (2.5 g) and Goshenol GL03 (5 g) in de-ionised water (250 cm^3) while shearing (using a Heidolph radial flow impeller, 50 mm) at 800 rpm for 2 min. The resulting oil-in-water emulsion was paddle-stirred at rt for 16 h. The polyurea microcapsules obtained were filtered though a polyethylene frit (20-micron porosity) and were washed with de-ionised water, acetone, ethanol, ether and dried.

‡ Representative procedure for Suzuki type cross-coupling reactions using microencapsulated (MC) Pd(OAc)$_2$ (MC-[Pd]): To a solution of 4-bromoanisole (1 mmol), 4-methoxybenzene boronic acid (1.5 mmol), K$_2$CO$_3$ (3 mmol) in toluene–water–ethanol (4 : 2 : 1, 7 cm^3) was added MC Pd(OAc)$_2$ (5 mol%, based on palladium content) and the reaction mixture stirred at 80 °C for 12 h. The reaction mixture was diluted with ether (25 cm^3) and filtered though a polyethylene frit (20-micron porosity). The filtrate was extracted with ether (2 × 20 cm^3) and the combined organic layers were washed with brine (20 cm^3) and dried (MgSO$_4$). Evaporation under reduced pressure and purification by column chromatography gave 4,4'-dimethoxybiphenyl (87% yield). ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 7.47$ (d, $J = 8.7$ Hz, 4H), 6.96 (d, $J = 8$ Hz, 4H), 3.84 (s, 6H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 159.1, 157.8, 128.1, 114.5, 55.7$; MS(EI): m/z(%): 214(100) [M$^+$]; HRMS(EI): calcd for C$_{14}$H$_{14}$O$_2$ [M$^+$] 214.099, found: 214.099.

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