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Scalable synthesis of catalysts for the Mizoroki–Heck cross coupling reaction: palladium nanoparticles assembled in a polymeric nanosphere†

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Palladium nano-spheres 160 nm in diameter, as an assembly of uniform 5 nm nanoparticles, are accessible using a facile one step method under continuous flow on a spinning disc with hydrogen gas as the reducing agent. The stable colloidal system is an effective catalyst for the Mizoroki–Heck reaction, as established for the reaction between several aryl halides and *n*-butyl acrylate, and can be readily recycled without a change in their catalytic activity.

Introduction

Heterogeneous catalytic systems have an advantageous practical convenience over homogeneous systems because of their ease of separation which is usually through simple filtration.¹⁻³ The recovery and reusability of catalysts is a very important factor especially in the case of noble metal (Pd) catalysed C-C coupling reactions like the Mizoroki-Heck and Suzuki cross coupling reactions, and heterogeneous systems also dispense with the need for the design and synthesis of often expensive ligands that feature in homogeneous systems.4-12 The interest and study of supported palladium catalysts for applications in C-C cross coupling reactions had its origins in 1990's, where initially palladium was often embedded on or in to supporting materials such as zeolite and inorganic oxides, including graphite oxide, MgO, Al₂O₃ and SiO₂.^{13–18} With nano-materials exhibiting unique physical and chemical properties relative to their larger counterparts, the synthesis and application of these supported palladium catalysts is attracting ever increasing interest.^{19–22} Bradley et al.¹⁹ have recently developed amino modified resins as supported materials for in situ reduction of Pd(OAc)₂ to 7 nm Pd nano-particles, which are stable and can be reused

in a variety of Suzuki reactions. More recently, Wan *et al.* reported 3 nm palladium nanoparticles supported on ordered mesoporous silica–carbon nano-composites exhibiting high catalytic activity for coupling reactions.²² However, the problem of catalytic recovery is not completely resolved using the aforementioned supported-heterogeneous systems. An inherent challenge in using supported palladium nanoparticles is their disassociation from the substrate support, resulting in catalyst leaching from the substrate over time. This leaching is often associated with a drop in catalytic activity and reusability.

The use of palladium nanoparticles as heterogeneous catalysts in C-C coupling reactions is an area of current interest due to the possibility of fine tuning the shape and size of the colloidal system to control the catalytic efficacy. The first well-known case for the use of colloidal Pd catalysts was independently reported by Beller et al. and Reetz et al. in 1996. In the former case palladium nano-particles were stabilized by tetra-octyl ammonium chloride,²³ whereas in the latter they were stabilized in propylene carbonate.²⁴ More recently palladium clusters stabilized in polymer micelles, dendrimers and ionic liquids have been widely studied as recyclable catalysts.²⁵⁻²⁷ The synthesis of colloidal palladium systems usually avoids the multi-step method for generating supported systems with their associated leaching problem, but they are thermodynamically unstable leading to aggregations, especially at high temperatures. Such aggregations can result in the loss of active surface area for effective catalysis, thereby diminishing their potential for recycling.

Poly(vinylpyrrolidone) (PVP) has been shown to be an effective matrix in stabilising palladium nanoparticles as catalyst for cross coupling reactions.^{28–31} Here we report the synthesis of novel palladium composite nano-spheres using spinning disc processing (SDP) as a facile one step process with hydrogen gas as the reducing agent for scalable size controlled synthesis of heterogeneous catalysts. The nano-spheres herein are held together by a PVP scaffold. We

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[†] Electronic supplementary information (ESI) available: Schematic of spinning disc processor, TEM image of as-prepared palladium nanoparticles using hydrazine as the reducing reagent, TEM image of a typical palladium nanomaterials synthesized using PVP with a molecular weight of 360000, TEM images of palladium–PVP spheres synthesized *via* mechanical stirring, EDS data of palladium nanospheres, ¹H NMR data and GC-MS data of the product of Mizoroki–Heck reactions in Table 1–5. See DOI: 10.1039/c0nj00898b

anticipated that the PVP scaffold is likely to prevent catalytic leaching with time, with the prospect of maintaining high colloidal stability, structural integrity and reusability.

Results and discussion

Synthesis and characterization of palladium composite nano-spheres

SDP is a microfluidic process intensification strategy with a continuous flowing film (1 to 200 µm) on a rapidly rotating disc surface (usually up to 3000 rpm) (Fig. S1, ESI⁺). It facilitates controlled nucleation and growth of nanoparticles for the fabrication of different nano-materials,^{32,33} and has potential for the large scale synthesis of a range of nanomaterials/nanoparticles. Such a microfluidic platform offers an alternative approach in alleviating the obstacles and limitations of the relaxed fluid dynamic regimes associated with conventional batch processing. In essence SDP offers improved micromixing environments on a rapidly rotating surface which ensures that there is a very high surface area to volume ratio for the reacting fluid, resulting in supersaturation of the gas phase reagents and nanocrystal nucleation and growth at room temperature. The mixing for SDP is achieved by feeding the reagents close to the centre of a rapidly rotating disc. The behavior of a thin film on a rapidly rotating disc can be associated with two zones: (i) The injection zone where the reagents hit the surface close to the centre of the spinning disc forming a spin-up pool with the flow of liquid from the pool controlled by viscous drag associated with centrifugal forces where rapid nucleation and instantaneous growth initiation occur. (ii) The acceleration and synchronized flow zone where the fluid film initially experiences an increase in the radial flow velocity with the liquid then rotating close to the disc velocity with the flow becoming similar to the Nusselt model.³⁴ The shear forces and viscous drag between the moving fluid layer and the disc surface create turbulence and ripples which gives rise to highly efficient mixing within the thin fluid layer. The turbulent waves thereby provide a high degree of growth control in zone (ii).

In a typical experiment aqueous solutions of H₂PdCl₄ were mixed with PVP at various molecular ratios of PVP relative to palladium, and then fed through a jet feed onto the spinning disc. Simultaneously the hydrogen gas reducing agent was fed through another jet feed slightly above ambient pressure, which resulted in the formation of palladium nano-spheres of uniform size and shape (Fig. 1). The nano-spheres result from the spontaneous assembly of a large number of 5 nm palladium particles within the dynamic thin films on the surface of the disc in the presence of PVP, rather than discrete individual palladium nanoparticles. The role of the PVP is multifunctional, in acting as a scaffold preventing leaching of palladium during catalysis from the confines of the nanospheres into the solution and in acting as a stabiliser maintaining high colloidal stability thereby preventing loss of activity due to agglomeration. TEM images (Fig. 1a-c) reveal an assembly of palladium nano-particles with a mean diameter of 5 nm. The XRD pattern (Fig. 1d) shows that the palladium nanoparticles are highly crystalline.



Fig. 1 (a) TEM image, (b) cross-section TEM image, (c) high resolution TEM image, (d) X-ray diffraction pattern of the typical palladium nano-spheres used in Mizoroki–Heck cross coupling reactions.

The use of hydrogen gas as the reducing agent is noteworthy for the following reasons: (1) high purity palladium catalysts are accessible void of reaction by-products associated with traditional reducing agents and (2) it presumably influences the growth of this unique nanostructure of palladium nanospheres in the present case, noting that other reducing agents such as hydrazine result in individual nanoparticles (Fig. S2, ESI†) rather than nano-spheres. It is noteworthy that the wavy thin film generated on the spinning disc surface has been demonstrated to enhance the hydrogen gas uptake,³⁵ which in turn is important for effective and rapid reduction of H₂PdCl₄.

The molar ratio of PVP to palladium was varied in order to optimise the synthesis of the palladium nano-spheres. SEM images show that a molar ratio (PVP : H₂PdCl₄) of 20:1 gave a more uniform shape than for a ratio of 10:1, for a fixed disc speed of 2000 rpm. For a molar ratio of 30:1, the mono-dispersity of the nano-spheres decreased compared to the ratio of 20, due to coalescence in the presence of excess of polymer (Fig. 2a–c). Varying the disc spinning speed also affected the size and distribution of the nano-spheres when investigating the fixed molar ratio of 10 resulted in a more uniform and separated nano-spheres than for disc speeds of 2000 rpm. This phenomenon is attributed to shorter residence times on the disc with increasing speed, resulting in a decrease in the time for the reacting mixture to equilibrate.

The effect of varying the average molecular weight of the PVP polymer was also investigated. Using a lower average molecular weight of PVP (10000) resulted in smaller nanospheres, as expected with a shorter scaffolding structure, with the average size of 120 nm (Fig. 3), in contrast to 160 nm (Fig. 2d) for an average molecular weight of 40000 for the PVP. Increasing the speed resulted in a decrease in size



Fig. 2 SEM images of palladium nano-sphere hybrids: (a)–(c) molar ratio of PVP to palladium 10, 20 and 30, respectively (disc speed 2000 rpm; 40 000 MW PVP), (d) and (e) disc speeds of 1500 rpm and 2500 rpm, respectively (molar ratio of PVP to palladium 10; 40 000 MW PVP). Scale bar indicated is 200 nm.

distribution, with uniform nano-spheres obtained at 2500 rpm. The time needed for forming uniform nano-spheres decreased (higher speed) for shorter chains (2500 rpm for PVP 10 000 and 1500 rpm for PVP 40 000). This establishes that the time needed to equilibrate in forming uniform nano-spheres using SDP is a function of the polymer chain length. Indeed, using a much higher molecular weight, PVP360 (MW 360 000), resulted in non-uniform and poorly-dispersable nano-spheres for all accessible disc speeds, ≤ 2500 rpm (Fig. S3, ESI†). High colloidal stability and uniformity in size is an important parameter to test catalytic efficacy. The 160 nm nano-spheres (Fig. 2d, PVP to palladium 10, disc speed 1500 rpm, 40 000 MW PVP) were used in Mizoroki–Heck cross coupling reactions.

In further studying the effect of the use of SDP in fabricating the nano-spheres, a control batch experiment was undertaken whereby hydrogen gas was bubbled into a rapidly stirred aqueous mixture of H_2PdCl_4 and PVP 40000 for 30 to 60 seconds. During this time the solution turned from yellow to black which is indicative of reduction of H_2PdCl_4 , with the resulting palladium/polymer composite spheres varying in size from several hundred nano-metres to micro-metres (Fig. S4, ESI[†]). Thus rapid stirring in batch processing does



Fig. 3 SEM images of palladium nano-spheres: (a)–(c) disc speed 1500, 2000 and 2500 rpm, respectively (10 : 1 molar ratio of PVP to Pd; 10 000 MW PVP). Scale bar indicated is 200 nm.

not provide the intense micro-mixing associated with SPD, and moreover the reaction time using SDP is much shorter which relates to the high mass transfer of hydrogen gas associated with the breakdown of surface tension arising from waves and ripples on the dynamic thin films.

Catalytic activity

The catalytic activity of the optimised 160 nm palladium nanospheres was first trialled for the Mizoroki–Heck cross coupling reaction between iodobenzene and *n*-butyl acrylate. All reactions were carried out at 60 °C overnight with a range of catalyst loading, as indicated in mol%.³⁶ In each case the isolated yield of 1,2-disubstituted olefinic product 1 is shown in Table 1.

Given the success of using one mole percent of the catalyst for iodobenzene and *n*-butyl acrylate, this loading was chosen in studying the Mizoroki–Heck cross coupling reaction with a range of iodobenzenes (Table 2). Excellent catalytic activity was established for both activated (containing a para-electron withdrawing group) and deactivated iodobenzene derivatives

 Table 1
 Isolated yield of the Mizoroki–Heck reaction involving iodobenzene and butyl acrylate as the mole percent of the catalyst is varied

| l | | O U |
|---|----------------------------------|--------|
| | Et ₃ N, Pd-PVP, 60 °C | |
| | | |

| Entry | Mol% of Pd catalyst | Yield (%) |
|-------|---------------------|-----------|
| 1 | 3.3 | 97 |
| 2 | 1 | 96 |
| 3 | 0.67 | 96 |
| 4 | 0.33 | 93 |
| 5 | 0.1 | 89 |

Table 2 Mizoroki-Heck reaction of iodobenzene derivatives with

5 6 95 ⁴ Reaction conditions: Iodobenzene derivatives (0.98 mmol, 1 eq.),

(2–6). In all cases the products (7-11) were characterized by ¹H NMR and GC-MS, and the isolated yield was reported. As

n-butyl acrylate (1.18 mmol, 1.2 eq.), Et₃N (2.45 mmol, 2.5 eq.), and 1 mol% Pd nano-sphere catalyst in DMF (2 mL), 60 °C, overnight.

expected none of the 1,1-disubstituted product was observed. The palladium/PVP nano-sphere catalyst showed a lower catalytic activity in the bromobenzene system, as normally observed in the Mizoroki–Heck reactions,^{37–41} using the identical conditions to the study of iodobenzene. Additionally, there was a little effect on increasing the reaction temperature from 60 °C to 135 °C. However, greater activity was evident when switching the base from triethylamine to K₂CO₃ in the presence of a phase transfer agent, namely tetra-*n*-butylammonium chloride (TBAC) (entry 5, Table 3). The use of tetraalkylammonium salts in general as phase transfer agents in increasing the reaction rate in the Mizoroki–Heck type

Table 3 Outcome of the Mizoroki–Heck reaction involving bromobenzene and *n*-butyl acrylate, and the effect of various bases and phase transfer agents^a

| Entry | Base | Phase transfer agent | Time/h | Yield (%) |
|-----------------|--------------------------------|----------------------------------|---------------|-------------|
| 1 | (Et) ₃ N | | 24 | Trace |
| 2 | K ₂ CO ₃ | | 24 | 20 |
| 3 | K_2CO_3 | TBAB | 24 | 25 |
| 4^b | K_2CO_3 | TBAB | 24 | 26 |
| 5 | K_2CO_3 | TBAC | 24 | 76^c |
| 6 | K_2CO_3 | $TBAA^{e}$ | 20 | 34 |
| $7^{b,d}$ | K_2CO_3 | TBAC | 24 | 38 |
| 8^b | NaOAc | TBAC | 24 | 4^c |
| 9^b | NaOAc | TBAC | 48 | 5^c |
| 10^{b} | NaHCO ₃ | TBAC | 24 | 9^c |
| 11^{b} | NaHCO ₃ | TBAC | 48 | 15^{c} |
| <i>a</i> 0.98 m | nmol bromobe | enzene, 1 47 mmol <i>n</i> -buty | l acrylate (1 | 5 eq.) 2 mL |

DMF, base 2.45 mmol (2.5 eq.), tetra-*n*-butyl acrylate (1.5 eq.), 2 mL DMF, base 2.45 mmol (2.5 eq.), tetra-*n*-butylammonium bromide (TBAB) or tetra-*n*-butyl ammonium chloride (TBAC) 0.98 mmol (1 eq.), 135 °C. ^b 2.0 eq. *n*-butyl acrylate. ^c GC-MS yield. ^d Recycled catalyst from entry 5 was used. ^e Tetra-*n*-butyl ammonium acetate (TBAA).

 Table 4
 Mizoroki–Heck reaction of bromobenzene derivatives^a

| R | Br 0 K ₂ CO ₃ , 1 mol% Pd-PVF | P, 135 °C R | |
|-------|--------------------------------------------------------|-------------|------------------|
| Entry | Aryl halide | Time/h | Conversion (%) |
| 1 | `О-{Вг 12 | 24/48 | 25/30 |
| 2 | →→-Br 13 | 4 | 100 ^b |
| 3 | HO-Br 14 | 24 | 11 |
| 4 | | 24/48 | 9/40 |
| 5 | N- 16 | 24 | 42 ^c |

^{*a*} 0.98 mmol bromobenzene, 1.47 mmol *n*-butyl acrylate (1.5 eq.), 2 mL DMF, K₂CO₃ 2.45 mmol (2.5 eq.), tetra-*n*-butyl ammonium chloride TBAC 0.98 mmol (1 eq.), 135 °C. ^{*b*} Methyl acrylate was used. ^{*c*} Isolated yield.

reaction has been thoroughly studied by Jeffery *et al.* in phosphine free systems.^{42–44} The improved reaction efficiency of TBAC relative to the bromide analogue (TBAB) was also observed in our system. This effect of the quaternary ammonium salt is consistent with previous work, which depends both on the nature of the anion and the cation. Using sodium acetate or sodium carbonate as the base failed to improve the reaction conditions even in the presence of TBAC.

After optimizing the reaction conditions for bromobenzene, several bromobenzene and chlorobenzene derivatives (12–16) were investigated, Table 4. As expected, for electron poor aryl bromides (13) the yields were very high, and conversely for electron rich bromobenzenes (12, 14–16) the yields were relatively low. There was no activity detected in the case of chlorobenzenes.

Kinetic and recycling studies

Recycling the palladium nano-sphere catalyst was investigated, along with the kinetics of the reaction of iodobenzene with *n*-butyl acrylate. After each reaction, the catalyst was recovered by centrifugation, washed by DMF three times, stored under argon and used for the next reaction without further treatment. We have established that the Pd nanosphere catalyst can be recycled five times involving 16 hour reactions, without losing any catalytic activity, Table 5, and can be easily re-dispersed in DMF or water after each reaction. The size of palladium nanoparticle within the nano-spheres slightly increases after the first run, and remains the same size from the second to fifth recycle, Fig. 4. The reason for the particle growth is widely postulated that the Ostwald ripening effect at elevated temperatures may be a dominant force resulting in a slight increase in the particle size in the initial catalytic cycles.45,46

 Table 5
 Recycling of palladium nano-spheres for the Mizoroki–Heck

 cross coupling reaction of iodobenzene with *n*-butyl acrylate^a

| Reaction number | Time/h | Conversion determined by GC-MS (%) |
|-----------------|--------|---------------------------------------|
| 1st | 16 | 100 |
| 2nd | 16 | 100 |
| 3rd | 16 | 99 |
| 4th | 16 | 96 |
| 5th | 16 | 100 |

^{*a*} Reaction conditions: Iodobenzene (0.98 mmol, 1 eq.), *n*-butyl acrylate (1.18 mmol, 1.2 eq.), Et_3N (2.45 mmol, 2.5 eq.), and 1 mol% Pd nano-sphere catalyst in DMF (2 mL), 60 °C.



Fig. 4 TEM images of reused palladium nano-spheres (a and b, after first run; c and d, after fifth run).

Tracking the conversions for each recycling provides an insight into the catalytic system. Although the final conversions of recycling is at the same level, there is a significant change in the catalytic activity between the 1st run and subsequent runs during the first several hours, as can be seen from GC-MS analysis, Fig. 5. Energy dispersive spectroscopy (EDS) shows the presence of iodine in the recycled catalyst (Fig. S5, ESI⁺), and iodine is retained even after vigorous washing. It is assumed this hydrido-palladium iodide species⁴⁷ does not react with the base, triethylamine, so still remains on the surface after reaction completion. Therefore, it's likely that the residual iodine hinders the oxidative addition of iodobenzene in the next recycling. XPS studies were undertaken on the pristine catalyst and on the catalyst recovered from the reactions after recycling. The as-prepared material shows a dominant Pd(0) peak (BE = 335.5 ± 0.1 eV) in the Pd $3d_{5/2}$ region, and an additional Pd(II) peak (BE = $336.7 \pm 0.1 \text{ eV}$), Fig. 6. The latter presumably corresponds to PdO,^{30,48} noting that the palladium nano-spheres were exposed to an oxygencontaining atmosphere before the XPS test. The peak at 338.0 ± 0.1 eV only appears in the recycled catalyst, and according to the literature data, it can be assigned to the peak



Fig. 5 Kinetic and recycling studies for the Mizoroki–Heck cross coupling reaction involving iodobenzene and *n*-butyl acrylate (reaction conditions are defined in Table 2).



Fig. 6 Curve-fitting of the Pd 3d spectra obtained for pristine nanospheres (a), and after being recycled five times (b).

of PdI_2 ,⁴⁹ which is consistent with the formation of palladium iodide species in the catalytic cycle, including hydrido-palladium iodide.

We have established that the catalytic activity of the nanospheres does not change after the first cycle for at least another four cycles. The small palladium nano-particles in the nanospheres retain their high volume-to-surface ratio, with no apparent agglomeration of the nano-particles and formation of palladium black, and with no significant leaching of the metal in any form (determined by using ICP-AAS). For reactions involving 1 mol% palladium, 2.5 ppm palladium was found in the undiluted mixtures for the first cycle, and less than 2.0 ppm for subsequent cycles, the overall leaching being less than 0.05% of palladium.

Conclusions

We have established a simple method for preparing novel palladium-polyvinylpyrrolidone (Pd–PVP) composite nanospheres of uniform size using a microfluidic spinning disc platform under an atmosphere of hydrogen. This processing platform is ideal for large scale synthesis of uniform Pd nanocatalysts under continuous flow conditions. The turbulent mixing within the dynamic thin films arising from the high centrifugal forces results in the long chains of PVP forming a compact scaffold which entangles and traps a large number of 5 nm palladium nano-particles within the composite. We have established that these nano-spheres are effective recyclable colloidal catalysts for Mizoroki–Heck cross coupling reactions. The polymeric scaffold maintains the morphology and integrity by minimising catalytic loss caused by leaching of the precious metal.

Experimental section

Reagents and conditions

Polyvinylpyrrolidone (PVP, average molecular weight 10000, 40000, and 360000), 4-iodotoluene, methyl 4-iodobenzoate, 4'-iodoacetophenone, 4-iodoanisole, bromobenzene, methyl 4-bromobenzoate, 4-bromoanisole, 4'-bromoacetophenone, 4-bromo-N,N-dimethylaniline, chlorobenzene, and 4'-chloroacetophenone, tetrabutvlammonium bromide (TBAB), tetrabutylammonium acetate (TBAA), butyl acrylate, and iodobenzene were purchased from Sigma-Aldrich. Triethylamine (Et₃N), 4-bromphenol, 4-bromotoluene, and tetrabutylammonium chloride (TBAC) were purchased from Fluka. 4-Iodophenol is from Alfa Aesar. Potassium carbonate (K_2CO_3) , sodium acetate (NaOAc), sodium bicarbonate (NaHCO₃), and magnesium sulfate (dried) are from Ajax Finechem Pty Ltd. Palladium precursor solution (palladium dissolved in aqua regia) was provided by AGR Matthey. All chemicals were used without further purification except N,N-dimethylformamide (DMF) which was purified by approved procedures.⁵⁰

Synthesis of palladium composite nano-spheres

In a typical experiment H_2PdCl_4 solution (50 mL, 0.6 mmol L⁻¹) was mixed with PVP40 (34 mg, molecular weight is 40 000) (molar ratio of PVP monomer to palladium is 10 : 1) and then fed into a jet feed at a flow rate of 0.7 mL s⁻¹ onto the spinning disc for which the speed was set at 1500 rpm, with hydrogen gas fed into another jet feed, affording a colloidal suspension of composite nano-materials. Products were collected from beneath the disc through an exit port. The as-synthesised palladium composite nano-spheres were washed using MilliQ water (>18 MΩ) three times and then freeze dried. The nanoparticles were highly stable for several months and could be used as catalyst directly.

Characterization of the composite nano-materials

The freeze dried materials were re-dispersed in water and the size and morphology of the samples were determined using transmission electron microscopy (TEM, JEOL 3000F) operating at 300 kV and scanning electron microscopy (SEM, Zeiss 1555) applying with an acceleration voltage of 2 kV, respectively. Powder XRD patterns were measured using an Oxford Diffraction Gemini-R CCD diffractometer (using Cu K α = 1.54178 Å radiation).

General procedure for Mizoroki-Heck reaction

(a) Aryl iodides: Iodobenzene or an iodobenzene derivative (0.98 mmol, 1 eq.), butyl acrylate (1.18 mmol, 1.2 eq.), Et₃N (2.45 mmol, 2.5 eq.) in DMF (2 mL) were treated in one portion with the palladium nano-sphere catalyst (varying mol%). The reaction mixture was degassed (freeze-pump-thaw method) before heating to 60 °C for the designated time.

The ensuing reaction mixture was centrifuged and the palladium nano-sphere catalyst washed three times with DMF $(3 \times 5 \text{ mL})$. The combined DMF were washed by HCl (0.1 M) and ethyl acetate (V : V = 1 : 4) once and water and ethyl acetate (V : V = 1 : 4) twice. The ethyl acetate layers were collected and concentrated under reduced pressure and the resulting mixture subjected to column chromatography (2%, 10%, 5%, 3%, 6%, and 4%, ethyl acetate in hexane for iodobenzene, 4-iodotoluene (2), 4-iodophenol (3), methyl 4-iodobenzoate (4), 4'-iodoacetophenone (5), and 4-iodoanisole (6), respectively). The products (7-11) were characterized by ¹H NMR (for data see ESI[†]) and GC-MS (for data see ESI[†]), and matched authentic samples found in the literature.^{51–55} The isolated yield is reported. For recycling studies, the palladium nano-sphere catalyst was separated by centrifugation, washed by DMF three times, and stored in DMF under argon prior to the next catalytic run. (b) Aryl bromides: The same procedure was carried out for the reaction between aryl bromides (bromobenzene and 12-16) and acrylates except the reaction temperature and the reaction time varied (135 °C for the designated time). For 4-bromo-N,N-dimethylaniline (16), the mobile phase of 5% ethyl acetate in hexane was used.

Kinetic studies

To monitor the reaction, 10 μ L samples were taken at regular intervals, washed with 0.1 M HCl, diluted with ethyl acetate, centrifuged to remove the palladium nano-sphere catalyst, and analyzed by gas chromatography and mass spectrometry (GC-MS).

X-Ray photoelectron spectra (XPS) measurements

High resolution XPS measurements were preformed on a Kratos Axis-Ultra spectrometer using a Dual anode Mg K α X-ray source (1253.6 eV) with 12 kV operational voltage and 12 mA emission current. The working pressure in the analysing chamber was better than 10^{-10} Torr. The pass energies were 80 eV for the survey scan and 20 eV for the Pd 3p, Pd 3d, O 1s and C 1s in the high resolution scans. A hybrid lens mode with a top lens set at 0° was utilised. Samples were mounted horizontally by the double side sticky carbon tape and the external surfaces were examined as introduced without any further treatment. All spectra were processed by using a Powell peak-fitting algorithm provided by the spectrometer software.

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