Palladium nanoparticles captured onto spherical silica particles using a urea cross-linked imidazolium molecular band†

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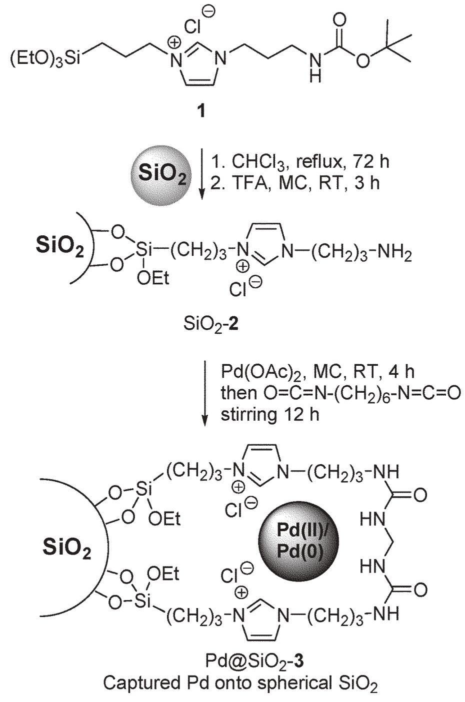
Palladium nanoparticles were captured onto spherical silica particles using a molecular band composed of imidazolium chloride and urea moieties to form raspberry-like Pd@SiO$_2$ composites, which can be recovered and reused without any loss of catalytic activity in Suzuki–Miyaura coupling.

Due to the increasing environmental requirements for waste minimization, heterogeneous catalysts have attracted more and more attention.[1] Palladium particles are among the most popular transition metals, and known to present a very high catalytic activity toward a wide range of applications.[2] However, there are difficulties associated with recovery and recycling. One promising solution to this problem consists in immobilizing the particles on a solid support. Although a number of support materials have been investigated, adsorption onto porous materials such as activated carbons, silica or alumina is the most generally employed method to immobilize palladium particles.[3] However, the micro- or mesoporosity of these materials often reduces the diffusion of the substrates toward the active particles.[3a]

Nanoparticles stabilized by imidazolium cation-based ionic liquids have been reported, and used as active catalysts for hydrogenation in ionic liquids.[4] A number of recent studies have indicated that the imidazolium-based ionic liquids stabilized metal nanoparticles not only electrostatically, but also by coordination involving the cations.[5] Although imidazolium-based ionic liquids are thought to be effective stabilizers for nanoparticles, it has often been found that aggregation still leads to loss of activity. Recently, it has been demonstrated that the task-specific functionalization of imidazolium ILs[6] with coordinating groups could cooperatively stabilize metal nanoparticles *via* the interaction of the nitrile functional group with the surface of nanoparticles.[7] In this context, the urea moiety would be a very promising functional group for the ligating and/or stabilization of nanoparticles. Ley and co-workers found the urea functionality of polyurea backbone could ligate Pd(OAc)$_2$, and thus retain palladium species in polyurea microcapsules.[8] Similarly, Davis Jr., Rogers and co-workers also showed that the urea groups attached into imidazolium cation could be ligated with heavy metal ions such as Hg^{2+} and Cd^{2+}, and thereby extracted the heavy metal ions from water.[9]

Quite recently, Bradley and co-workers elegantly demonstrated that palladium particles could be permanently immobilized onto the PS-PEG resin by using an amide molecular 'band', and minimized the leaching of the palladium.[10] Based on these observations, we anticipated that by modification of spherical silica surfaces with an amine-functionalized imidazolium salt, amino groups on the silica could be used to capture palladium species through the formation of molecular bands composed of imidazolium salt and urea moieties, which might be able to stabilize the palladium nanoparticles cooperatively. Moreover, the palladium particles immobilized on spherical surfaces would enable exposure toward substrates, avoiding diffusion problems.

The spherical silica nanoparticles (average diameter: ~200 nm) were synthesized according to the reported sol–gel method.[11] The surfaces of the silica particles were modified by grafting of the *N*-Boc-protected amine and triethoxysilyl bifunctionalized ionic liquid **1** (Scheme 1), which was synthesized by reaction of the commercially available 3-aminopropylimidazole with (Boc)$_2$O, followed by reaction with 3-chloropropyltriethoxysilane. A solution of **1** in chloroform was added to a suspension of silica particles in chloroform. After refluxing for 72 h under a nitrogen atmosphere, the silica particles were separated and washed several times with methylene chloride by repeated centrifugation



Scheme 1 Synthesis of captured Pd nanoparticles on spherical silica nanoparticles using urea-linked imidazolium chloride molecular bands.‡

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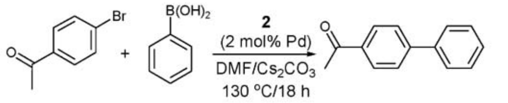

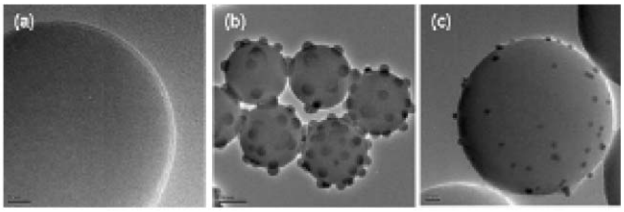

Fig. 1 TEM images of Pd@SiO$_2$-**3** (a) before (scale bar: 20 nm), (b) after first (scale bar: 100 nm) and (c) after fifth (scale bar: 20 nm) coupling reactions.

(10 000 rpm, 500 s). The Boc protection group was removed by treatment with trifluoroacetic acid to provide silica particles SiO$_2$-**2** modified with the amine-functionalized imidazolium moiety with 0.238 mmol g^{-1} content (determined by elemental analysis). IR spectra indicated the disappearance of the carbonyl band ($\nu_{C=O}$ 1681 cm^{-1}) after deprotection. To capture the Pd(OAc)$_2$ on silica particles using urea-linked imidazolium chloride, a suspension of the aminoimidazolium chloride-functionalized silica particles and Pd(OAc)$_2$ in methylene chloride was stirred for 4 h, then an excess amount of 1,6-diisocyanatohexane (10 equiv. to amine group) was added, and stirred for 12 h. The Pd(OAc)$_2$ captured spherical silica particles (Pd@SiO$_2$-**3**) were isolated through filtration, and washed with methylene chloride several times, then dried under a vacuum for 12 h. The IR spectrum was indicative of the formation of urea bonds ($\nu_{C=O}$ 1690 cm^{-1}). Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis showed 6.846 × 10^{-2} mmol g^{-1} of Pd, consisting of about 43% of the added Pd(OAc)$_2$ was captured onto the silica particles. As shown in the high resolution transmission electron microscope (HR-TEM) image of Pd@SiO$_2$-**3**, no Pd particles were observed (Fig. 1(a)).

To test the catalytic activity of the captured palladium species, Suzuki–Miyaura coupling between phenylboronic acid and 4-bromoacetophenone was carried out in the presence of Pd@SiO$_2$-**3** (5 mol% based on Pd content) in DMF at 130 °C for 18 h under a nitrogen atmosphere.§ After the completion of the reaction, the Pd@SiO$_2$-**3** was recovered by simple filtration, and washed with methylene chloride, water–methanol and methanol successively. TEM analysis of the recovered Pd@SiO$_2$-**3** revealed that the nano-sized palladium particles (mean size of 15 nm ± 3 nm) were immobilized onto the spherical silica surfaces, presenting the raspberry-like shape of the Pd@SiO$_2$ composites (Fig. 1(b)).

Surprisingly, X-ray photoelectron spectroscopy (XPS) measurement indicated that the captured palladium is a mixture of Pd^{II} (336.5 ± 0.5 and 341.5 ± 0.5 eV) and Pd^0 (334.5 ± 0.5 and 339.5 ± 0.5 eV) in *ca.* 1.2 : 1 ratio (Fig. 2(a)). As shown in Fig. 3, the X-ray absorption near-edge structure (XANES) spectroscopy experiment of the captured Pd@SiO$_2$-**3** showed that the edge jump of Pd@SiO$_2$-**3** appears between those of Pd metal and Pd^{II}Cl$_2$, indicative of the mixed Pd oxidation state of Pd^0/Pd^{II}. This result is in good accord with the XPS results, implying, although the reason for this is not yet clear, that Pd^{II} reduced to Pd^0 during capturing. ICP-AES analyses of the recovered Pd@SiO$_2$-**3** (5.04 × 10^{-2} mmol g^{-1}) recovered from the first coupling reaction revealed that about 26% of the palladium was leached out, which may largely be due to the uncaptured palladium. Importantly, the catalytic activity of the recovered Pd@SiO$_2$-**3** did not change at all, and could be reused four more times without any loss of catalytic activity. XPS measurement showed that the amounts of the Pd^0 species were slightly increased upon reuse of the Pd@SiO$_2$-**3**, implying that the Pd^{II} was reduced to Pd^0 during the Suzuki–Miyaura coupling reaction (compare Fig. 2(b) with (c)). Moreover, ICP-AES analyses of the recovered Pd@SiO$_2$-**3** from the second (4.94 × 10^{-2} mmol g^{-1}) and third runs (4.83 × 10^{-2} mmol g^{-1}) indicated that minimal amounts of palladium were released from the Pd@SiO$_2$-**3** composites. As shown in Fig. 1(c), the raspberry-like morphology was not significantly changed after five times reuse, and moreover the size of Pd nanoparticles decreased to 8–10 nm suggesting more nucleation of Pd^{II} occurred to form Pd^0 species. In order to understand the effects of the imidazolium–urea molecular band on the capturing of palladium nanoparticles, Pd(OAc)$_2$ was immobilized onto the amine-functionalized **2** (Pd@SiO$_2$-**2**) and unmodified (Pd@SiO$_2$-unmodified) spherical silica, and used as a catalyst for the same Suzuki–Miyaura coupling. It was revealed that significant amounts of palladium

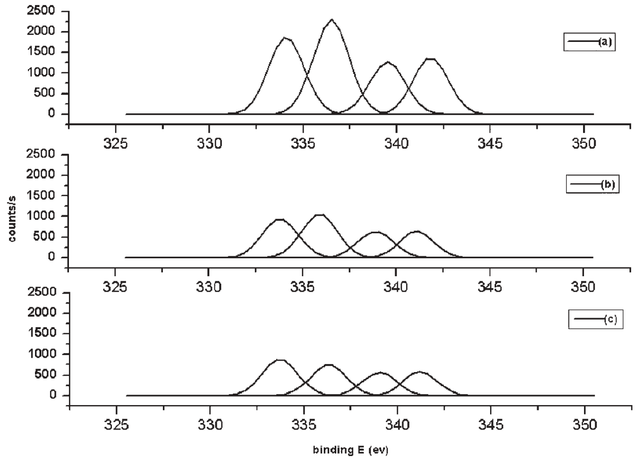

Fig. 2 X-Ray photoelectron spectroscopy (XPS) spectra (Pd 3d reagion) of Pd@SiO$_2$-**3** (a) before coupling reaction, (b) after first coupling reaction, (c) after second coupling reaction.

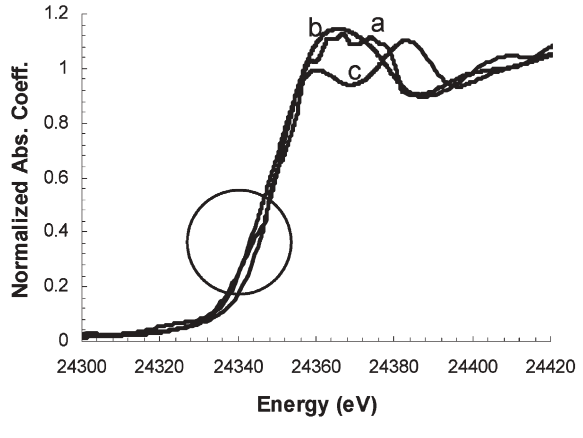

Fig. 3 X-Ray absorption near-edge structure (XANES) spectra of (a) Pd@SiO$_2$-**3**, (b) PdCl$_2$ and (c) Pd metal. Circle: absorption edge.

that adsorbed onto the silica surfaces were leached out after the coupling reaction. ICP-AES analyses of the recovered Pd@SiO$_2$-**2** from the first run (Pd content: before 4.035×10^{-2} mmol g^{-1}, after 2.188×10^{-2} mmol g^{-1}) and second run (1.695×10^{-2} mmol g^{-1}) indicated that about 46 and 23% of Pd leached out, respectively. after the first and second runs from Pd@SiO$_2$-**2**, respectively. Over 90% of the Pd adsorbed onto the unmodified silica, Pd@SiO$_2$-unmodified, was leached out after the first coupling reaction. These results clearly indicate that although the amine group is also capable of capturing Pd, the molecular band between the imidazolium chloride and urea moiety was responsible for not only capturing but also stabilizing the palladium nanoparticles.

In conclusion, palladium nanoparticles were captured and stabilized onto spherical silica nanoparticles using a molecular band composed of imidazolium chloride and urea moiety. The captured palladium particles formed raspberry-like Pd@SiO$_2$ composites after the Suzuki–Miyaura coupling reaction, and were not leached out from Pd@SiO$_2$-**3** composites, meaning that they can be recovered and reused several times without any loss of catalytic activity. Although it is not clear at the present time whether the captured palladium species are nucleated within the molecular band, or whether the molecular band reservoired the palladium nanoparticles, this approach will be extrapolated to other supported-nanocatalysts and might provide a new direction for the development of a recoverable catalyst

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Notes and references

‡ *Representative procedure* for the preparation of captured palladium particles onto spherical silica particles (Pd@SiO$_2$-**3**): 1-(3-*N*-*tert*-Butoxycarbonylaminopropyl)-3-(triethoxysilylpropyl)imidazolium chloride **1** (4.5 mL) was added to a suspension of spherical SiO$_2$ (4.5 g) in chloroform (30 mL). The resulting mixture was refluxed for 72 h under a nitrogen atmosphere. After cooling to room temperature, the SiO$_2$ particles were separated and washed four times with dichloromethane by repeated centrifugation (10 000 rpm, 500 s), and dried under a vacuum at room temperature to give *N*-Boc protected aminoimidazolium-functionalized SiO$_2$ particles (4.5 g) as a white solid. For deprotection of the *N*-Boc group, trifluoroacetic acid (0.8 mL) at room temperature was added to a suspension of *N*-Boc protected aminoimidazolium-functionalized SiO$_2$ particles (0.5 g) in dry methylene chloride (8.0 mL). After 3 h of stirring gently, the SiO$_2$ particles were separated by centrifugation and washed successively with 10% Et$_3$N–CH$_2$Cl$_2$ (20 mL) and dichloromethane (50 mL × 5), then dried under a vacuum to give SiO$_2$ particles SiO$_2$-**2** (0.5 g) with a free amine group. In order to capture palladium onto the spherical SiO$_2$ particles, Pd(OAc)$_2$ (36 mg) was added to a suspension of aminoimidazolium-functionalized SiO$_2$ particles SiO$_2$-**2** (0.36 g) in dry dichloromethane (5 mL). After stirring gently for 4 h at room temperature, 1,6-diisocyanatohexane (20 mg) was added and stirred for a further 12 h. The SiO$_2$ particles were separated by centrifugation and washed several times with dichloromethane to remove unreacted diisocynatohexane and uncaptured Pd(OAc)$_2$. After drying under vacuum at room temperature, the resulting Pd@SiO$_2$ composite Pd@SiO$_2$-**3** was subjected to ICP-AES analysis, which indicated 6.846×10^{-2} mmol g^{-1} of Pd captured onto the silica particles.

§ *Suzuki–Miyaura cross-coupling reactions* using captured Pd@SiO$_2$-**3**: To a solution of 4-bromoacetophenone (55.8 mg, 0.27 mmol), phenylboronic acid (39.0 mg, 0.30 mmol), Cs$_2$CO$_3$ (116.3 mg, 0.36 mmol) in dimethylformamide (1.6 mL) was added Pd@SiO$_2$-**3** (197.2 mg, 5 mol%, based on palladium content), and the reaction mixture stirred at 130 °C for 18 h. The reaction mixture was filtered through a membrane filter (0.2 μm porosity) and the filter cake was washed with methylene chloride first, and subsequently washed with water–methanol (3 : 7, v/v), and methanol to recover the captured Pd@SiO$_2$, which was used for the next run after drying under vacuum at room temperature. The water–methanol filtrate was evaporated, and extracted with ethyl acetate. The methylene chloride filtrate and ethyl acetate were combined. Evaporation under reduced pressure and purification by short silica column chromatography gave 4-phenylacetophenone (52 mg, 95% yield).

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