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Highly reactive heterogeneous Heck and hydrogenation catalysts constructed through 'bottom-up' nanoparticle self-assembly†

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Polymer-mediated self-assembly of functionalized Pd and SiO_2 nanoparticles provides highly active hydrogenation and Heck coupling catalysts.

The high surface area to volume ratio of noble metal nanoparticles makes them highly attractive tools for catalysis. One key challenge in the application of these particles is agglomeration. While aggregation can be overcome through surface functionalization,[1] this introduces mass transport issues that limit the catalytic efficiency of the catalytic system. Heterogeneous noble metal catalysts, on the other hand, are typically prepared by deposition of metal onto preformed supports,[2] resulting in limited control over metal particle size and dispersion. The use of directed self-assembly to construct heterogeneous catalysts in a 'bottom-up' fashion presents a promising alternative, preventing agglomeration while providing the inherent advantages of heterogeneous catalysts, such as ease of product separation and catalyst recycling.

Mixed Monolayer Protected Clusters (MMPCs)[3] are inherently versatile 'building blocks' for self-organization. MMPCs bearing recognition moieties in the monolayer can be assembled into macroscopic aggregates through the use of suitable mediators.[4] In recent studies, we have shown that acid–base complementarity can be used to assemble Au and SiO_2 nanoparticles into binary and ternary nanoparticle–polymer composites.[5] These assembly processes were highly modular and tailorable, with control of aggregate structure provided by stoichiometry, composition of polymer and nanoparticle, and order of addition of components. Using both binary and ternary assembly strategies, large, highly porous extended superstructures were provided featuring extensive exposure of the more expensive noble metal component of the system. We report here the extension of this electrostatically-mediated assembly process to the creation of highly reactive, recyclable, heterogeneous catalysts in which palladium MMPCs are simultaneously used as building blocks and active catalytic units.

The required SiO_2 building block **2** and polymer **3** (Fig. 1) were synthesized using established procedures.[4] Pd nanoparticle **1** was fabricated by place exchange of 11-mercaptoundecanoic acid onto 1 nm octanethiol-covered particles[6] (see ESI for all syntheses and preparations).†

MMPC **1** was dissolved in MeOH to 2.4% w/v, silica particles **2** and polymer **3** were dissolved in DMF to 12 and 6% w/v, respectively. Mixing polymer **3** with carboxylic acid–silica colloids **2** followed by addition of **1** afforded the ternary systems *via* acid–base reaction followed by immediate charge pairing (Scheme 1).[7] The order of addition provides control over the distribution of the metal component; addition of the palladium colloid to a preformed silica colloid–polymer aggregate should lead to high concentrations of the metal near the surface of the final aggregates. Transmission Electron Microscopy (TEM) images of precalcinated aggregates (Fig. 2a) reveal highly open micron-scale superstructures.

Active catalysts were prepared through calcination of the nanocomposite materials. Thermal Gravimetric Analyses (TGA) of **1** and the precalcinated 1 : 1 : 3 and 1 : 1 : 5 **1·2·3** ternary aggregates show that a slow ramp temperature (20 to 500 °C; 9 h) and with a ceiling temperature of 500 °C (3 h) provided total removal of organics. Significantly, after calcination, the highly porous nature of the systems remained intact (Fig. 2b).

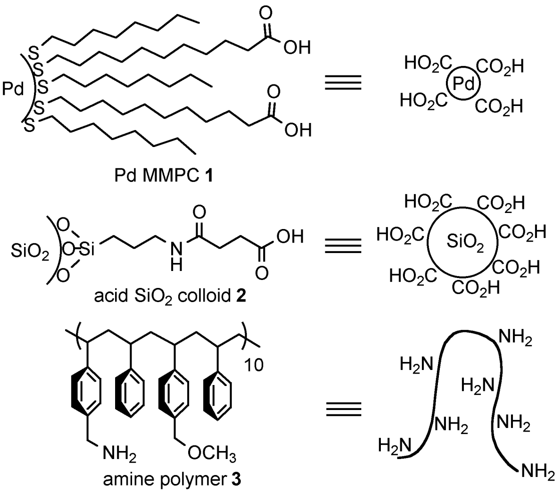
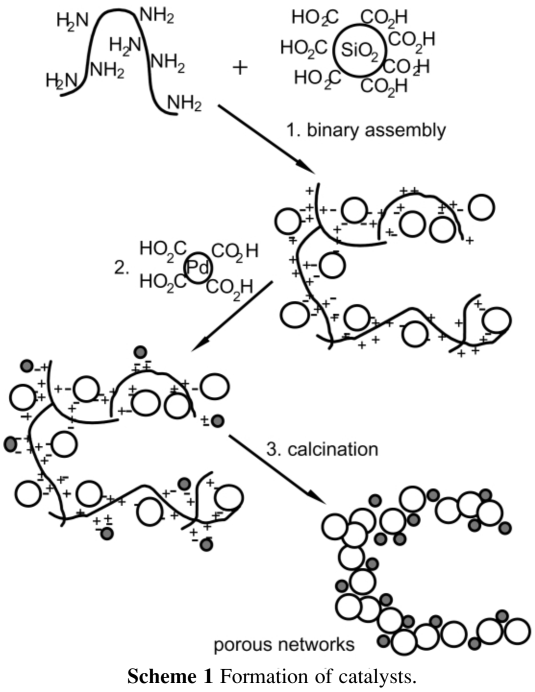


Fig. 1 Chemical structures of carboxylic acid-derived Pd–MMPC **1**, carboxylic acid-derived silica colloids **2**, and amine-functionalized polymer **3**.



Scheme 1 Formation of catalysts.

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† Electronic supplementary information (ESI) available: experimental methods. See http://www.rsc.org/suppdata/cc/b2/b200334a/

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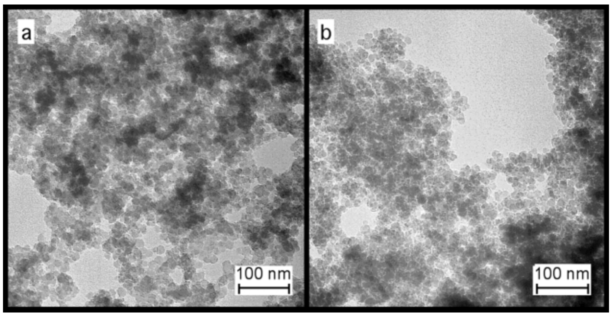
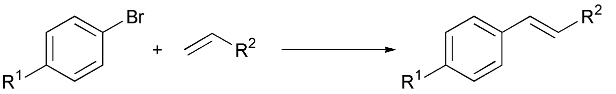


Fig. 2 Representative TEM images of (a) precalcinated 1 : 1 : 1 **1·2·3** aggregate; (b) calcinated 1 : 1 : 1 **1·2·3** catalyst.

Table 2 Coupling of bromoarenes with alkenes in the presence of calcinated 1 : 1 : 5 **1·2·3**[a]



R^1	R^2	Time/d	% Yield
$-NO_2$	$-C_6H_5$	1	88[b]
$-NO_2$	$-C_6H_5$	1.5	94[b]
$-NO_2$	$-C_6H_5$	1.5	89[bc]
$-NO_2$	$-CO_2CH_3$	1	96[d]
–H	$-C_6H_5$	2	30[d]
–H	$-CO_6CH_3$	2	25[d]

[a] 5 mmol bromoarene, 7.5 mmol alkene, 5.5 mmol NBu_3, 0.045 mol% Pd relative to bromoarene, PhMe, sealed tube. [b] Isolated yield. [c] Yield using recycled catalyst. [d] Yield determined by NMR.

To assess the catalytic activity of these systems, a series of hydrogenation reactions were carried out. In these studies, the calcinated 1 : 1 : 1, 1 : 1 : 3 and 1 : 1 : 5 **1·2·3** systems (1.6% Pd, determined by elemental analysis) were employed as catalysts for the hydrogenation of 9-decen-1-ol under zero order conditions (excess substrate over catalyst, see Table 1 and Fig. 3). Rapid stirring of the reaction mixtures at different rates showed no effect on the reaction rate, demonstrating the absence of a mass transport limit of hydrogen or substrate. The 1 : 1 : 1 and 1 : 1 : 3 systems exhibited extremely high efficiencies, with turnover frequencies (TOFs) of 10,100 and 9400 h^{-1}, respectively, after correction for catalyst loading. These values are substantially higher than the 7200 h^{-1} found under the same conditions with commercial 1% Pd/C, a highly evolved industrially important catalyst. Increasing the polymer content to the 1 : 1 : 5 system resulted in a reduced, albeit still high TOF of 7600 h^{-1}, consistent with the denser structure observed with this system.[5b]

Carbon–carbon bond formation reactions provide a further test for the utility of our nanocomposite catalysts. Previous investigations have shown that commercial Pd/C and Pd/SiO_2 supports are not effective catalysts in Heck coupling reactions.[8] Therefore, we investigated the ability of the 1 : 1 : 5 **1·2·3** system to undergo Heck reactions. Table 2 shows the results obtained for coupling activated and electronically neutral bromoarenes with styrene and methyl acrylate. As expected, the nitroarene coupled most efficiently, requiring only 0.045 mol% of Pd, a dramatic improvement over their commercial counterparts, Pd/C and Pd/SiO_2. Most importantly, the catalyst required no activation, no toxic ligand, and could be recycled with only a small decrease in activity. While this system was less efficient in catalyzing the coupling of non-activated substrates, it is still significantly more active than previously reported polymer-stabilized nanoparticle systems.[8b]

In summary, we have demonstrated that directed self-assembly provides highly reactive, recyclable heterogeneous catalysts for both hydrogenation and carbon–carbon bond formation reactions. Extension of the method to the creation of additional catalytic systems is currently being explored and will be reported in due course.

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Table 1 All turnover frequencies of catalysts

Catalyst	TOF/h^{-1}[a]
1 : 1 : 1 **1·2·3**	10154 ± 32
1 : 1 : 3 **1·2·3**	9419 ± 337
1 : 1 : 5 **1·2·3**	7622 ± 67
1% Pd/C	7202 ± 36

[a] Under above conditions, calculated as $mol_{product}\ mol_{Pd}^{-1}\ h^{-1}$.

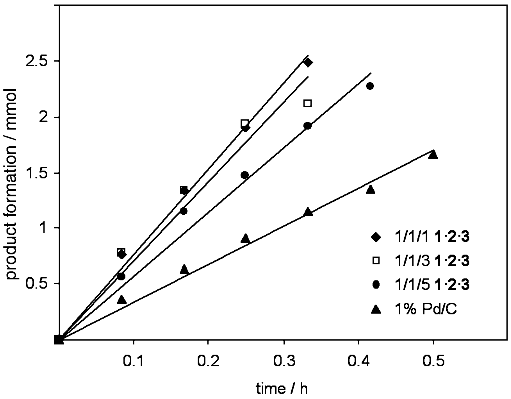

Fig. 3 Graphs of initial product formation *versus* time under conditions for zero order kinetics for substrate (5.6 mmol 9-decen-1-ol, 0.013 mol% Pd (0.008 for Pd/C), MeOH, 1 atm H_2) monitored by GC. Reduced substrate to 98% yield.

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