

Converting homogeneous to heterogeneous in electrophilic catalysis using monodisperse metal nanoparticles

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A continuing goal in catalysis is to unite the advantages of homogeneous and heterogeneous catalytic processes. To this end, nanoparticles represent a new frontier in heterogeneous catalysis, where this unification can also be supplemented by the ability to obtain new or divergent reactivity and selectivity. We report a novel method for applying heterogeneous catalysts to known homogeneous catalytic reactions through the design and synthesis of electrophilic platinum nanoparticles. These nanoparticles are selectively oxidized by the hypervalent iodine species PhICl_2 , and catalyse a range of π -bond activation reactions previously only catalysed through homogeneous processes. Multiple experimental methods are used to unambiguously verify the heterogeneity of the catalytic process. The discovery of treatments for nanoparticles that induce the desired homogeneous catalytic activity should lead to the further development of reactions previously inaccessible in heterogeneous catalysis. Furthermore, a size and capping agent study revealed that Pt PAMAM dendrimer-capped nanoparticles demonstrate superior activity and recyclability compared with larger, polymer-capped analogues.

The field of homogeneous catalysis is a source of easily tuned, selective catalysts with high activity. Heterogeneous catalysts also offer many advantages, some of which are not displayed by their homogeneous counterparts, including recyclability, ease of separation from the reaction mixture and their use in continuous flow processes. It is highly desirable to develop new systems that blend the many advantages of heterogeneous catalysis with the versatility of homogeneous catalysts^{1–3}.

Most efforts approach from the homogeneous side and use immobilized homogeneous catalyst species that promote reactions already accessible in solution-state conditions^{1,4}. We sought to use an alternative method whereby heterogeneous catalysts are extended to reactions previously only catalysed by homogeneous species. Metal nanoparticles (NPs) that serve as heterogeneous catalysts and whose particle size and oxidation state can be characterized are well suited to our study. It is known that the reactivity and selectivity of monodisperse metal NPs can be altered by changes in their size and shape^{5–15}. Although Pd and Au NPs have been demonstrated to catalyse a range of cross-coupling and oxidation/reduction reactions in solution^{16–25}, studies have not yet yielded the control necessary to develop new NP catalysts applicable to a wider variety of reactions.

A further challenge involves the specific nature of the catalyst. In particular, the distinction between homogeneous and heterogeneous catalysis is often difficult to determine. This is due to the possibility that metal leaches from a heterogeneous catalyst into solution and acts as the catalytically active homogeneous species. Thus, it was important for us to consider in our studies the fact that for many of the NPs used in carbon–carbon bond-forming reactions, formation of a catalytically active homogeneous species from the NP precursor cannot be excluded. For example, it is generally accepted that Pd nanoparticles, when used in solution, degrade into various homogeneous species and provide a strong case for the assumption that a nanoparticle catalyst is leaching in solution

until proven heterogeneous^{2,16,17,25}. Thus, we aimed to design and synthesize truly heterogeneous NPs—which show no leaching—capable of catalysing an alternative yet broad class of reactions for functionalizing π -bonds, which, to date, has been achieved exclusively with homogeneous catalysts.

To accomplish this goal, the NP catalysts would require significant electrophilic character, which could be imparted by an increase in metal oxidation state, similar to that found in electron-deficient, late-metal homogeneous catalysts. Through this, we would obtain new activity from heterogeneous metal NP catalysts resulting in selective, solution-phase carbon–carbon and carbon–heteroatom bond-forming reactivity not previously observed with known heterogeneous catalysts.

Results and discussion

Catalyst development and reactivity. Given that the aforementioned set of desired transformations are currently known to be catalysed by Pt halides, we focused our study on Pt NPs. Two general types of NPs were prepared in a range of sizes that allow for thorough investigation of the effects of various parameters on reactivity. These Pt NPs were synthesized using two techniques: dendrimer and polymer encapsulation (Fig. 1a).

Fourth-generation hydroxyl-terminated polyamidoamine (PAMAM) dendrimers (G4OH) were used as capping agents^{4,17,26} for small 1.0 nm, 40 atom Pt (Pt_{40}) NPs. Alternatively, polyvinylpyrrolidone (PVP) was used to generate 1.5, 2.9 and 5.0 nm-sized NPs by existing procedures²⁷. Fabrication of the NPs was followed by deposition onto SBA-15, or in the case of the larger 5.0 nm NPs, MCF-17 mesoporous silica. Notably, NPs capped with PAMAM dendrimers are active for a variety of reactions when supported on SBA-15 silica, and calcinations or other similar manipulations of the NPs are not necessary, unlike NPs capped with PVP or other agents^{26,28}. In addition to allowing for recycling of the catalyst,

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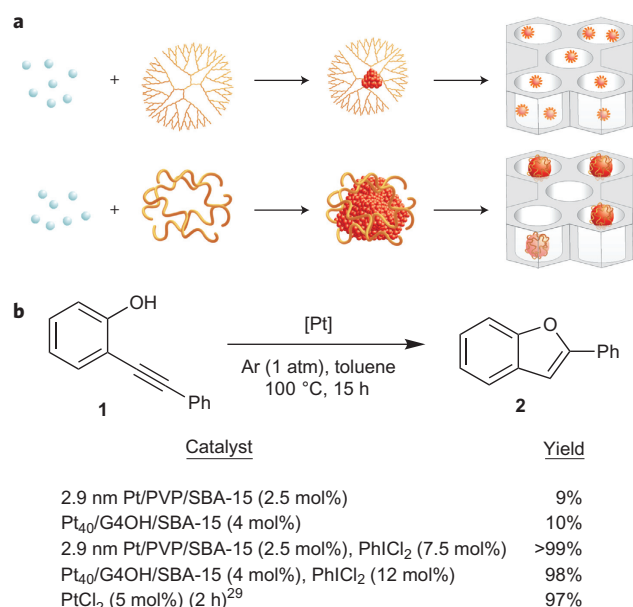


Figure 1 | Depiction of the two nanoparticle synthesis techniques used and the initial reactivity results for electrophilic catalysis. **a**, In the top scheme, Pt ions are loaded onto a PAMAM dendrimer and reduced to form a dendrimer-encapsulated NP. Sonication deposits the NPs on the mesoporous silica SBA-15 to generate the NP catalysts. In the bottom scheme, polyvinylpyrrolidone encapsulates the NP. Deposition on SBA-15 follows to produce the catalyst. In both cases, the NPs are synthesized before loading onto SBA-15. **b**, Hydroalkoxylation of **1** with Pt NPs. To obtain electrophilic activity from the Pt NPs, treatment with the mild oxidant PhICl₂ is required. Pt₄₀/G4OH/SBA-15 NPs must be further reduced under H₂ atmosphere at 100 °C for 24 h before reaction. This treatment generates catalytically active NPs that activate the π -bond in **1** resulting in hydroalkoxylation to benzofuran **2**. Yields were determined by NMR versus internal standard.

deposition of the PAMAM dendrimer NPs on SBA-15 imparts additional thermal stability against aggregation^{4,26,28}. Furthermore, as PAMAM dendrimers are normally soluble only in protic liquids, loading the NPs on SBA-15 allows for their use in organic solvents.

Our initial studies focused on a hydroalkoxylation reaction in which an electrophilic Pt catalyst activates an alkyne towards nucleophilic attack by an oxygen functionality²⁹. When 1.5 nm Pt/PVP/SBA-15 NPs were used, no appreciable reaction was observed. Given that the homogeneous Pt catalysts for this type of reaction exist in the +2 or +4 oxidation state, we hypothesized that the failure of the NPs was due to an overabundance of Pt in the 0 oxidation state. In fact, X-ray photoelectron spectroscopy (XPS) studies on these Pt/PVP NPs have confirmed that >90% of the metal exists in a metallic Pt(0) oxidation state. Thus, we turned to the Pt₄₀/G4OH NPs, which are >70% oxidized as determined by XPS^{30–32}. However, exposure of alkyne **1** to 1.0 nm Pt₄₀/G4OH NPs generated only a 10% yield of product. This result is most likely due to the presence of catalytically inactive Pt oxide species on the Pt₄₀/G4OH NP surface.

To address this lack of activity, we postulated that known oxidizing agents for metals might be used to selectively modify the NP surface to produce a catalyst species with the requisite activity. Recent work has shown the formation of oxidized [PtCl₄]² layers on Pt surfaces with Cl₂ etching³³, as well as oxidation of Pd catalysts to form Pd–Cl bonds with the hypervalent iodine species iodosobenzene dichloride (PhICl₂)³⁴. These precedents serve to reinforce the ability of PhICl₂ to act as a mild oxidant to transform the Pt NP surface into a catalytically active state. We found that PhICl₂ successfully generated the desired electrophilic catalyst species. Treatment of either Pt₄₀/G4OH/SBA-15 (further reduced under H₂ atmosphere at 100 °C for 24 h before reaction) or Pt/PVP/SBA-15 NPs with three equivalents (relative to catalyst loading) of PhICl₂ resulted in an excellent yield of >95% for benzofuran **2** (Fig. 1b). Further evidence for the oxidation of the Pt NPs was obtained from an XPS spectrum of 1.5 nm Pt/PVP NPs treated with PhICl₂ showing that >25% of the Pt was oxidized.

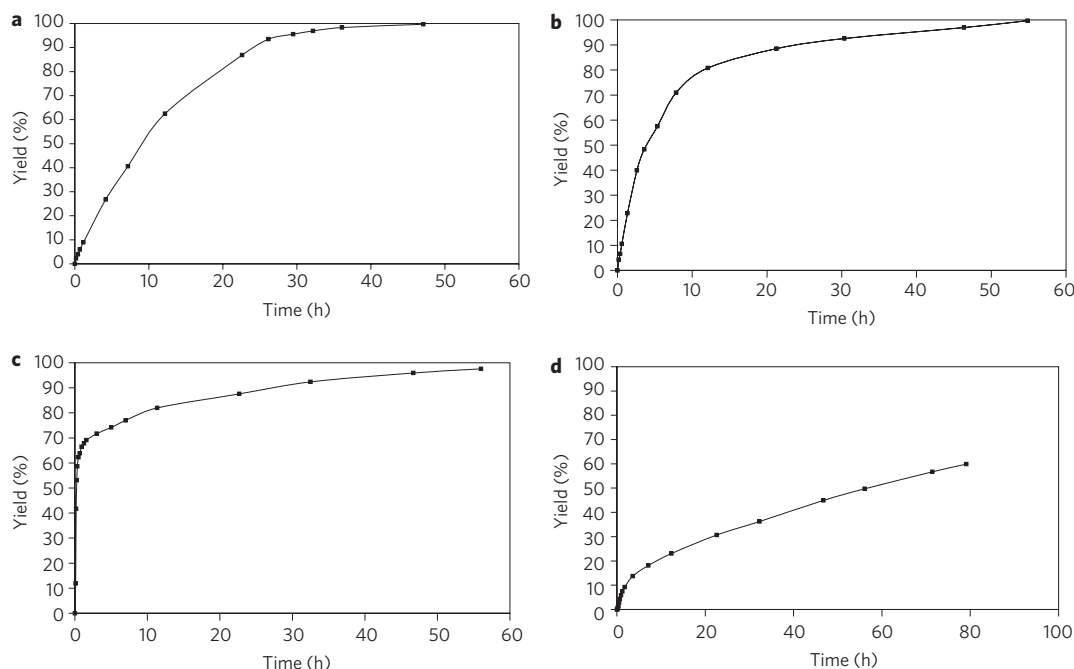


Figure 2 | Monitoring the Pt nanoparticle catalysed reaction to show size and capping-agent effects as well as recyclability. Graphs display the reaction yield of **2** from **1** as a function of time. All catalysts were treated with PhICl₂ (three catalytic equivalents). **a,b**, Initial run of Pt₄₀/G4OH/SBA-15 (3 mol%) (**a**), and recycled run (**b**). **c,d**, Initial run of 1.5 nm Pt/PVP/SBA-15 (1 mol%) (**c**), and recycled run (80 h reaction time) (**d**). Note the excellent recyclability of the Pt₄₀/G4OH catalyst as opposed to the significant deactivation of the Pt/PVP NPs.

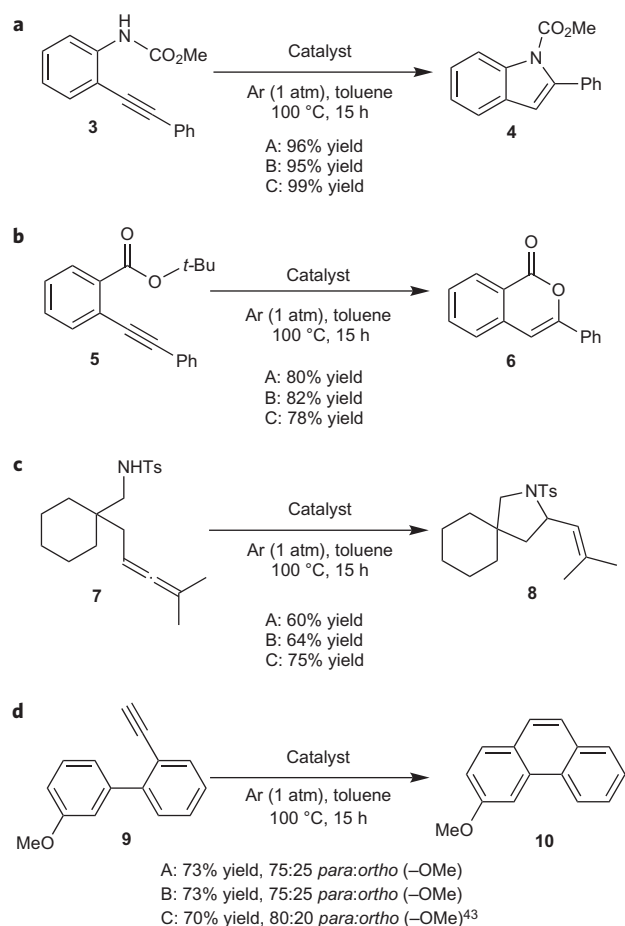


Figure 3 | Cyclization reactions using Pt nanoparticles. a–d, Using either PVP- or dendrimer-encapsulated NPs results in good to excellent yields of nitrogen- and oxygen-containing heterocycles through π -bond activation by electrophilic Pt. Catalyst systems: A: Pt₄₀/G4OH/SBA-15 (4 mol%), PhICl₂ (12 mol%); B: 2.9 nm Pt/PVP/SBA-15 (2.5 mol%), PhICl₂ (7.5 mol%); C: PtCl₂ (5 mol%). Pt₄₀/G4OH/SBA-15 NPs must be further reduced under H₂ atmosphere at 100 °C for 24 h before reaction. Yields were determined by NMR versus internal standard. In **d**, the catalyst system C reacted at 80 °C for 17 h⁴³.

As predicted, the oxidized NP catalysts demonstrated a size and capping-agent effect on catalytic activity. Although multiple studies conducted on various reactions in both the gas and solution phase have demonstrated the importance of NP parameters for reactivity and selectivity, fewer discuss supported NPs in solution^{5–15,35}. Under our oxidative modification conditions, additional size and capping-agent effects were found for the PVP- and dendrimer-capped, SBA-15-supported Pt NPs. Results from detailed reaction monitoring indicate that smaller dendrimer-capped NPs are more stable in higher oxidation states than larger NPs and remain in this catalytically active state for prolonged times. Based on previous observations, this trend may be due to stability imparted by the PAMAM dendrimers^{26,28,30–32}.

It is also possible that, under the reaction conditions, the dendrimer could decompose. Any decomposition, however, does not seem to affect the catalytic activity as shown by the similar activity of the Pt₄₀/G4OH/SBA-15 NP catalyst after recycling and its consistent difference from the PVP-capped NPs. Furthermore, recent reports suggest more harsh conditions are required for complete dendrimer removal^{31,36,37}. Regardless, Pt₄₀ proved to be the most robust catalyst and, after oxidative modification with PhICl₂, a steady rate of reaction was maintained, which only decreased as the reaction neared complete consumption of the starting material (Fig. 2a).

The stability of the Pt₄₀ catalyst was additionally tested by isolation of the SBA-15-supported catalyst and immediate resubmission to a new solution of substrate. In this case, an overall decrease in activity was observed, but the catalyst remained consistently active until all substrate was consumed with no further deactivation.

The Pt₄₀/G4OH PAMAM NPs, when supported on SBA-15, showed excellent recyclability over multiple cycles after simple filtration, reduction and retreatment with PhICl₂ (Fig. 2b). A sample of Pt₄₀/G4OH/SBA-15 NPs has been recycled four times with a consistent yield of >90% under the reported reaction conditions. In addition, a single batch of catalyst was active for a month, and a turnover number of 400 (per metal basis) was obtained. Monitoring of the reaction indicated no loss of activity after recycling compared to the initial catalyst use, and simple filtration of the catalyst through a glass microfibre filter was sufficient to separate the metal species from the product solution.

Much like their use in the gas phase, PAMAM dendrimers show significant advantages as NP capping agents in solution. This templating strategy allows for the generation of monodisperse NPs as small as 1 nm and is complemented by the resulting performance enhancements and potential for further catalyst development in combination with the oxidative modification.

For larger NP sizes, PVP capping was required. However, the 1.5, 2.9 and 5.0 nm Pt/PVP/SBA-15 NPs had distinctly different activity from the smaller, dendrimer-capped NPs. In addition to a decrease in activity as NP size increased, these larger NPs demonstrated a marked initial spike in activity, followed by rapid deactivation and prolonged time to reach completion (Fig. 2c). For example, when only 1 mol% of 1.5 nm Pt/PVP/SBA-15 NPs treated with PhICl₂ were used, approximately 70% yield was reached in the first 1.5 hours. However, nearly 60 hours were required to reach complete conversion to product. Immediate resubmission of the PVP NPs to a new batch of substrate did indeed prove the catalyst was deactivated as the reaction was extremely slow and reached a lower level of completion in significantly more time than initially required. Even after reduction and PhICl₂ retreatment of the recycled catalyst, substantial deactivation of the catalyst was observed (Fig. 2d). In comparison, 2 mol% of PhICl₂-oxidized 5.0 nm Pt/PVP/SBA-15 NPs generated only ~14% yield in the initial activity spike, and after 70 hours, only 60% yield was obtained, demonstrating the decrease in activity resulting from larger NP sizes. It is important to note that although the PVP-capped catalyst did show a more rapid deactivation, a batch of 2.9 nm Pt/PVP/SBA-15 NPs treated with PhICl₂ remained active for one month. A turnover number of 415 (per metal basis) was obtained. For these larger NP sizes, we believe that the NP has more metallic character and tends to revert to the Pt(0) oxidation state^{38–40}. With smaller sizes, the NP more readily retains its oxidized state as the electronic valency of the surface atoms is less saturated and more atomic character is present. It is also likely that the increased activity of smaller NPs is due to the larger number of Pt atoms, and therefore active sites after treatment with PhICl₂,

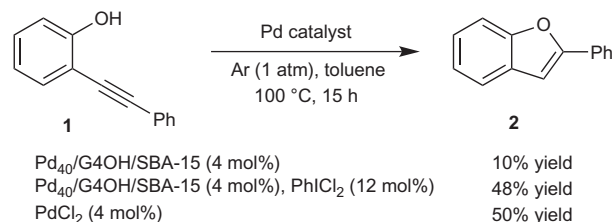


Figure 4 | Cyclization reaction using Pd nanoparticles. Reaction with Pd NPs demonstrates generality for the oxidative modification. Pd₄₀/G4OH/SBA-15 NPs must be further reduced under H₂ atmosphere at 100 °C for 24 h before reaction. Yields were determined by NMR versus internal standard.

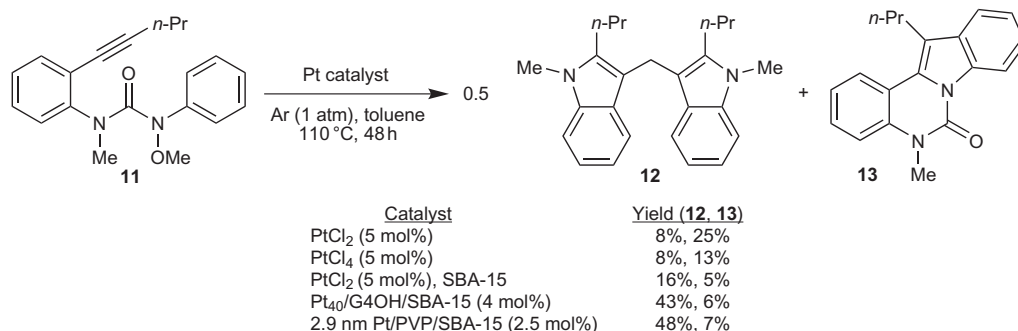


Figure 5 | Oxidatively modified Pt nanoparticle catalysed cyclization of phenylurea 11. Whereas homogeneous catalysts provided low yields of tetracycle 13, the NPs result in an unprecedented reaction to the methylene-bridged bisindole compound 12.

present on the surface of the NP. Beyond size considerations, the increased rate of deactivation and limited recyclability for the PVP capping agent renders the oxidatively modified PAMAM dendrimer-capped NPs as the optimal catalyst system.

Having developed two highly active Pt NP catalysts, we sought to test them for a range of π -bond activation reactions previously known to occur only with electrophilic homogeneous catalysts. The NPs were found to catalyse several reactions in the solution phase under relatively mild conditions with minimal or no side reactions. Figure 3 shows the results of these reactions with both G4OH PAMAM dendrimer and PVP capping agents. Five- and six-membered-ring heterocycles were formed by addition of nitrogen and oxygen nucleophiles to alkynes and allenes (Fig. 3a–c)^{41,42}, activated by the Pt nanoparticle catalysts. Carbon–carbon bond formation has also been accomplished with a hydroarylation reaction (Fig. 3d)⁴³. It is important to note that all reactions are catalysed by Pt NPs in yields comparable to, if not slightly better than those obtained with homogeneous PtCl₂. Furthermore, in the case of the cyclization of compound 9, our NP catalysts show selectivity favouring the *para*-isomer 10 over the *ortho*-isomer that is nearly equivalent to that observed in homogeneous PtCl₂ systems. This highlights the potential of unique heterogeneous catalysts to offer similar selectivities relative to homogeneous species. Generality for the oxidative treatment was shown when Pd₄₀/G4OH/SBA-15 NPs were used for the formation of 2 from 1 (Fig. 4). Just as was found for Pt, the Pd NPs required further reduction (H₂ (1 atm), 100 °C, 24 h) followed by *in situ* treatment with PhICl₂ to generate electrophilic catalytic activity. The yield obtained with the Pd NPs (48%) was comparable to that obtained with PdCl₂ homogeneous catalyst.

Additionally, we found that when urea 11 was treated with either PtCl₂ or PtCl₄ homogeneous catalyst in toluene at 110 °C, both 13 (ref. 44) and a previously unreported product, the bis-indole 12, were observed, although in low yields. However, addition of SBA-15 resulted in a suppression of the formation of 13 and a subsequent increase in the yield of bis-indole 12 (Fig. 5). Interestingly, the use of either Pt/PVP/SBA-15 or Pt₄₀/G4OH/SBA-15 NPs oxidatively modified with PhICl₂ resulted in a much higher 43–48% yield after 48 h for the bis-indole 12. Although a small amount of tetracycle 13 was still formed by the NP catalysts, the majority of the consumed starting material went towards this alternative catalytic reaction pathway. In this case, the NPs selectively catalyse a reaction cascade that generates several new carbon–carbon bonds and combines aspects of two starting material molecules to afford 12. Furthermore, by utilizing supported NPs for this process, we have developed a recyclable catalyst system that can access this reactive pathway in yields greater than those obtained by simply mixing homogeneous catalyst with SBA-15.

Leaching tests. Although the remarkably consistent recyclability of the PhICl₂-treated Pt₄₀/G4OH/SBA-15 NPs is a strong indication

of its heterogeneity, we wanted further verification that the NPs were not leaching to form a homogeneous active catalyst. The first example is the striking improvement in long-term activity of the smaller-sized PAMAM dendrimer-capped NPs over the larger PVP-capped NPs, which is complemented by the differing recycling ability based on capping agent. Both results illustrate the effect of size and capping agent, which would not be possible if homogeneous catalysts were generated as the active species even if a ‘release and capture’ dynamic were present. In a more rigorous test for the formation of a homogeneous species, a three-phase test^{45,46} was used with Wang resin-bound substrate 14 (Fig. 6a). In the presence of homogeneous PtCl₂, 26% conversion of resin-bound substrate to product was observed. However, both 2.9 nm Pt/PVP/SBA-15 and Pt₄₀/G4OH/SBA-15 NPs oxidized with PhICl₂ resulted in <2% conversion. In addition, transmission electron microscopy images of supported Pt₄₀/G4OH/SBA-15 NPs before and after reaction do not show any appreciable aggregation or leaching (Fig. 6b).

Furthermore, an experiment was conducted in which a Pt₄₀/G4OH/mesoporous silica pellet was used to allow for facile removal of the reaction solution from the NP catalyst under the reaction conditions and inert atmosphere. In this case, detailed in Fig. 6c, a solution of starting material, PhICl₂ and solvent are added to the catalyst pellet in a reactor (A) and begin to generate product. After 42% yield is achieved, the reaction solution in A is transferred to a new vessel with no catalyst (B). The oxidized catalyst pellet remains in A. A fresh solution of starting material and solvent is then added into A. Now, the solution in A begins to convert to product while the solution in B does not react and remains at 42% yield. This further indicates the active catalyst is heterogeneous. If any homogeneous leached species were present, it would have also been transferred to B and an increase in yield would have been observed for the solution after it was removed from the heterogeneous catalyst pellet in A. Moreover, the new solution added to A begins to react, showing that the active catalyst has, in fact, remained in A.

Finally, elemental analysis by inductively coupled plasma of a centrifuged solution (1 with Pt₄₀/G4OH/SBA-15 and PhICl₂ in toluene) after reaction was unable to detect any significant amount (<1 ppm) of Pt above the instrument’s detection limits. By the same analytical method, no loss of Pt was observed from the Pt₄₀/G4OH/SBA-15 catalyst when it was isolated after the reaction.

All together, this collection of experiments strongly indicates that no homogeneous catalytically active species had leached from the treated/oxidized Pt₄₀/G4OH/SBA-15 NPs during the reaction, and that the catalytically active species is the heterogeneous NP.

Conclusion

We have contributed to the larger goal of bridging the gap between homo- and heterogeneous catalysis with a strategy for developing catalytically active NPs capable of performing reactions previously

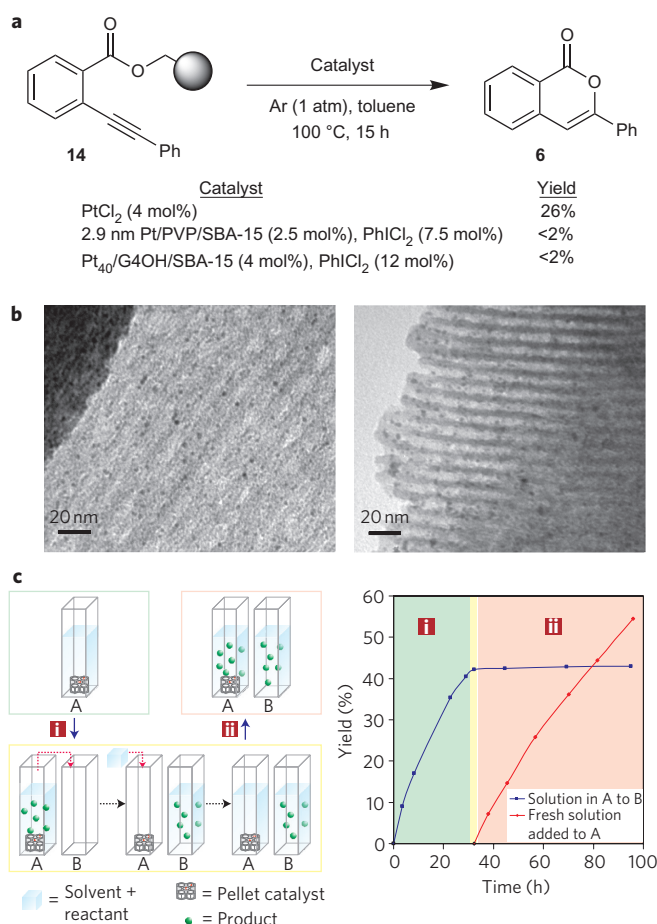


Figure 6 | Results from catalyst heterogeneity tests. **a**, A three-phase test to determine the presence of a homogeneous catalyst by leaching or release and capture. The reaction rate between the heterogeneous catalyst and polymer-bound substrate should be negligible. Yields were determined by NMR versus internal standard. **b**, Transmission electron microscope (TEM) images of Pt₄₀/G4OH/SBA-15 before reaction (left), and after treatment with PhICl₂ and reaction with **1** (right). No leaching or aggregation is observed. Further TEM data including average diameters and standard deviations can be found in the Supplementary Information. **c**, A filtrate transfer test. A reaction vessel (A) was charged with a substrate. Into this vessel was added a pellet of Pt₄₀/G4OH/mesoporous silica catalyst and PhICl₂ oxidant (blue section). The mixture was stirred and the yield monitored (i). When the reaction in vessel A reached 42% yield, the solution was removed and placed into a new vessel (B). A fresh solution of starting material was added to vessel A where the catalyst pellet remained (yellow section). Both vessel A and B were then stirred and monitored (ii). The yield in B remained constant, whereas product was generated in A (red section). The yield was determined by gas chromatography versus internal standard. All transfers and reactions were conducted under Ar at 100 °C. The catalyst pellet was pre-reduced under H₂ atmosphere at 100 °C for 36 h before reaction.

in the exclusive purview of homogeneous chemistry. To this end, we have successfully identified novel electrophilic Pt NPs that catalyse a range of π -bond activation reactions with equivalent or superior yields and selectivities relative to reported homogeneous variants. Instrumental to this success were NP structural analyses and mechanistic insights that uncovered the importance of treatment with the hypervalent iodine oxidizing agent PhICl₂. Moreover, reaction kinetic analysis confirmed the capability of tuning nanoparticle size and capping agent to improve catalytic ability. Multiple experimental results indicate the heterogeneity of the dendrimer-encapsulated NP catalyst supported on SBA-15. These discoveries,

most notably the oxidative modification, illustrate the ability to obtain new reactivity from existing NP systems, and, in some cases, divergent reaction pathways are accessible.

In a broader sense, this concept represents a significant advancement in the solution-phase applications of supported NPs, and further application with other metals and treatment methods may facilitate the development of heterogeneous catalysts with novel activity or selectivity in an even larger array of chemical reactions. Efforts are underway to better understand the nature of the oxidation in order to further increase as well as maintain catalyst activity to allow for the development of a continuous flow system. Future studies can also move beyond traditional homogeneous ligand control and use NP shape or dendrimer composition to provide opportunities for selective solution-phase reactions.

Methods

Synthesis of dendrimer-templated NPs. Fourth-generation dendrimers (G4OH) were purchased from Dendritech as 10.2% (mass) methanol solutions. A dendrimer stock solution (250 μ M) was prepared by adding water to the dendrimer methanol solution. The dendrimer stock solution was mixed with 15–40 mole equivalents of an aqueous solution of 0.01 M K₂PtCl₄ in a 20 ml vial. The vial was purged with Ar for 30 min, tightly sealed with a septum and left for 66 h for complexation. Then a 20-fold excess of freshly prepared 0.5 M NaBH₄ (stored at 0 °C before use) was injected dropwise into the vial with vigorous stirring. The reaction solution was stirred for an additional 8 h after which the reaction solution (10 ml) was purified by dialysis against 2 l of deionized water in cellulose dialysis sacks with a molecular weight cutoff of 12,000 (Sigma-Aldrich). Dialysis occurred over 24 h with the water changed four times.

Synthesis of PVP-capped NPs. Chloroplatinic acid (H₂PtCl₆·6H₂O, 99.9% pure on metals basis) and polyvinylpyrrolidone (PVP) with a molecular weight of 29,000 were purchased from Sigma-Aldrich.

For the synthesis of 1.5 nm Pt particles, NaOH was dissolved in ethylene glycol (12.5 ml, 0.5 M). This solution was added to an ethylene glycol solution (12.5 ml) containing H₂PtCl₆·6H₂O (0.25 g, 0.48 mmol). During N₂ purging, this combined solution was heated to 160 °C and held for 3 h. The resulting NPs were precipitated with 2 M HCl and dispersed in an ethanol/PVP mixture.

For the synthesis of 2.9 nm Pt particles, aqueous H₂PtCl₆·6H₂O (20 ml of 6.0 mM) was added into 180 ml of methanol. PVP (133 mg) was then dissolved in this mixture and refluxed for 3 h.

For the synthesis of 5.0 nm Pt particles, freshly prepared 2.9 nm Pt particles were mixed in a 90% methanol/10% water solution (100 ml). Methanol (90 ml) and a solution of H₂PtCl₆·6H₂O (36.9 mg) in water (10 ml) were added and the combined mixture refluxed for 3 h.

Synthesis of mesoporous SBA-15 silica. Pluronic P123 (6.0 g, BASF) was dissolved in deionized water (45 g) and 2 M HCl (180 g) while stirring at 35 °C for 1 h. Tetraethylorthosilicate (12.8 g, Sigma Aldrich, 98%) was added to the solution and allowed to stir for 20 h. The mixture was then aged at 100 °C for 24 h. The mixture was filtered to give a white powder, which was further purified by washing with ethanol and deionized water. This purified product was dried in air at 100 °C and then calcined at 550 °C for 12 h. The white powder was stored in a desiccator.

Preparation of Pt/SBA-15 catalysts. Pt NPs were loaded onto the mesoporous SBA-15 silica before the catalytic studies. SBA-15 was added to a colloidal solution of the Pt NPs and the resulting slurry was sonicated for 3 h at room temperature. The NP supported SBA-15 was separated from the solution by centrifuge at 4,200 rpm for 6 min. After centrifugation, the solution was clear. The solution was then decanted and the catalyst was dried under ambient conditions and then at 100 °C.

PVP-encapsulated NPs were loaded to 1.0 wt% Pt. SBA-15 was used for 1.5 and 2.9 nm NPs. MCF-17 was used for 5.0 nm NPs. The larger size mesoporous silica was required for successful loading of the larger NPs.

Dendrimer-encapsulated NPs were loaded to 0.7 wt% Pt. SBA-15 was used as the support.

Representative procedure for catalytic reactions. To a dry 10 ml glass reaction tube with stirbar and Teflon screwvalve cap under Ar was added 2-(phenylethynyl)phenol (**1**) (20 mg, 0.1025 mmol), Pt(2.9 nm)/PVP/SBA-15 (50 mg, 0.0026 mmol, 2.5 mol%), PhICl₂ (2.1 mg, 0.0077 mmol, 7.5 mol%), mesitylene (15 μ l, internal standard, Aldrich) and toluene-d₈ (2 ml, Cambridge Isotopes). The reaction mixture was degassed (freeze/pump method) three times and placed under 1 atm of Ar. The reaction tube was sealed and the mixture heated with stirring to 100 °C for 15 hours. The mixture was then cooled to room temperature and the solid catalyst filtered by glass microfibre filter. The filtrate was transferred to a NMR tube for analysis.

For the Pt₄₀/G4OH/SBA-15 catalyst, before addition of all other reaction materials, the catalyst was added to the dry 10 ml glass reaction tube and placed under 1 atm of H₂. The catalyst was then heated to 100 °C for 24 hours. After

cooling to room temperature and replacing the H₂ atmosphere with Ar, the reaction setup was continued as discussed above.

2-Phenylbenzofuran (**2**) can be isolated in the following manner. The toluene solution containing the product from the catalytic reaction was concentrated and purified by flash chromatography (5% ethyl acetate/hexanes, Fisher ACS grade).

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Author contributions

C.A.W., W.H., C.-K.T. and J.N.K. performed the experiments and synthesized materials, substrates and catalysts. F.D.T. and G.A.S. supervised the research. All authors contributed to the conception of the experiments, discussed the results and commented on the manuscript.

Additional information

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