

Nesting Well-Defined Pt Nanoparticles within a Hierarchically Porous Polymer as a Heterogeneous Suzuki–Miyaura Catalyst

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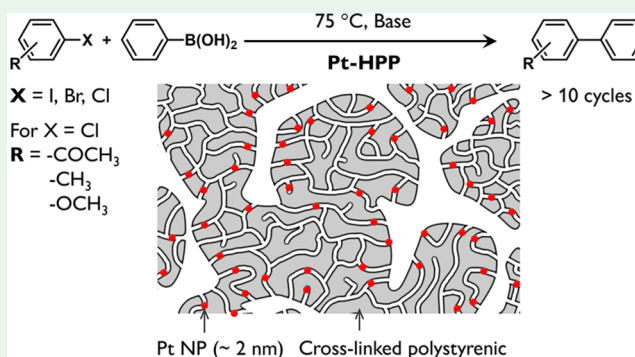
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Supporting Information

ABSTRACT: A hierarchically porous polymer (HPP) consisting of micropores (~1 nm) within a 3D continuous mesoporous wall (~15 nm) was used to support well-defined Pt nanoparticles (2 nm in diameter) as a heterogeneous catalyst for the Suzuki–Miyaura cross-coupling reaction in the liquid phase. The ligand-capped nanoparticles were loaded into the polymer and treated with plasma to expose the active surface. The dual porosity was essential: the block polymer-templated mesopores provided the reactants facile access to the nanoparticle center, which was firmly immobilized by the microporous surface. Compared to inorganic mesoporous silica supports, which are intrinsically susceptible to basic hydrolysis, the Pt-HPP featured higher activity for all halide leaving groups, even in green solvents, as well as excellent recyclability. Only 5% decrease in activity was observed after 10 cycles. Pt-HPP was one of the most active heterogeneous catalysts for aryl chloride substrates compared to literature Pt or Pd examples.

KEYWORDS: hierarchically porous polymer, block polymer self-assembly, Pt nanoparticle, Suzuki–Miyaura cross-coupling, heterogeneous catalysis



INTRODUCTION

Immobilization of metal nanoparticles onto solid supports has received much attention to overcome stability issues and difficulties in recovery in the homogeneous reactions. The heterogenized catalyst can offer easy purification and recyclability, while retaining excellent activity of the nanoparticles.^{1,2} Mesoporous oxides such as silica have been widely studied as the solid support because of their high specific surface area and excellent thermal stability. One particular application is the Suzuki–Miyaura cross-coupling of aryl halides with arylboronic acids for the synthesis of biaryls.³ Compared to immobilizing the catalytically active metal complex, metal nanoparticles can be loaded ligand-free in a synthetically more feasible manner and produce purer products.^{4,5} However, the oxide framework is intrinsically sensitive to the aqueous base which is typically used in the Suzuki–Miyaura reaction. The base can induce restructuring of the pore structure and even pore collapse, blocking reactant access to the nanoparticle, resulting in the loss of catalytic activity.⁶ This raises serious issues about recycling of the mesoporous oxide-supported metal nanoparticle catalysts.

Porous polymers constructed by C–C bonds can be an appealing alternative to mesoporous oxides. They typically feature high stability in aqueous environments and strong resistance against hydrolysis. Polymeric materials can be

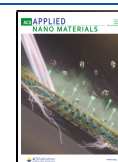
processed into various form factors, and the variety of synthetic methods available for tailoring pore functionality can be also beneficial for applications.^{7–9} In contrast to their inorganic counterparts, however, reports on metal nanoparticle-loaded mesoporous polymer supports have been scarce, including only two examples of heterogeneous catalysis via Suzuki–Miyaura coupling.^{10–13} Nonporous polystyrene,¹⁴ macroporous polystyrenics,^{15–17} and hyper-cross-linked polymers consisting of microporous cavities (<2 nm)^{4,18–22} have been previously used as metal nanoparticle supports such as Pd. While nanoparticles could be prepared within the swollen micropores by reducing the impregnated precursors, microporous channels inherently suffer from limited diffusion. The *in situ* nanoparticle synthesis also prevented the precise control of shape and dimension.

The synthesis of mesoporous polymers from block polymer precursors is an appealing methodology that offers exquisite control of pore size.^{23–25} Advanced controlled polymerization

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techniques allow for the precise synthesis of block polymers with target molecular weight and composition. A microphase-separated precursor with controlled domain size can be obtained and transformed into a mesoporous polymer upon the removal of the sacrificial block, while retaining the initial morphology. This approach has proven highly beneficial for lithographic and membrane applications in the form of thin films.^{26,27} However, this material class has rarely been used as a nanoparticle support for heterogeneous catalysis.^{28,29} Synthetically feasible and scalable routes to robust mesoporous polymers with high chemical and thermal stabilities have been missing. Access to aligned or 3D continuous porous channels has also been challenging and thus limited their use.

Here we present block polymer-based polymers with tunable micro- and mesopore structure as a metal nanoparticle-loaded catalyst support (Figure 1a). We harness a hierarchically

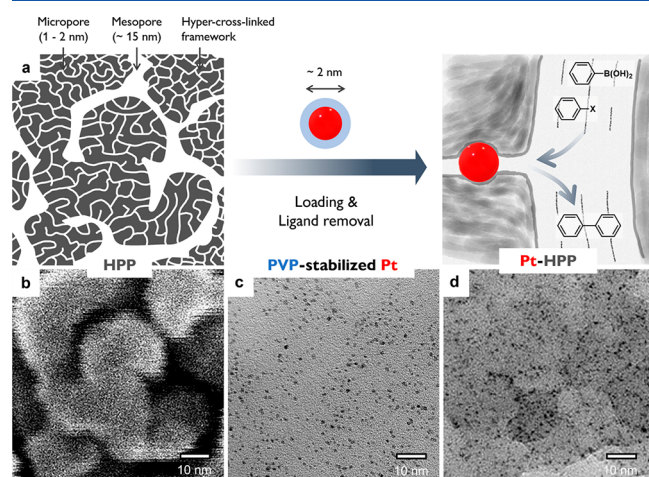


Figure 1. (a) Schematic depiction for preparing Pt-HPP as a heterogeneous catalyst for Suzuki–Miyaura cross-coupling. HPP consisting of micropores within the mesoporous framework is prepared. Then Pt nanoparticles stabilized by PVP are loaded into the micropores by sonication. The PVP ligand is removed by plasma etching to produce Pt-HPP, where the Pt surface is readily accessed by the reactants through the 3D continuous mesopores. (b) SEM image of HPP obtained after Os coating (~ 1 nm thick). Note that only the mesopore structure is visible in this condition. (c) HRTEM image of PVP-stabilized Pt nanoparticles. (d) HRTEM image of as-prepared Pt-HPP. The micrographs are on the same scale.

porous polymer (HPP) consisting of micropores within a 3D continuous mesoporous wall, which was synthesized by combining the polymerization-induced microphase separation (PIMS)³⁰ process with hyper-cross-linking.^{31–34} The hierarchical pore structure allows the reactants to rapidly diffuse through the mesoporous space and access the large surface area provided by the micropores, where the nanoparticles are hosted. The robust hyper-cross-linked framework provides chemical and thermal stability in the reaction condition, which is composed of both organic and aqueous solvents. We studied the Suzuki–Miyaura cross-coupling reaction catalyzed by Pt nanoparticles. In contrast to the conventional Pd-catalyzed systems, Pt nanoparticles were selected to take advantage of their stability and the tunability of electron-transfer reactions, which contribute to recyclable coupling reactions under mild conditions.^{35–37} To exploit the highly advanced nanoparticle chemistry, which can produce well-defined metal nanoparticles with exquisite control, we developed a methodology for

loading solution-synthesized Pt nanoparticles into the porous polymer and removing the capping agent in mild conditions by plasma treatment. The particle size was controlled to be ~ 2 nm to ensure uptake in the swollen micropores of HPP. This also allowed us to rigorously investigate the support effect without variation in the nanoparticles. While Pd nanoparticle-supported systems are more common for the cross-coupling reactions, we note that well-defined synthesis of Pd nanoparticles with comparable size is less straightforward.³⁸

The Pt-loaded polymer support, denoted Pt-HPP, outperformed the mesoporous and the microporous polymer supports, showing higher turnover frequency (TOF) and better recyclability, confirming the importance of the hierarchical pore structure. It also exhibited superior catalytic performance compared with mesoporous silica analogues SBA-15 and MCF-17 in terms of TOF, substrate scope, compatibility to green solvents, and recyclability.

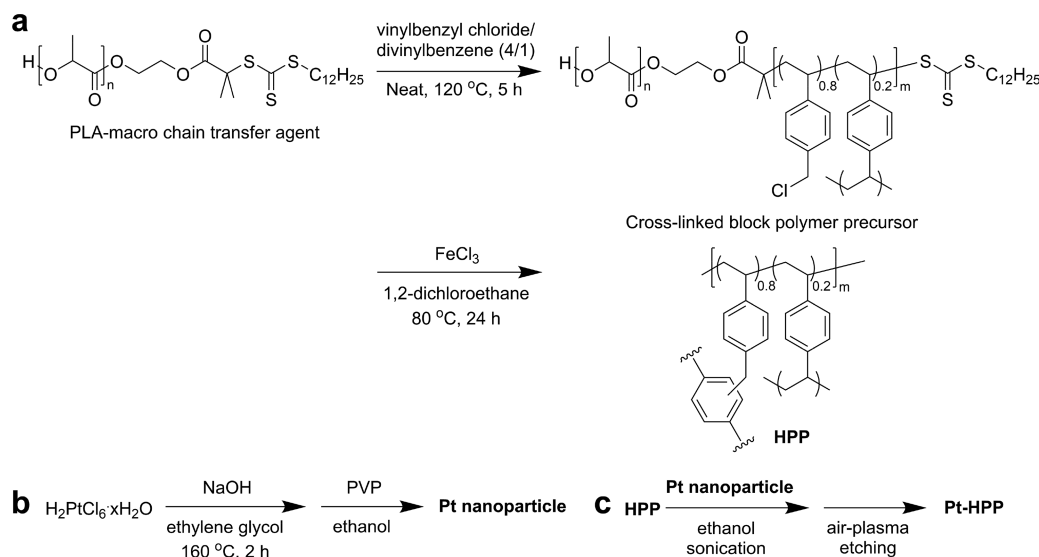
Remarkable recyclability was particularly noted in successive reactions, more than 10 times with only marginal activity loss. The prepared Pt-HPP turned out to be one of the most reactive and reusable heterogeneous catalysts for aryl chloride substrates. Thanks to the fine tunability of the hierarchical pore characteristics and tailorable surface chemistry, our results suggest HPP is a promising support for heterogeneous catalysis.

RESULTS AND DISCUSSION

Scheme 1 depicts synthetic routes to HPP and Pt nanoparticles used in this study. We synthesized HPP with a mode mesopore diameter (D) of 15.1 nm and a specific surface area of $690 \text{ m}^2 \text{ g}^{-1}$ (see the Supporting Information and Figures S1 and S2 for the synthetic details). Briefly, HPP was synthesized by neat reversible addition–fragmentation chain transfer (RAFT) copolymerization of vinylbenzyl chloride with divinylbenzene (4:1 in molar ratio) in the presence of poly(lactide) (PLA) macro-chain transfer agent (number-average molar mass of 50 kg mol^{-1} , 30 wt % in the reaction mixture) following the procedure published previously.^{31,32} The RAFT copolymerization grows a polystyrenic block off from the PLA chain end, inducing microphase separation, and also arrests the emerging disordered bicontinuous morphology by *in situ* cross-linking with divinylbenzene. Cross-linked block polymer precursor consisting of PLA and the cross-linked polystyrenic microdomains is obtained in high yield. Then Friedel–Crafts alkylation of the precursor with FeCl_3 as a Lewis acid generates micropores in the polystyrenic framework via hyper-cross-linking and simultaneously degrades the PLA to form the mesopores.

A representative scanning electron micrograph of the HPP is presented in Figure 1b, showing its 3D continuous mesopore structure (see Figure S2a for a low-magnification image). Micropores are not visible since the specimen is coated with Os for imaging. Nonetheless, the large uptake at small relative pressure in the nitrogen sorption isotherm clearly indicates the presence of micropores (Figure S2b). We prepared reticulated mesoporous polymer (RMP)^{30,31} and hyper-cross-linked polymer (HCP)³² as reference materials to investigate the contribution of the hierarchical pore structure to the catalytic performance (Figure S3). RMP contains only mesopores, and HCP exclusively develops micropores. We also prepared SBA-15 and MCF-17 as mesoporous silica analogues for comparison (Figure S4). Table S1 summarizes the pore characteristics of the porous materials used in this study.

Scheme 1. Synthetic Routes to HPP (a), Pt Nanoparticles (b), and HPP-Supported Pt Nanoparticles (Pt-HPP, c)



Pt nanoparticles with average diameter of 1.9 ± 0.3 nm and spherical shape were successfully synthesized by the polyol method using polyvinylpyrrolidone (PVP) as a capping agent³⁹ and were characterized by transmission electron microscopy (TEM) (Figure 1c and Figure S5). A stable suspension was obtained in ethanol without aggregation. The nanoparticles were then loaded into the porous support by sonication (see the Supporting Information for the synthetic details). The amount of Pt incorporated in the support was set as 2 wt % by adjusting the concentration of the suspension, as corroborated by inductively coupled plasma mass spectrometry (ICP-MS). The TEM image of as-prepared Pt-HPP supports that the Pt nanoparticles were well dispersed over the support (Figure 1d). Clustering of the nanoparticles was not noticeable.

The Pt nanoparticles could also be stably loaded into the HCP, but deposition was unstable in RMP. Micropores appear to be necessary to anchor the nanoparticles firmly. This suggests that the nanoparticles are hosted within the micropores of the HPP, not on the mesopore surface. Swelling of the hyper-cross-linked framework even in a nonsolvent such as ethanol seems to facilitate nanoparticle uptake into the micropores.⁴ For the mesoporous silica supports, a homogeneous dispersion of the nanoparticles on the surface was generally observed.⁴⁰

We developed a plasma treatment technique to effectively remove PVP from the Pt nanoparticle surface without damaging the porous structure. Degradation of the PVP during the air-plasma etching was tested with PVP film deposited on silicon wafer and monitored by Raman spectroscopy as well as by extent of weight loss (Figure S6). In the Raman spectra, the vibrational frequency at 2928 cm^{-1} corresponding to CH_2 stretching quickly diminished over time and became nearly indiscernible after 165 min. This was in good agreement with the mass decay, indicating successful degradation.

This condition was applied to the Pt-loaded supports, and their structural integrity was examined by small-angle X-ray scattering (SAXS). The characteristic scattering pattern of the HPP including a broad principal peak followed by a second-order shoulder persisted after the plasma treatment, indicating that the pore structure was well preserved (Figure S7a). The

extracted length scale was in good agreement with the mesopore size measured by BJH analysis (Table S2). Only minor changes in the roughness of ca. 0.5 nm were observed from the Porod plots (Figure S7b). In contrast, thermal degradation of the PVP at 230 °C destroyed the micropores.

To determine the catalytic capability of the Pt-HPP, the ligand-free Suzuki–Miyaura cross-coupling reaction of iodobenzene and phenylboronic acid was chosen as a test reaction (Scheme S1).⁴¹ The reactions were performed under gradual heating from 30 to 120 °C, systematically varying the reaction time from 1 to 5 h in the presence of appropriate amount (mol %) of Pt content. Combinations of different bases (1.4 equiv) and solvents (2 mL) were screened, and Bu_4NCl was applied as a phase transfer catalyst if necessary. The observations are collected in Figures S8–S12. The HPP itself was not active in the cross-coupling reaction without Pt loading. With increasing Pt content, the biphenyl yield rapidly increased and became saturated above 0.3 mol %. A mixture of polar aprotic *N,N*-dimethylformamide (DMF) with water (4:1 in volume) gave the best results for Pt-HPP, where the highest reactivity was observed. The reaction reached 100% conversion after 3 h with Cs_2CO_3 as a base at 100 °C. Other inorganic bases also showed good yields. Organic bases significantly decreased the conversions, except for Et_3N . These observations are consistent with previously published results.^{42–44} Lowering the reaction temperature to 75 °C still gave 96% conversion after 3 h. Under this condition, the catalytic performance of the Pt-HPP was further examined and compared to Pt-SBA-15 and Pt-MCF-17.

The Pt-HPP system was found to be the most efficient composite among the tested catalysts, as shown in Figure 2 (see also Figures S8–S12). While Pt-MCF-17 showed moderate activity in a single solvent medium, Pt-HPP outperformed both Pt-SBA-15 and Pt-MCF-17 when water was added as a cosolvent. The addition of protic solvents such as water and ethanol was generally much more effective for Pt-HPP. The different behavior may be related to the relatively hydrophobic HPP surface lacking hydroxyl groups. When a mixture of DMF and water was used, a TOF of 640 h^{-1} was achieved with Pt-HPP per surface Pt atom.⁴⁵ This was a 57% increase in value compared with Pt-SBA-15, which is well-

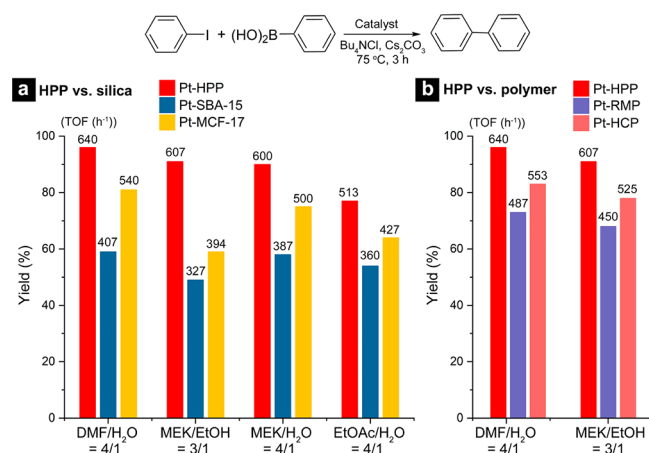


Figure 2. Suzuki–Miyaura cross-coupling reaction catalyzed by porous host-supported Pt nanoparticle: solvent and support effects. (a) HPP vs silica supports (SBA-15 and MCF-17). (b) HPP vs polymer supports (RMP and HCP). Reaction conditions: 1.0×10^{-3} mol of iodobenzene, 1.2×10^{-3} mol of phenylboronic acid, 1.2×10^{-3} mol of Bu_4NCl , 1.4×10^{-3} mol of Cs_2CO_3 , 0.3 mol % catalyst, 2.0 mL of solvent, $T = 75^\circ\text{C}$, and $t = 3$ h.

known for its 1D pore channels. Pt-HPP was also superior to Pt-MCF-17, which possesses a topologically similar 3D continuous mesopore structure, while the difference is much smaller than the Pt-SBA-15 case. The higher activity of Pt-MCF-17 compared with Pt-SBA-15 supports the importance of the 3D continuous mesopore structure.^{46,47}

Inspired by the remarkable activity of Pt-HPP and the absence of side reactions, we also screened some “green” solvents other than DMF, following the Pfizer solvent selection guide. Results obtained from the mixtures of methyl ethyl ketone (MEK) with ethanol (EtOH) (3:1), MEK with water (4:1), and ethyl acetate (EtOAc) with water (4:1) are shown (Figure 2a). The Pt-HPP system retained a catalytic activity similar to the level of DMF/H₂O. The MEK/EtOH mixture was a particularly effective medium for Pt-HPP, showing a TOF of 607 h^{-1} . In contrast, TOF values for Pt-SBA-15 and Pt-MCF-17 were only 54 and 65% that of Pt-HPP.

We posit that the relatively hydrophobic HPP surface can provide a more feasible environment for the cross-coupling reaction than the silica. The polystyrenic hydrocarbon HPP framework exposes the Pt nanoparticle to the aromatic reactants with enhanced affinity. Removal of the PVP was important to uncover the Pt surface and achieve high reactivity. Without the plasma treatment, Pt-HPP was only slightly active, showing more than 5 times smaller TOF (113 h^{-1}) (Figure S13). The high reactivity of Pt-HPP compared with the mesoporous Pt-RMP and the microporous Pt-HCP suggests there is a synergistic effect in the hierarchical pore structure of the HPP (Figure 2b). While the larger surface area provided by the micropores may be primarily more important, the 3D-interconnected mesopores seem to also enhance catalytic activity by promoting material transport.^{32,46}

Pt-HPP also exhibited superior recyclability compared to the mesoporous silica-supported catalysts in the MEK/EtOH mixture (Figure 3a). The yield in the model reaction only decreased by 5% from 91 to 86% after 10 cycles, supporting the stability of the HPP hydrocarbon framework in the basic medium. No significant Pt leaching, sintering, or deposition on the external HPP surface was observed from the used catalyst

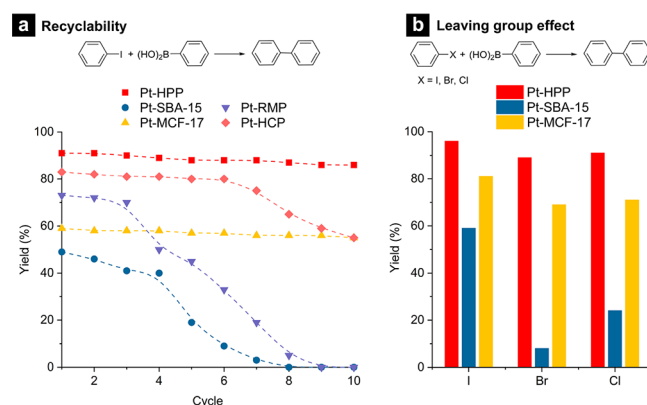


Figure 3. (a) Recyclability of Pt-HPP. Reaction conditions: 1.0×10^{-3} mol of iodobenzene, 1.2×10^{-3} mol of phenylboronic acid, 1.2×10^{-3} mol of Bu_4NCl , 1.4×10^{-3} mol of Cs_2CO_3 , 0.3 mol % catalyst, 2.0 mL of MEK:EtOH = 3:1, $T = 75^\circ\text{C}$, and $t = 3$ h. (b) Substrate scope. Reaction conditions: 1.0×10^{-3} mol of halobenzene, 1.2×10^{-3} mol of phenylboronic acid, 1.2×10^{-3} mol of Bu_4NCl , 1.4×10^{-3} mol of Cs_2CO_3 , 0.3 mol % catalyst, 2.0 mL of DMF:H₂O = 4:1, $T = 75^\circ\text{C}$, and $t = 3$ h.

and after hot filtration (Figure S14). In the filtered solution, 311.6 ± 2.8 ppb of Pt was detected by ICP-MS analysis. The reaction did not proceed further after filtration, supporting Pt nanoparticles catalyze the reaction (Figure S15). In contrast, the catalytic activity of Pt-SBA-15 decreased with the increasing number of cycles. The catalyst became completely inactive after the eighth cycle, presumably due to Pt leaching and restructuring of the pore structure.^{35,48,49} The 3D continuous pore structure of Pt-MCF-17 seemed helpful for retaining the activity, but a much lower yield (<60%) than Pt-HPP was observed.

Interestingly, the activities of the mesoporous and microporous analogues also dropped after three and six cycles, respectively. Pt-RMP was not stable under the reaction condition and showed no activity after nine cycles. These observations support that the micropore framework is more suitable for stably immobilizing the Pt nanoparticles but is inadequate for repeated use because it is more resistant to diffusion. HPP offers the ideal environment for heterogeneous catalysis, allowing facile diffusion to the active center, which is strongly bound to the support.

Preliminary screening also indicated higher reactivity of Pt-HPP to more challenging aryl halides, bearing industrially more relevant chloride and bromide leaving groups. In the DMF/water mixture, chlorobenzene and bromobenzene were successfully reacted with phenylboronic acid to produce biphenyl with 91 and 89% yield, respectively (Figure 3b). Again, the mesoporous oxide-supported catalysts showed inferior performances with low biphenyl selectivity, particularly in the case of Pt-SBA-15.

While it would be challenging to prove unambiguously, our data favor the heterogeneous mechanism for Pt-HPP by showing support-dependent reactivity and stability over successive reaction cycles, low level of Pt leaching, and much higher reactivity compared to homogeneous Pt catalysis.^{43,50} To our knowledge, this is the first study of Suzuki–Miyaura cross-coupling reactions catalyzed by heterogenized Pt nanoparticles on a porous polymer support. The high catalytic reactivity of Pt-HPP to challenging aryl chloride substrates is striking, where higher C–Cl bond strength disfavors oxidative

addition.⁵¹ Brief screening of the substrate scope indicated Pt-HPP generally works well, while electron-deficient substrates lowered the yield of the desired product (Figure S16). The catalytic activity showed almost no change over 10 cycles even with chlorobenzene (Figure S17). We have compared performances of Pt-HPP to some relevant examples^{4,17,20,52–59} reporting the Suzuki–Miyaura reaction with chlorobenzene or 4'-chloroacetophenone catalyzed by Pd nanoparticle-immobilized supports in Table S3. The key parameters are plotted in Figure 4. It is apparent that Pt-HPP is one of the best reactive

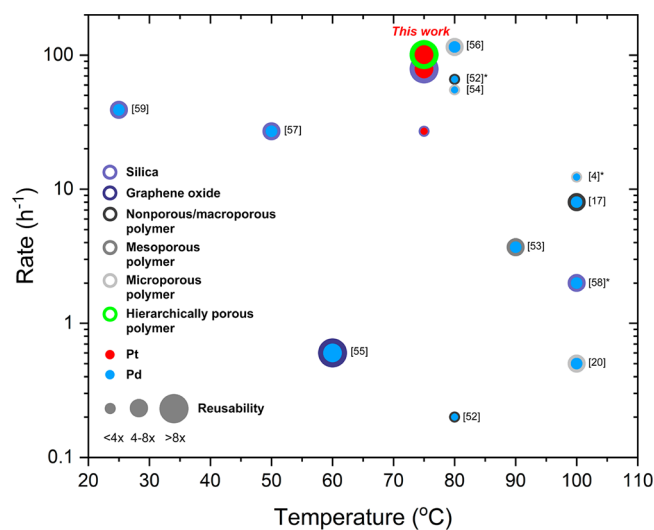


Figure 4. Reaction temperature–rate plot of Pt-HPP, Pt-SBA-15, and Pt-MCF-17 with some Pd nanoparticle-immobilized supports reported in the literature. Rate (h^{-1}) is given per total catalyst loading for comparison. Recyclability is also indicated as the size of the data point. Data obtained with chlorobenzene and/or 4'-chloroacetophenone (marked with *) were chosen. See Table S3 for the detailed reaction conditions.

catalysts as well as having excellent recyclability and mild reaction conditions. The tailorable pore surface chemistry and framework composition of HPP suggest there is huge room for further enhancement of catalytic performance.

CONCLUSIONS

In conclusion, a heterogenized Pt nanoparticle catalyst supported on a well-defined hierarchically porous polymer was prepared and used in ligand-free Suzuki–Miyaura cross-coupling reactions. Uniform Pt nanoparticles with 2 nm diameters were separately synthesized in solution, and successfully loaded into the support, consisting of micropores within a 3D continuous mesoporous framework. We developed a plasma treatment as a mild yet effective method for removing the capping agent of the Pt nanoparticle immobilized in the support, thus exposing the active center to the reactants. We note that we have not experienced noticeable challenges in multigram scale synthesis, and we do not see fundamental bottlenecks for scaling up further. The Pt-HPP system achieved a cross-coupling product with excellent yield and presented remarkable catalytic behavior under mild reaction conditions and in green solvents. Moreover, the as-prepared catalyst proved to be more active to aryl chloride substrates and—more importantly—was highly stable, running 10 times in successive reactions without any changes, unlike the majority of previous supported Pt and Pd nanoparticle systems.

Compared to silica-supported systems susceptible to basic hydrolysis, and other micro- and mesoporous polymer analogues, the hierarchically porous polymer framework stably hosted Pt nanoparticles on the microporous surface in a readily accessible environment provided by the percolating mesopores. We envision that this newly developed methodology will open a route to new heterogeneous catalytic systems, with precise tuning of the structure and functionality of the polymer support, in combination with a variety of well-defined metal nanoparticles with complex shapes and compositions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsnm.1c00396>.

Synthesis and characterization data of supports and Pt nanoparticles, loading of Pt nanoparticles onto supports, monitoring of PVP removal by Raman and SAXS analyses, screening and optimization of Suzuki–Miyaura cross-coupling reaction conditions, comparison of reaction conditions for aryl chloride substrates (PDF)

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S.K. and G.V. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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