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Palladium Nanoclusters Supported on Propylurea-Modified Siliceous Mesocellular Foam for Coupling and Hydrogenation Reactions

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Abstract: This paper describes the synthesis, characterization and applications of palladium (Pd) nanoparticles supported on siliceous mesocellular foam (MCF). Pd nanoparticles of 2–3 nm and 4–6 nm were used in reactions involving molecular hydrogen (such as hydrogenation of double bonds and reductive amination), transfer hydrogenation of ketones and epoxides, and coupling reactions (such as Heck and Suzuki reactions). They successfully catalyzed all these reactions with excellent yield and selectivity. This heterogeneous catalyst was easily recovered by filtration, and recycled several times without any significant loss in activity and selectivity. The palladium leaching in the reactions was determined to be much less than the FDA-approved limit of 5 ppm. Furthermore, the catalyst can be stored and handled under normal atmospheric conditions. This immobilized catalyst allows for ease of recovery/reuse and minimization of waste generation, which are of great interest in the development of green chemical processes.

Keywords: C−C coupling reactions · heterogeneous catalysis · hydrogenation · mesoporous materials · palladium nanoparticles

Introduction

The pharmaceutical industry produces 25–100 kg or more of waste for every kg of active pharmaceutical ingredient (API) manufactured.[1] According to a leading practitioner of the industry, the potential waste co-produced with APIs is in the range of 500 million to 2 billion kg per year.[2] Thus, the potential savings associated with waste reduction would be significant compared to pharmaceutical industry's annual sales (US$500 billion in 2003).[2] Most pharmaceuticals syntheses involve the use of homogeneous catalysts, which are difficult to separate from the products. The resulting metal contamination of the products poses a serious concern in the pharmaceutical industry.[3] Heterogeneous catalysts may be more stable, less expensive, and more easily separated from the products.[4] However, their activity and selectivity are often lower than that of homogeneous catalysts.[5] Thus, increasing efforts have been devoted towards developing more efficient heterogeneous catalysts.[6,10] Immobilized homogeneous catalysts would provide for ease of catalyst recovery and reuse, and would minimize the waste generation and use of toxic chemicals, which is of great interest in the development of green chemical processes.[7]

This work is focused on designing supported palladium catalysts. Palladium-catalyzed reactions have become an important tool in organic synthesis, owing to their high efficiency, selectivity, and their ability to perform a range of possible transformations.[8] Palladium-based catalysts have shown remarkable performance in coupling and hydrogenation reactions.[9] However, despite their high activity, the homogeneous palladium-based catalysts suffer from low stability and high costs, which prevent their application in industrial processes. As a heavy metal, palladium is also highly undesirable as a contaminant of pharmaceutical products. To overcome these challenges associated with conventional palladium-based catalysts, heterogeneous and heterogenized catalysts have been developed.[10] Palladium has been supported on materials such as carbon, zeolites, silicates and polymers for catalytic applications.[11] Although these supported palladium catalysts allowed for ease of recovery, palladium leaching remained a significant problem.[12]

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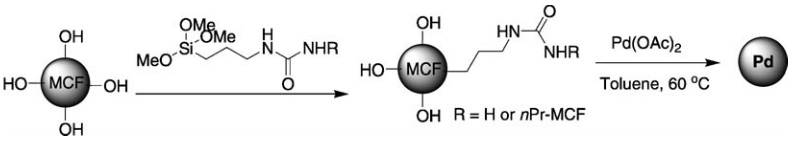
Results and Discussion

In this study, palladium was immobilized on siliceous mesocellular foam (MCF) through the use of urea ligands (see Scheme 1). MCF was selected as the support, as it possesses a three-dimensional, interconnected pore structure with ultralarge cell-like pores (24–42 nm) connected by windows of 9–22 nm.[13] Templated by oil-in-water microemulsions, MCF also has a high surface area of 500–800 m^2g^{-1} and a high surface concentration of silanols. The urea groups were introduced onto the pore surface of spherical MCF microparticles[14] by reacting $(CH_3O)_3Si(CH_2)_3NHCONH_2$ or $(CH_3O)_3Si(CH_2)_3NHCONH(CH_2)_3Si(OCH_3)_3$ with 550°C-calcined MCF in toluene at 80°C for 24 h. The urea ligand loading in the resulting Urea-MCF was determined by elemental analysis to be 1.8 $mmol\,g^{-1}$. $Pd(OAc)_2$ (1.5 mmol) was dissolved in toluene/ethyl acetate, and introduced to Urea-MCF (1 g). The mixture was stirred at room temperature for 30 min, and then heated at 60°C for 24 h. The initially dark brown palladium acetate solution was reduced to elemental palladium, and was deposited onto the MCF support via the urea ligands. The Pd/Urea-MCF was filtered, washed and dried. The supernatant was clear after the reaction, indicating the complete formation and immobilization of Pd on MCF after the heating and drying processes.



Scheme 1. Immobilization of Pd nanoclusters on Urea-MCF.

The Pd nanoclusters deposited on Urea-MCF have a size distribution in the range of 4–6 nm (Figure 1), and were dispersed uniformly on the support (see Figures S1 and S2 in the Supporting Information). The size of the nanoclusters could also be controlled by changing the $Pd(OAc)_2$ concentration during the synthesis. For example, if the amount of $Pd(OAc)_2$ was reduced by half, a similar procedure would result in the formation of 2–3 nm Pd particles (Figure 2). Scanning transmission electron microscopy (STEM) (Figure S3 in the Supporting Information) and Si and Pd mapping by transmission electron microscopy (TEM) (see the Movie S1 in the Supporting Information) illustrated the uniformity of the Pd particles dispersed within the mesopores of MCF. Scanning electron microscopy (SEM) (Figure 3) and nitrogen adsorption-desorption isotherms (Figures S4 and S5 in the Supporting Information) illustrated that the uniform, ultralarge mesopores of the MCF support were retained in the Pd/Urea-MCF catalysts. X-ray diffraction (XRD) studies confirmed the ultrafine grain size and high dispersion of Pd nanoclusters in the Pd/Urea-MCF catalyst (see Figures S6 and S7a in the Supporting Information).

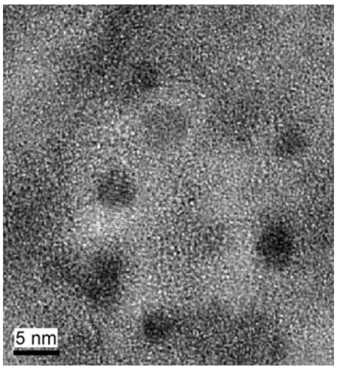


Figure 1. TEM micrograph of Pd/Urea-MCF with Pd nanoclusters of 4–6 nm.

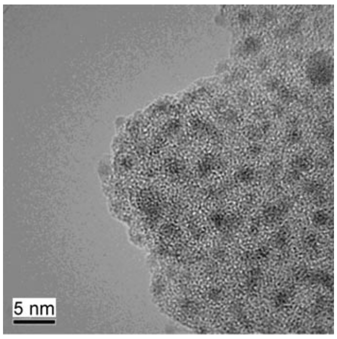


Figure 2. TEM micrograph of Pd/Urea-MCF with Pd nanoclusters of 2–3 nm.

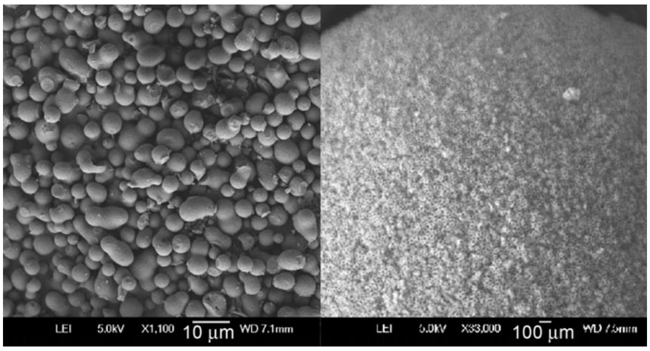
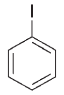
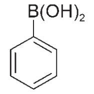
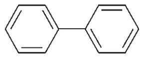
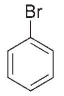
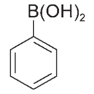
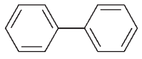
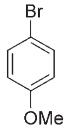
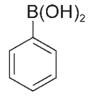
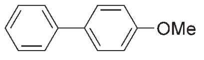
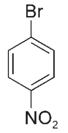
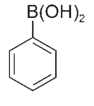
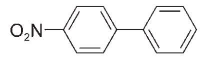
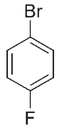
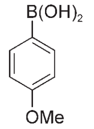
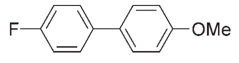
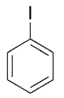
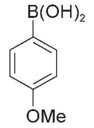
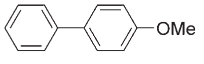


Figure 3. SEM micrographs of Pd/Urea-MCF microparticles.

The catalytic activity of Pd/Urea-MCF was examined for the Suzuki coupling reaction of iodoanisole and phenyl boronic acid in an ethanol/water mixture (9:1 volume ratio), by using Na_2CO_3 as the base (Table 1). After 24 h, the coupling product was isolated in 99% yield (Table 1, entry 1). Pd/

Table 1. Suzuki coupling of aryl halides with aryl boronic acids.[a]

Entry	Aryl halide	Aryl boronic acid	Product	t [h]	Yield [%][b]
1				6	99
				0.167[c]	99[c]
2				12	89
3				12	97
4				12	94
5				12	91
6[d]				12	99
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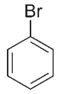
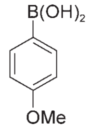
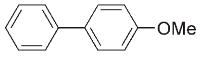
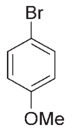
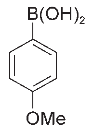
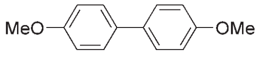
7				20	96
8				12	92

[a] Reaction conditions: 1 mol% of 5 wt% Pd/Urea-MCF catalyst with Pd nanoclusters of 2–3 nm, 1 mmol of aryl halide, 1.25 mmol of aryl boronic acid, 1.5 mmol of sodium carbonate, 5 mL of ethanol/water mixture (volume ratio = 9:1), 80 °C, argon atmosphere. [b] Isolated yield. [c] Under microwave conditions. [d] Recycled five times without any loss in the product yield. [e] Volume ratio of ethanol/water mixture used = 1:1.

Urea-MCF catalysts with 2–3 nm and 4–6 nm Pd nanoclusters were compared to commercial 10 wt% Pd/C catalyst (Sigma-Aldrich) with 2–3 nm Pd nanoclusters for the Suzuki coupling of iodobenzene and phenylboronic acid. Pd/Urea-MCF with 2–3 nm Pd nanoclusters outperformed the commercial 10 wt% Pd/C catalyst and the Pd/Urea-MCF catalyst with 4–6 nm Pd nanoclusters (Figure 4). Pd leaching was examined by analyzing the supernatant of the reaction. No Pd was found to have leached from the Urea-MCF support even after 5 days of a blank experiment under similar reaction conditions. The Suzuki reaction proceeded faster when the solvent was changed to an ethanol/water mixture of 1:1 volume ratio at 80 °C (Table 1, entry 6), giving a 98% yield in 6 h instead of 24 h under the typical homogeneous reaction conditions.[15]

Pd/Urea-MCF catalyst also provided excellent yields for the Heck coupling of iodoarenes (Table 2). Coupling of iodo and bromoarenes with acrylates resulted in the corresponding cinnamate esters in good to excellent yields. The catalyst was recycled without any significant loss in activity and selectivity in the coupling reaction of iodobenzene with *n*-butyl acrylate (Table 2, entry 5).

Excellent yields were achieved for the transfer hydrogenation of various ketones over Pd/Urea-MCF. Typically, transfer hydrogenation of ketones was carried out using 10 mol% of the 5 wt% Pd/Urea-MCF catalyst and 5 equivalents of formic acid/triethylamine mixture as the hydrogen source in ethyl acetate at room temperature. The heterogeneous catalyst was easily recovered and reused several times without any loss in reactivity and selectivity (Table 3). After 10 runs of transfer hydrogenation of acetophenone (Table 3, entry 1), the Pd nanoclusters remained highly dispersed on Urea-MCF (Figure 5), and the catalyst demonstrated negligible loss in activity. The X-ray diffraction (XRD) pattern of Pd/Urea-MCF consisted of Pd^0 peaks. Peak broadening analysis by Scherrer's method indicated that the average Pd crystallite

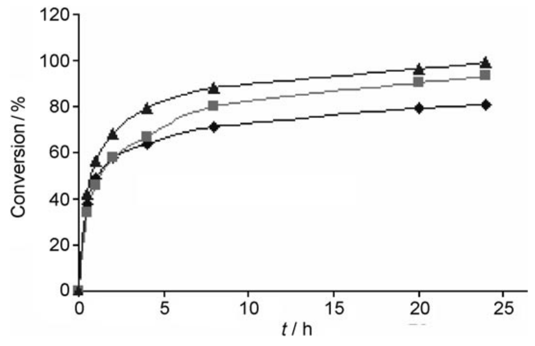
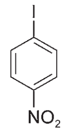
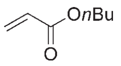
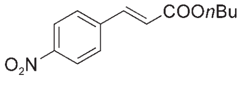
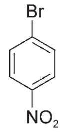
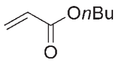
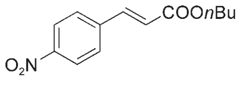
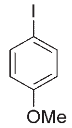
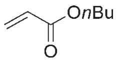
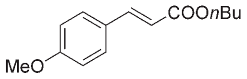
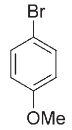
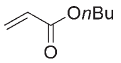
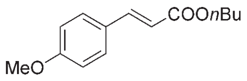
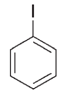
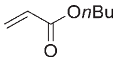
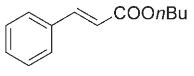
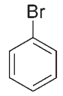
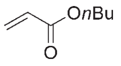
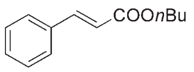
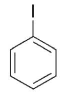
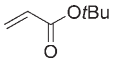
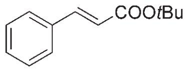
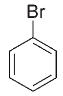
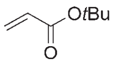
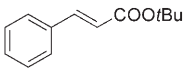


Figure 4. Suzuki coupling of iodobenzene and phenylboronic acid (first run) over (◆) 10% Pd/C, and Pd/Urea-MCF with (▲) 2–3 nm and (■) 4–6 nm Pd nanoclusters.

Table 2. Heck coupling of aryl halides and alkenes.[a]

Entry	Aryl halide	Alkene	Product	t [h]	Yield [%][b]
1				18	96
2				24	92
3				18	95
4				24	89
5[c]				20	92
6				24	88
7				20	93
8				24	84

[a] Reaction conditions: 1 mol% of 5 wt% Pd/Urea-MCF catalyst with Pd nanoclusters of 2–3 nm, 1 mmol of aryl halide, 1.25 mmol of olefin, 2 mmol of triethylamine, 5 mL of toluene, 100 °C, argon atmosphere. [b] Isolated yield. [c] Recycled five times without loss in activity and selectivity.

size grew slightly from 2–3 nm to 4–5 nm after 10 runs (see Figure S7a,b in the Supporting Information). The filtrate of the reaction system was clear (see Figure S8b in the Supporting Information); inductively coupled plasma mass spectrometry (ICP-MS) confirmed that only a total of 1.25% of the Pd loaded in 5 wt% Pd/Urea-MCF was leached after 10 runs. In contrast, the filtrate of the reaction system containing 10 wt% Pd/C was brown in color (see Figure S8a in the Supporting Information), owing to almost 90% leaching of the Pd loaded after just one run. Interestingly, when the transfer hydrogenation of various ketones was performed in water at 60 °C with ammonium formate as the hydrogen source instead of formic acid/triethylamine mixture, the reaction was completed more rapidly (i.e., in 2 h instead of 24 h), giving an excellent yield of the corresponding alcohol.

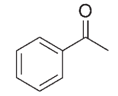
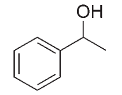
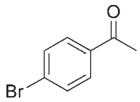
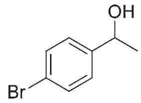
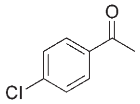
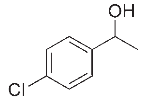
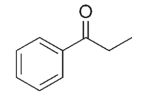
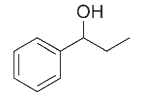
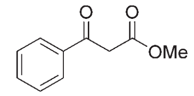
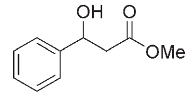
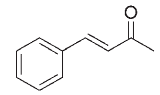
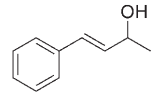
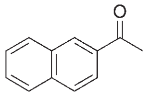
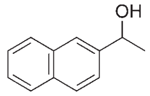
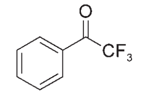
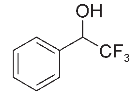
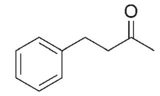
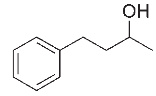
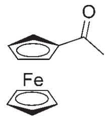
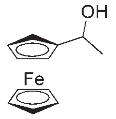
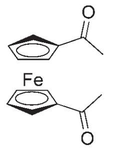
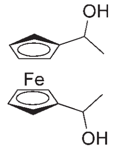
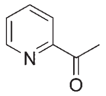
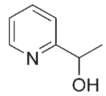
Pd/Urea-MCF was also examined for the hydrogenation of activated olefins (Table 4) such as dimethylitaconate (Table 4, entry 1) under a low pressure (40 psi). The hydrogenated product, 1-methyl-dimethylsuccinate, was obtained in 99.9% yield, and the catalyst was successfully recycled and reused for 10 runs without any loss in activity. Hydrogenation also proceeded with excellent yield and catalyst recyclability for a variety of olefins (Table 4).

Next, the catalytic activity of Pd/Urea-MCF for the reductive amination of aldehydes and amines was examined. This reaction is very important for producing secondary amines in the pharmaceuticals and specialty chemicals industry. Excellent conversions and yields of the corresponding amines were achieved under mild conditions, and the catalyst was recycled 10 times without any significant loss in reactivity and selectivity (Table 5).

The reductive ring opening of epoxides to the corresponding alcohols has emerged as a powerful tool in organic synthesis. It is of great interest to develop a practical, economical, and environmentally friendly process for this reaction. The efficiency and stability of Pd/Urea-MCF catalyst were examined with *trans*-stilbene oxide as a substrate (Table 6, entry 4). Notably, the hydrogenolysis reaction reached completion with excellent yields in 10 successive runs. The catalyst could be recovered by simple filtration, and be reused without loss of activity. A variety of benzylic epoxides were then subjected to the same hydrogenolysis conditions, and good yields of homobenzylic alcohols were obtained consistently. To further extend the scope of this catalytic system, we turned our attention to the hydrogenolysis of chiral epoxides, which are used for the synthesis of anti-inflammatory arylpropionic acids. Hydrogenolysis of chiral α-methylstyrene oxide generated the corresponding terminal alcohol with the retention of configuration in excellent yield (Table 6, entry 8).

In the cases of transfer hydrogenation, hydrogenation, hydrogenolysis, and reductive amination, the total Pd leached after 10 recycles was determined by ICP-MS to be <1.5% of the total Pd loaded in the catalyst. In the cases of Heck and Suzuki coupling reactions, the total Pd leached after 5 recycles was <5% as determined by ICP-MS. The supernatant of the heterogeneous reaction systems containing Pd/Urea-MCF was very clear (Figures S8 and S9 in the Sup-

Table 3. Transfer hydrogenation of ketones.[a]

Entry	Ketone	Product	t [h]	Yield [%][b]
1[c]			24	87
			0.25[d]	85
			2[e]	82
2			24	88
			2[e]	84
3			24	88
4			24	84
			2[e]	80
5			18	96
6[c]			18	99
7			24	92
			2[e]	94
8			48	99
9			24	95
10[c]			12	99
11			12	99
12			15	99

[a] Reaction conditions: 10 mol % of 5 wt % Pd/Urea-MCF catalyst with Pd nanoclusters of 2–3 nm, 1 mmol of ketone, 5 mmol of formic acid/triethylamine (volume ratio = 1:1), 5 mL of ethyl acetate, 25 °C. [b] Isolated yield. [c] Recycled 10 times without any loss in activity and selectivity. [d] Under microwave conditions. [e] Used ammonium formate as hydrogen source and water as solvent at 60 °C.

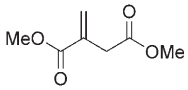
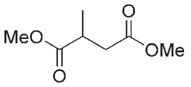
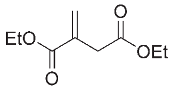
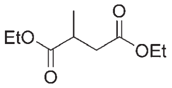
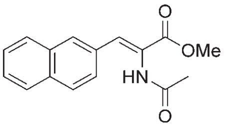
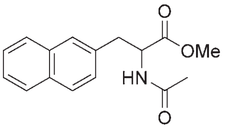
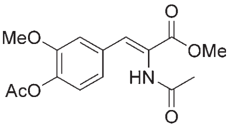
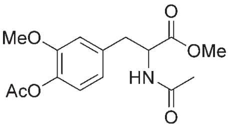
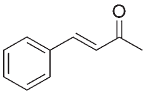
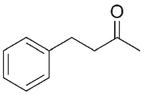
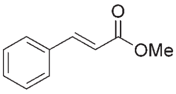
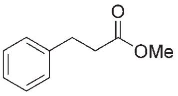
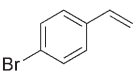
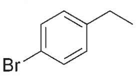
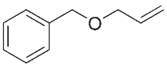
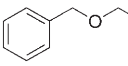
porting Information). Negligible leaching of Pd was observed, and this novel catalyst could be easily isolated and recycled. A comparative study of Pd/Urea-MCF with Pd/silica gel and Pd/unmodified MCF in the Suzuki coupling of iodobenzene and p-methoxyphenyl boronic acid as well as the transfer hydrogenation of acetophenone demonstrated the advantage of urea ligand in the formation and stabililization of nanoparticles (Table S1 in the Supporting Information).

Pd/Urea-MCF was found to provide even faster reaction rates for coupling reactions and transfer hydrogenations with the aid of microwave. Excellent conversions were achieved under low frequency and short reaction period. For example, 99 % conversion was attained in 10 min in the Suzuki coupling of iodobenzene and phenylboronic acid (Table 1, entry 1). 85 % yield of the corresponding alcohol was achieved in 15 min for the transfer hydrogenation of acetophenone under microwave (Table 3, entry 1). In contrast, 87 % yield would be obtained in 24 h under normal reaction conditions at room temperature.

Conclusion

In conclusion, active Pd nanoclusters could be easily prepared with high yields on urea-modified MCF. They were formed by the reduction of Pd-$(OAc)_2$, and were stabilized by the urea ligands on the MCF surface. The ultralarge mesopores of MCF facilitated reactions involving bulky substrates. The resulting Pd/Urea-MCF catalyst demonstrated excellent activity for transfer hydrogenation, hydrogenation and C−C coupling reactions, and were superior to commercially available 10 wt % Pd/C or polymer-supported Pd-Encat.[16] The facile synthesis and novel design of supported metal catalyst described herein might be widely applied to derive metallic nanoclusters supported on modified MCF for a wide variety of catalytic reactions in chemical syntheses. We are currently examining other Pd-catalyzed reactions, and im-

Table 4. Hydrogenation of olefins.[a]

Entry	Olefin	Product	t [h]	Yield [%][b]
1[c]			6	99.9
2			6	99.9
3			6	99.9
4			6	99.9
5			8	99.9
6[c]			8	99.9
7			18	99
8			18	99

[a] Reaction conditions: 1 mol% of 5 wt% Pd/Urea-MCF catalyst with Pd nanoclusters of 2–3 nm, 1 mmol of olefin, 40 psi or 100 psi of hydrogen (for entries 1–6 and 7–8, respectively), 5 mL of methanol/ethanol, 25 °C. [b] Isolated yield. [c] Recycled 10 times without any loss in product yield.

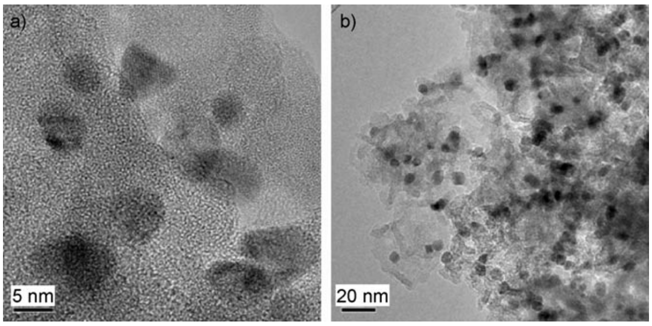


Figure 5. TEM micrographs of Pd/Urea-MCF catalysts with Pd nanoclusters of a) 4–6 nm and b) 2–4 nm after 10 runs of transfer hydrogenation of acetophenone at room temperature.

mobilizing other metals (e.g. Rh, Ru, Cu, Ir, and In) on MCF for various catalytic applications.

Experimental Section

All chemicals were purchased from Aldrich, and used as received without further purification. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy (Bruker 400 MHz Spectrometer), Fourier-transform infrared (FTIR) spectroscopy (Digilab FTS7000 FTIR spectrometer equipped with MTEC 300 photoacoustic detector), XRD (Philips XPert PRO X-ray diffraction system), N_2 adsorption-desorption analysis (Micromeritics ASAP 2020M system), elemental analysis (Exeter Analytical CE440 CHN analyzer), TEM and STEM (FEI Tecnai G20, 200 kV), SEM (JEOL JSM-6700F) and ICP-MS (Elan DRCII, PerkinElmer SCIEX) were employed in catalyst characterization. Products from catalytic reactions were analyzed by GC (Agilent 6890N).

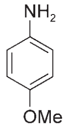
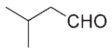
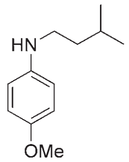
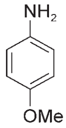
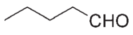
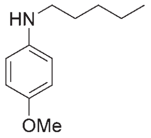
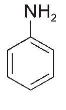
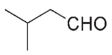
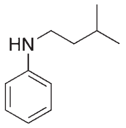
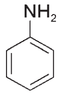
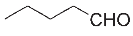
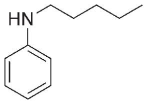
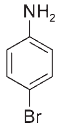
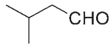
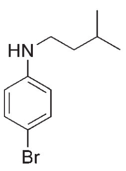
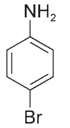
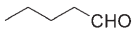
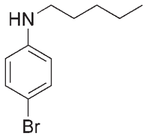
Synthesis of Urea-MCF: Spherical MCF microparticles (1 g) synthesized according to the method reported[14] were dried for 24 h at 100 °C, and cooled to room temperature under argon. Dry toluene (20 mL) was added to the MCF. Next, a solution of trimethoxysilylpropyl urea (2.2 mmol) in toluene (2 mL) was introduced. The mixture was stirred under argon for 10 min, and then heated at 80 °C for 24 h. It was cooled to room temperature, filtered, and washed several times with toluene, ethanol, acetone and dichloromethane to remove any unreacted precursor. The resulting material was suspended in ethanol, and heated at 60 °C overnight, filtered, washed and dried. Elemental analysis showed a loading of 1.80 mmol of urea per gram of MCF.

Synthesis of Pd/Urea-MCF: Urea-MCF (1 g) was suspended in dry toluene (20 mL), and a solution of palladium acetate (0.55 or 1.10 mmol depending on the requirement) in CH_2Cl_2 (2 mL) was added dropwise. The mixture was heated at 60 °C until the supernatant became colorless under argon (24 h). It was then cooled to room temperature, filtered, washed and dried to obtain a dark brownish black solid, Pd/Urea-MCF. Elemental analysis showed 0.55 or 1.10 mmol of Pd loading per gram of Urea-MCF, corresponding to 5 wt% Pd/Urea-MCF or 10 wt% Pd/Urea-MCF, respectively.

General Procedure for Suzuki Coupling Reaction: An oven-dried reaction vial was charged with aryl halide (1 mmol), aryl boronic acid (1.25 mmol), sodium carbonate (1.5 mmol), catalyst (1 mol% of 5 wt% Pd/Urea-MCF), ethanol (4.5 mL) and water (0.5 mL) under argon. The resulting reaction mixture was stirred at room temperature for 10 min, and then heated at 80 °C for a desired period. The reaction was monitored by GC. After completion of the reaction, the mixture was cooled to room temperature, and was filtered through a sintered glass funnel, washed with water (5×5 mL) and ethanol (5×5 mL), and dried under vacuum. The catalyst was recycled five times.

General Procedure for Heck Coupling Reaction: An oven-dried reaction vial was charged with aryl halide (1 mmol), olefin (1.25 mmol), triethylamine (2 mmol), catalyst (1 mol% of 5 wt% Pd/Urea-MCF), and toluene (5 mL) under argon. The resulting reaction mixture was stirred at room temperature for 10 min, and then heated at 100 °C for a desired period. The reaction was monitored by GC. After completion of the reaction, the mixture was cooled to room temperature, and was filtered through a

Table 5. Reductive amination of aldehydes.[a]

Entry	Amine	Aldehyde	Product	t [h]	Yield [%][b]
1[c]				6	99.9
2[c]				8	99.9
3				6	99.9
4				8	99.9
5				6	99.9
6				8	99.9

[a] Reaction conditions: 1 mol% of 5 wt% Pd/Urea-MCF catalyst with Pd nanoclusters of 2–3 nm, 1.01 mmol of amine, 1.0 mmol of aldehyde, 40 psi of hydrogen, 5 mL of methanol, 25 °C. [b] Gas chromatography (GC) yield. [c] Recycled 10 times without any loss in activity and selectivity.

sintered glass funnel, washed with toluene (5×5 mL), and dried under vacuum. The catalyst was recycled five times.

General Procedure for Transfer Hydrogenation of Ketones: An oven-dried reaction vial was charged with ketone (1 mmol), formic acid/triethylamine mixture (volume ratio = 1:1) or ammonium formate (5 mmol), catalyst (10 mol% of 5 wt% Pd/Urea-MCF) and ethyl acetate or water (5 mL) under argon. The resulting reaction mixture was stirred at room temperature for 24 h, and the progress of the reaction was monitored by GC. After completion of the reaction, the mixture was filtered through a sintered glass funnel, washed with ethyl acetate (5×5 mL), and dried under vacuum. The catalyst was recycled 10 times.

General Procedure for Hydrogenation of Olefins: An oven-dried reaction vial was charged with olefin (1 mmol), catalyst (1 mol% of 5 wt% Pd/Urea-MCF) and methanol/ethanol (5 mL) under argon. The resulting reaction mixture was pressurized with 40–100 psi of hydrogen, and was stirred at room temperature for 6 h. The progress of the reaction was monitored by GC. After completion of the reaction, the mixture was filtered through a sintered glass funnel, washed with methanol (5×5 mL), and dried under vacuum. The catalyst was recycled 10 times.

General Procedure for Reductive Amination of Aldehydes under Hydrogen: An oven-dried reaction vial was charged with aldehyde (1.0 mmol), primary amine (1.01 mmol), catalyst (1 mol% of 5 wt% Pd/Urea-MCF) and methanol (5 mL) under argon. The resulting reaction mixture was pressurized with 40 psi of hydrogen, and was stirred at room temperature for 6 h. The progress of the reaction was monitored by GC. After completion of the reaction, the mixture was filtered through a sintered glass funnel, washed with methanol (5×5 mL), and dried under vacuum. The catalyst was recycled 10 times.

General Procedure for Hydrogenolysis of Epoxides and Diols: An oven-dried reaction vial was charged with epoxide or diol (1 mmol), ammonium formate (5 mmol), catalyst (10 mol% of 5 wt% Pd/Urea-MCF) and ethyl acetate (5 mL) under argon. The resulting reaction mixture was stirred at room temperature for 24 h, and the progress of the reaction was monitored by GC. After completion of the reaction, the mixture was filtered through a sintered glass funnel, washed with ethyl acetate (5×5 mL), and dried under vacuum.

Acknowledgements

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[1] This refers to the concept of atom efficiency applied to chemical synthesis presented by B. Trost and R. Sheldon. See for example, T. Collins, *Science* **2001**, *291*, 48–49.

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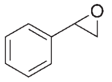
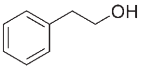
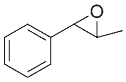
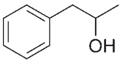
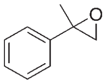
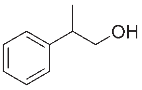
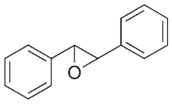
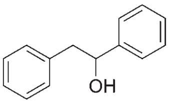
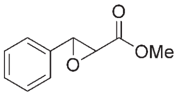
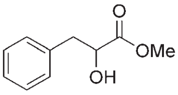
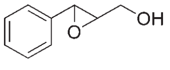
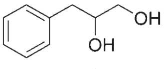
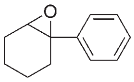
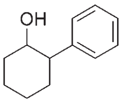
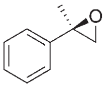
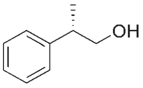
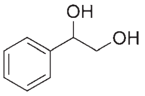
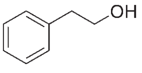
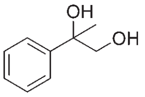
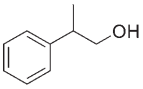
Table 6. Hydrogenolysis of epoxides and diols.[a]

Entry	Epoxide/diol	Product	t [h]	Yield [%][b]
1			12	91
2			12	94
3			12	97
4[c]			24	99
5			24	94
6			24	98
7			24	86
8[d]			12	98
9			12	88
10			12	94

[a] Reaction conditions: 10 mol% of 5 wt% Pd/Urea-MCF catalyst with Pd nanoclusters of 2–3 nm, 1 mmol of epoxide or diol, 5 mmol of ammonium formate, 5 mL of ethyl acetate, 25 °C. [b] Isolated yields. [c] Recycled 10 times without any loss in reactivity and selectivity. [d] Retention of configuration.

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