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Electronic Supplementary Information

Magnetically Recyclable Core-Shell Nanocatalysts for Efficient Heterogene ous Oxidation of Alcohols

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Synthesis of core-shell magnetic NPs with silica layer supported Pd NPs

These nanostructures were synthesized without polymer shell in which Pd NPs were loaded by NaBH $_4$ reduction process on the silica layer of the core-shell NPs. While vigorous stirring, 200 mg K₂PdCl₄ dissolved in water was added dropwise to the EtOH dispersed silica coated Fe₃O₄ NPs, and the mixtur e was stirred for 1 h at room temperature. To this solution, 25 mg NaBH₄ dissolved in water was direc tly added and the solution vigorously stirred at room temperature for 3 h to produce disordered Pd NP s supported on silica coated Fe₃O₄ NPs. The product was washed several times with water/ethanol and dried in vacuo. The palladium loading of the product was measured by ICP-AES.

Synthesis of Pd NPs using Pluronic copolymers

Pd NPs were synthesized by modification of a previously reported method.¹ The Pd NPs were synthes ized simply by mixing aqueous solutions of palladium salts and Pluronic copolymer P85 or F127. In a typical procedure, 0.1 ml of 0.1m K₂PdCl₄ was added to 10 ml aqueous solution containing 0.2 g of tri block Pluronic copolymer P85 or F127 at room temperature, and the resulting solution was vigorously stirred for 5 hours. Within several minutes, the color of the solution changed from light yellow to a de ep brown, indicating the formation of nanoparticles. The palladium concentration of the solution was measured by ICP-AES.

Synthesis of carbon supported Pd NPs

Carbon (300 mg) was dispersed in $H_2O/EtOH$ mixture (2:1) and stirred at room temperature for 1 h. While vigorous stirring, 50 mg K_2PdCl_4 dissolved in water was added to the vial and the mixture was stirred for 1 h at room temperature. To this solution, 25 mg NaBH₄ dissolved in water was directly ad ded and the solution vigorously stirred at room temperature for 3 h to produce Pd NPs supported on ca rbon. The product was washed several times with water/ethanol and dried in vacuo. The palladium loa ding of the product was measured by ICP-AES.

Synthesis of mesoporous carbon supported Pd NPs

Mesoporous carbon (300 mg) was dispersed in $H_2O/EtOH$ mixture (2:1) and stirred at room temperatu re for 1 h. While vigorous stirring, 50 mg K_2PdCl_4 dissolved in water was added to the vial and the mi xture was stirred for 1 h at room temperature. To this solution, 25 mg NaBH₄ dissolved in water was d irectly added and the solution vigorously stirred at room temperature for 3 h to produce Pd NPs suppo rted on carbon. The product was washed several times with water/ethanol and dried in vacuo. The pall adium loading of the product was measured by ICP-AES.

Synthesis of SBA-15 supported Pd NPs

SBA-15 was readily synthesized by modifying a previously reported method.² In a typical synthesis, 2 g of $EO_{20}PO_{70}EO_{20}$ (P123, Pluronic 123 from BASF) polymer was dissolved in 144 ml of an aqueous solution of 1.7 M hydrochloric acid and stirred for 4hrs at 40 °C. Then, the tetraethyl orthosilicate (TE OS) was added dropwise at the mass ratio of TEOS/P123=2 and the reaction mixture was stirred for 2 4 hrs. Next, the reaction gel was transferred to the Teflon autoclaves and kept at 100 °C for 24 hrs. Th e resulting product was filtered, washed with DI water and dried for 24 hrs at 60 °C. The template fro m as-synthesized SBA-15 sample was removed by calcination at 550 °C for 5hrs under air. Synthesize d SBA-15 (300 mg) was dispersed in H₂O/EtOH mixture (2:1) and stirred at room temperature for 1 h. While vigorous stirring, 50 mg K₂PdCl₄ dissolved in water was added to the vial and the mixture was stirred for 1 h at room temperature. To this solution, 25 mg NaBH₄ dissolved in water was directly ad ded and the solution vigorously stirred at room temperature for 3 h to produce Pd NPs supported on S BA-15. The product was measured by ICP-AES.

Synthesis of Hydroxyapatite supported Pd NPs

Hydroxyapatite (300 mg) was dispersed in $H_2O/EtOH$ mixture (2:1) and stirred at room temperature f or 1 h. While vigorous stirring, 50 mg K_2PdCl_4 dissolved in water was added to the vial and the mixtu re was stirred for 1 h at room temperature. To this solution, 25 mg NaBH₄ dissolved in water was dire ctly added and the solution vigorously stirred at room temperature for 3 h to produce Pd NPs supporte d on Hydroxyapatite. The product was washed several times with water/ethanol and dried in vacuo. T he palladium loading of the product was measured by ICP-AES.

Heterogeneous oxidation of alcohols catalyzed by catalysts

The oxidation of alcohols was carried out in a 25 round-bottom flask. In a typical procedure, 1 mol% of catalysts was dispersed in H_2O (5 mL). Then, alcohol (1 mmol), $H_2O_2 30\%$ (3 mmol) and a small sti rring bar were added to the flask. The flask containing reaction mixture was placed in an oil bath (80 ° C) and stirred under air atmosphere. After completion of reaction, the mixture was cooled to room te mperature and the nanocatalysts were separated using a magnet. The separated catalysts were washed several times. The products were analyzed by a GC-MS.



Figure S1. TEM (a) and HRTEM (b) images of Pd NPs supported on *N*-(3-Trimethoxysilylpropyl)-PPy.



Figure S2. XPS analyses of Si 2p (a), C 1s (b), N 1s (c), and Pd 3d (d) for Pd NPs supported on *N*-(3-Trimethoxysilylpropyl)-PPy.



Figure S3. XPS analyses of Pd 3d (a), Si 2p (b), C 1s (c), N 1s (d), and Fe 2p (e) for magnetically retr ievable Pd nanocatalysts.



Figure S4. HRTEM images of magnetically recyclable Pd nanocatalysts.



Figure S5. XRF spectrum of the magnetically recyclable Pd nanocatalysts.



Figure S6. XPS analyses of Si 2p (a), and Fe 2p (b) for silica-coated Fe₃O₄ NPs.



Figure S7. Field-dependent magnetization of the Pd nanocatalysts at 300 K.



Figure S8. TGA of The magnetically recyclable Pd nanocatalysts.



Figure S9. HRTEM images of Pd NPs synthesized by Pluronic copolymer P85 (a), and Pluronic copo lymer F127 (b).



Figure S10. TEM images of commercially available Pd/C catalyst (a), and commercially available Pd /charcoal catalyst (b).



Figure S11. TEM images of silica coated Fe_3O_4 NPs (a), and Pd NPs supported on silica layer of core-shell nanostructures (b).



Figure S12. HRTEM images of carbon (a), and Pd NPs supported on carbon (b).



Figure S13. HRTEM images of mesoporous carbon (a), and Pd NPs supported on mesoporous carbon (b).



Figure S14. HRTEM images SBA-15 (a), and Pd NPs supported on SBA-15 (b).



Figure S15. TEM images of Hydroxyapatite (a), and Pd NPs supported on Hydroxyapatite (b).



Figure S16. TEM image of FeO_xPd NPs catalyst synthesized by a previously reported method.³



Figure S17. Low magnification (a), high magnification (b), and high resolution sectioned (c) TEM images of hollow nanocomposite Pd catalyst synthesized by a previously reported method.⁴







Figure S19. Photograph of scale up synthesis for the magnetically recyclable Pd nanocatalysts.

Table S1. The CHN elemental analysis results of N-(3-Trimethoxysilylpropyl)-PPy, silica core-shell Fe₃O₄ NPs and the magnetically recyclable Pd nanocatalysts.

Samula	Elemental Contents (wt %)			
Sample	С	Н	Ν	
<i>N</i> -(3-Trimethoxysilylpropyl)-PPy Pd NPs	23.5	5.7	5.7	
Silica core-shell Fe ₃ O ₄ NPs	2.1	1.9	0.1	
Pd nanocatalysts	9.3	3.2	3.8	

Table S2. Continues Heterogeneous oxidation of heptanol catalyzed by the designed Pd nanocatalysts.^a

OH -	Nanoata	lysts	<i>S</i>		
Continues reactions	1st	2nd	3rd	4th	5th
Yield of product $(\%)^b$	99	97	95	91	87

^{*a*} Reaction conditions: heptanol (0.25 mmol), Pd nanocatalysts (1 mol%) only added on the first run, 12 h, 80 °C, H_2O_2 30% (0.75 mmol), H_2O (2.5 ml).

^b Yields were determined by GC-MS with respect to an internal standard (decane).

R	×+	B(OH) ₂ Nanocatal	ysts	\succ
X=I,	Br			
Entry	Aryl halide	Product	Time (h)	Yield (%) ^b
1			2	97
2			2	92
3			2	94
4	H ₃ CO	н ₃ со —	2	91
5	Br	$\bigcirc - \bigcirc \bigcirc$	4	95
6	Br		4	93
7	Br		4	91
8	NC		4	94

Table S3. Heterogeneous Suzuki cross-coupling reaction of aryl halides with phenylboronic acid.^a

^{*a*} Aryl halide (0.5 mmol), phenylboronic acid (0.6 mmol), Pd nanocatalysts (1 mol %), K₂CO₃ (2 mmo l), DMF/H₂O (3:1), 100 °C.

^b Yields were determined by GC-MS analysis using internal standard (decane).

Table S4. Heterogeneous Reduction of Substituted Nitrobenzene with Hydrazine.^a

R				
Entry	Substrate	Product	Yield (%) ^b	
1	NO ₂	NH ₂	99	
2	CI NO2	CI NH2	97	
3	Br NO ₂	Br NH ₂	95	
4	NO ₂	NH ₂	92	
5	NO ₂	NH ₂	94	

^{*a*} Reaction conditions: substituted nitrobenzene (1 mmol), hydrazine (2 equiv.), Pd nanocatalysts (1 mol %), EtOH (5 ml), 80 °C, 4 h.

^b The yields were determined by GC-MS with respect to an internal standard (decane).

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