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$PdCl_2(py)_2$ encaged in monodispersed zeolitic hollow spheres: a highly efficient and reusable catalyst for Suzuki–Miyaura cross-coupling reaction in aqueous media

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1. Experimental details

1.1 Synthesis of mesoporous silica spheres (MSS)

n-Hexadecylamine 1 g was dissolved in a mixture of 90 ml isopropanol and 100 ml water at room temperature. Afterwards 1.4 ml ammonia (25%-28%) and 5.8 ml TEOS were added stepwise under stirring, the white mixture was left for 24 h at room temperature. Then the solid was isolated by centrifugation and washed with ethanol and distilled water three times respectively. After drying at 80 °C for 4 h, the product was submitted to calcination in air at 600 °C for 4 h (heating rate: 2 °C/min)

1.2 Synthesis of silicalite-1 seeds

7 g TPAOH, 3 g H_2O and 5 g TEOS were mixed together and stirred at ambient temperature to form a clear solution, then the liquor was transferred into a flask to crystallize at 80 °C. After refluxing for 3 days, the milk was enclosed in a semipermeable membrane bag to low down pH.

1.3 Synthesis of SHS

The as-synthesised MSS were seeded with the silicalite-1 seeds through a layer-by-layer procedure to get silicalite-1 coated MSSs. Then the sample was treated through a two-step hydrothermal approach: 0.1 g of silicalite-1 coated MSSs were hydrothermally treated in 15 ml of 1.5 wt% TPAOH aqueous solution at 100 °C for 1 h, and then continuously treated in 15 ml aqueous solution with a molar composition of TPAOH:TEOS:H_2O = 3:10:2000 at 100 °C for 8 h. The solid product was separated by centrifugation and washed with distilled water three times. After drying at 60 °C for 2 h, templates in the samples were removed by calcination in air at 550 °C for 4 h (heating rate: 2 °C/min).

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2. Supplemental figures

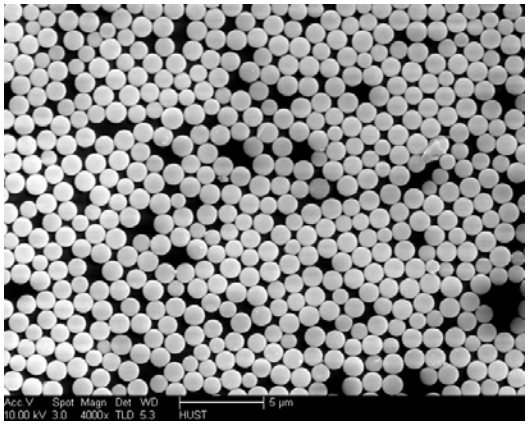

Fig. S1 SEM image of MSS.

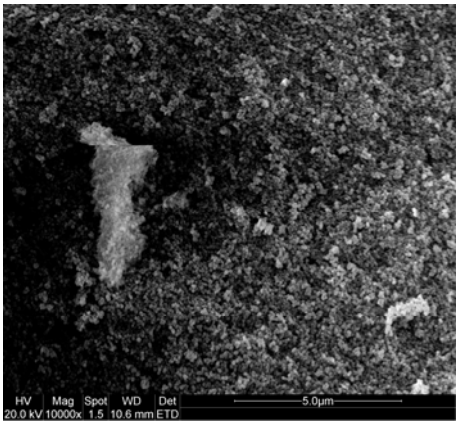

Fig. S2 SEM image of silicalite-1 seeds.

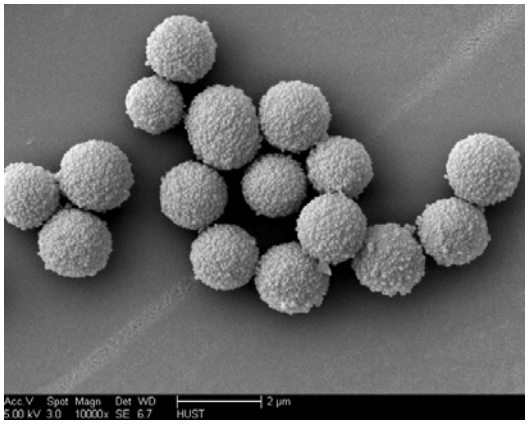

Fig. S3 SEM image of silicalite-1 coated MSS.

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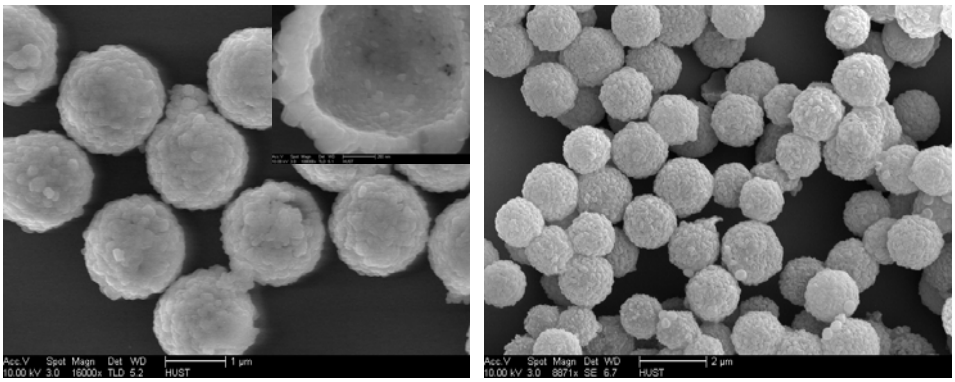

Fig. S4 SEM image of SHS. The inset represents a broken sphere.

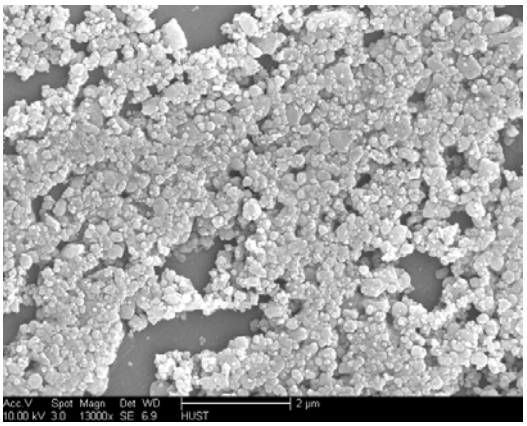

Fig. S5 SEM image of shell-crushed $PdCl_2(py)_2$@SHS by heavily grinding.

3. ^{1}H NMR data for the coupling products

Biphenyl.
White solid, mp 69–70 °C;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, 4 H, J = 7.2 Hz), 7.44 (t, 4 H, J = 8.0 Hz), 7.34 (tt, 2 H, J_a = 1.2 Hz, J_b = 7.6 Hz).

4-*tert*-Butylbiphenyl.
White solid, mp 49–50 °C;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55–7.62 (m, 4 H), 7.42–7.50 (m, 4 H), 7.34 (m, 1 H), 1.39 (s, 9 H).

4-Methoxybiphenyl.
White solid, mp 89–90 °C;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51–7.56 (m, 4 H), 7.39–7.43 (m, 2 H), 7.30 (t, 1 H, J = 7.6 Hz), 6.98 (d, 2 H, J = 8.8 Hz), 3.85 (s, 3 H).

4-Cynaobiphenyl.
White solid, mp 85–86 °C;
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.42 (m, 3 H), 7.50 (d, 2 H, J = 7.8 Hz), 7.53–7.64 (m, 4 H).

4-Biphenylcarboxaldehyde.
White solid, mp 57–58 °C;
^{1}H NMR (400 MHz, $CDCl_3$): δ10.07 (s, 1 H), 7.95 (d, 2 H, J = 7.8 Hz), 7.75 (d, 2 H, J

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= 7.8 Hz), 7.43–7.66 (m, 5 H).

4-Methylbiphenyl.

White solid, mp 46–48 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, 2 H, J = 6.8 Hz), 7.49 (d, 2 H, J = 8.0 Hz), 7.42 (t , 2 H, J = 7.2 Hz), 7.31 (tt, 1 H, J_a = 2.0 Hz, J_b = 7.2 Hz), 7.24 (d, 2 H, J = 8.4 Hz), 2.39 (s, 3 H).

4,4'-Dimethylbiphenyl.

White solid, mp 122–124 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, 4 H, J = 8.0 Hz); 7.23 (d, 4 H, J = 8.8 Hz); 2.39 (s, 6 H).

4-Methoxy-4'-Methylbiphenyl.

White solid, mp 109–110 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, 2 H, J = 8.8 Hz), 7.44 (d, 2 H, J = 8.0 Hz), 7.21 (d, 2 H, J = 8.0 Hz), 6.96 (d , 2 H, J = 8.8 Hz), 3.84 (s, 3 H), 2.38 (s, 3 H).

4-*tert*-Butyl-4'-Methylbiphenyl.

White solid, mp 75–76 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43–7.53 (m, 6 H), 7.23 (d, 2 H, J = 8.2 Hz), 2.38 (s, 3 H), 1.35 (s, 9 H).

4-Cynao-4'-methylbiphenyl.

White solid, mp 110–111 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64–7.72 (m, 4 H), 7.49 (d, 2 H, J = 8.4 Hz), 7.29 (d, 2 H, J = 8.8 Hz), 2.40 (s, 3 H).

4'-Methyl-4-biphenylcarboxaldehyde.

White solid, mp 105–107 °C;

^{1}H NMR (400 MHz, $CDCl_3$): 10.03 (s, 1 H), 7.91 (d, J = 8.4, 2 H), 7.2 (d, J = 8.4, 2 H), 7.53 (d, J = 8.0, 2 H), 7.28 (d, J = 8.4, 2 H), 2.42 (s, 3 H).

4-Trifluoromethylbiphenyl.

White solid, mp 69–70 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (s, 4 H); 7.57 (d, 2 H, J = 8.0 Hz); 7.37–7.47 (m, 3 H).

4-Chlorobiphenyl.

White solid, mp 75–76 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47–7.54 (m, 4 H), 7.31–7.43 (m, 5 H).

3,5-Dimethylbiphenyl.

Colorless oil;

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55–7.57 (m, 2 H), 7.37–7.42 (m, 2 H), 7.30–7.33 (m, 1 H), 7.20 (s, 2 H), 6.98 (s, 1 H), 2.36 (s, 6 H).

4-Methoxycarbonylbiphenyl.

White solid, mp 116–117 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, 2 H, J = 8.4 Hz), 7.63–7.69 (m, 4 H), 7.38–7.50 (m, 3 H), 3.95 (s, 3 H).

2-Methoxycarbonylbiphenyl.

White solid, mp 110–111 °C;

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.65 (m, 8 H), 3.67 (s, 3 H).