

Supporting information for

In-Situ encapsulation of Pd inside the MCM-41 channel

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Experimental section:

Chemicals: Cetyltrimethylammonium bromide ($\geq 99.0\%$), Ammonia solution (28%), Ethanol (A.R.) and Potassium carbonate anhydrous (A.R.) were purchased from Sinopharm Chemical Reagent Co., Ltd. Tetrathoxysilane (98%), Ammonium tetrachloropalladate (II) (Pd, 37%), Iodobenzene (A.R.) and Phenylboronic acid (A.R.) were purchased from Alfa Aesar. The super pure water (18.2 M Ω cm) was used as solvent.

Synthesis of Pd/MCM-41:

0.0675g CTAB and 30 mL deionized water were added into a 50 mL two-necked flask under stirring ($\omega=900$ rpm). When the solution became transparent, ammonium hydroxide (28 wt%) was added to adjust the pH to an appropriate range (10~12), and this system was heated to 60 °C in an oil bath. After stirring 0.5 h, 1 mL TEOS was added dropwise. And then after another 30 minutes' reaction, suitable amount of 0.5 M (NH₄)₂PdCl₄ aqueous solution was introduced to the system and continued to react for another 2 h. After the reaction, the product was separated by ultrasound and centrifugation (9000 rpm). And then, this product was washed by ethanol and repeated this centrifugation /washing cycle for 2 times. The obtained product was dried at 80 °C for 10 h, and then cooled to room temperature. Finally, the powder was calcined in air at 550 °C for 6 h to remove the organic materials, and then continued to reduce in an H₂/Ar flow for 2 h.

Synthesis of MCM-41:

0.0675g CTAB and 30 mL deionized water were added into a 50 mL two-necked flask under stirring ($\omega=900$ rpm). When the solution became transparent, ammonium hydroxide (28 wt%) was added to adjust the pH to an appropriate range (10~12), and this system was heated to 60 °C in an oil bath. After stirring 0.5 h, 1 mL TEOS was added dropwise. Continued to react for another 2 h, the product was separated by ultrasound and centrifugation (9000 rpm). After centrifuging, the product was washed by ethanol and repeated the centrifugation /washing cycle for 2 times. The obtained powder was dried at 80 °C for 10 h, and then cooled to room temperature. Finally, the powder was calcined in air at 550 °C for 6 h to move the organic materials.

Synthesis of Pd-SiO₂ spheres:

The silica spheres were prepared by Stöber method¹, and then suitable amount Pd precursor was introduced into this pre-prepared silica system and adjusted the pH to 10~11. After 2 hours' reaction, the product was centrifuged out and collected.

Characterizations:

Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) was recorded with a JEOL 2100 F instrument operating at 200 kV. X-ray diffraction (XRD) patterns was performed on a Rigaku D/max 2500 type instrument using CuK α radiation with a step size of 0.01. The Pd loading amount was measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES) on a Shimadzu ICPE-9000. The N₂

adsorption/desorption isotherms were carried out at liquid nitrogen temperature after sample was outgassed at 120 °C, by using a Micrometrics ASAP 2010 apparatus. The specific surface area of the samples was calculated by using the Brunauer–Emmett–Teller (BET) method. Pore size distribution was obtained by the Barrett–Joyner–Halenda (BJH) method from the adsorption branch. UV-vis spectrum was obtained from Shimadzu UV-2600. In the Suzuki reaction, the conversion was tested by High Performance Liquid Chromatography (HPLC) with an Agilent 1260 Infinity HPLC instrument.

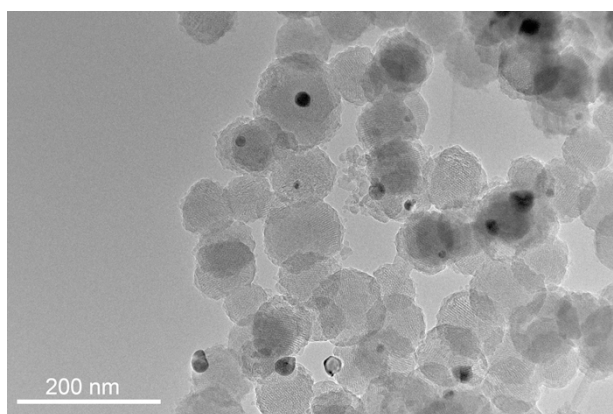


Fig. S1. TEM image of 1.1 wt% Pd/MCM-41 sample calcined at 900 °C. At this high temperature, most of the channels were destroyed, leaving no observable mesopores. Meanwhile, serious agglomeration of Pd nanoparticles happened as revealed by the big chunks of large particles.

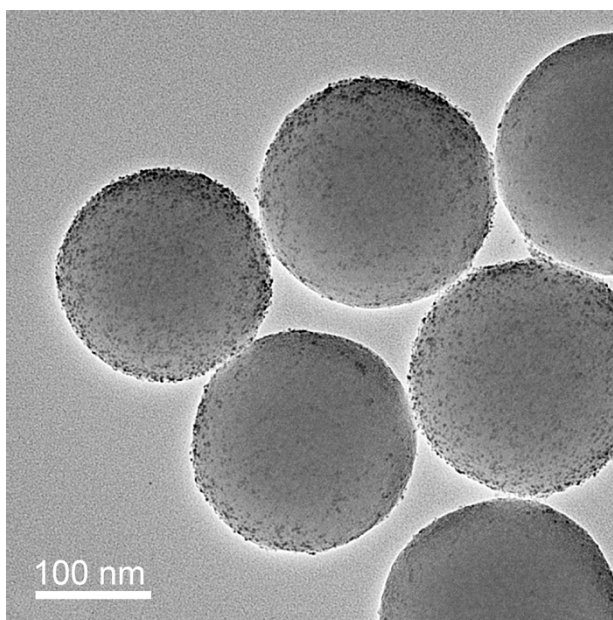


Fig. S2. TEM image of a contrast sample of Pd-SiO₂, which was prepared by supporting Pd nanoparticles onto the surface of pre-SiO₂ nanospheres. The supported Pd nanoparticles were very easy to sinter and a relatively low temperature heating at 600 °C would cause seriously sintering.

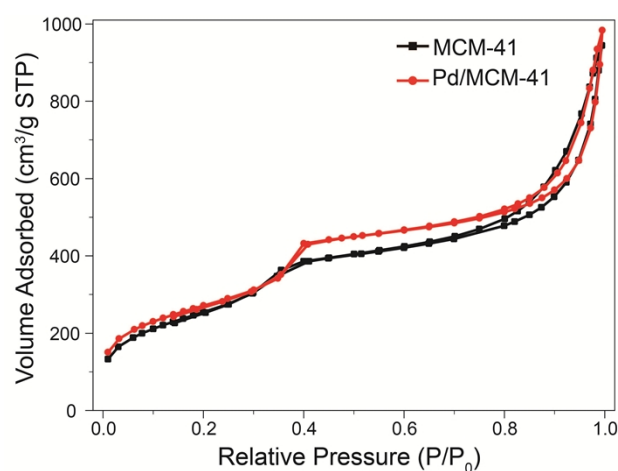


Fig.S3. The N_2 adsorption /desorption isotherms of MCM-41 and Pd/MCM-41. The specific surface area of these two samples was $935 \text{ m}^2/\text{g}$ and $984 \text{ m}^2/\text{g}$, respectively, changes barely after loading Pd, which indicated that the introduction of Pd did not destroy the structure and channels of MCM-41.

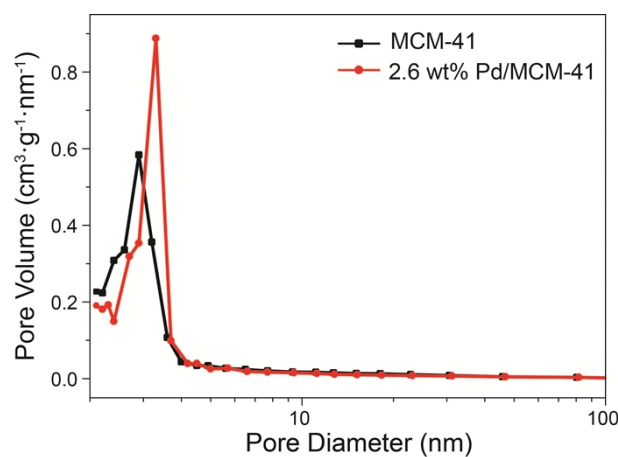


Fig. S4. The pore size distribution curves of MCM-41 and 2.6 wt% Pd/MCM-41. After the introduction of Pd, the Pd/MCM-41 remained mesoporous but showed an increased pore size of 3.3 nm (3.0 nm for that of MCM-41). The pore volume also increased a little from $935 \text{ m}^2/\text{g}$ and $984 \text{ m}^2/\text{g}$.

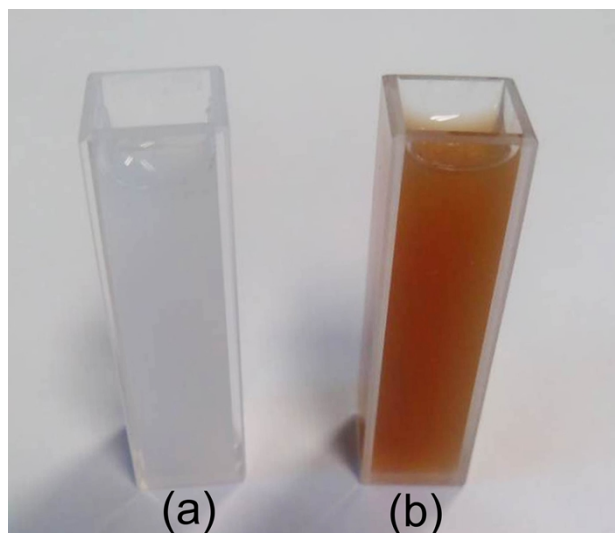


Fig. S5. The photos of two different suspensions formed by mixing a $(\text{NH}_4)_2\text{PdCl}_4$ solution with (a) MCM-41 containing CTAB and (b) MCM-41 with CTAB removed. The as-prepared MCM-41 from the hydrolysis of TEOS was originally white. After the adding of $(\text{NH}_4)_2\text{PdCl}_4$, the brown colour of $(\text{NH}_4)_2\text{PdCl}_4$ would quickly disappear, indicating that the palladium species had been effectively adsorbed into the channels of MCM-41. On the contrary, the removal of CTAB would lose the link between MCM-41 and Pd, forming a brown colour due to the existence of $(\text{NH}_4)_2\text{PdCl}_4$ in the solution.

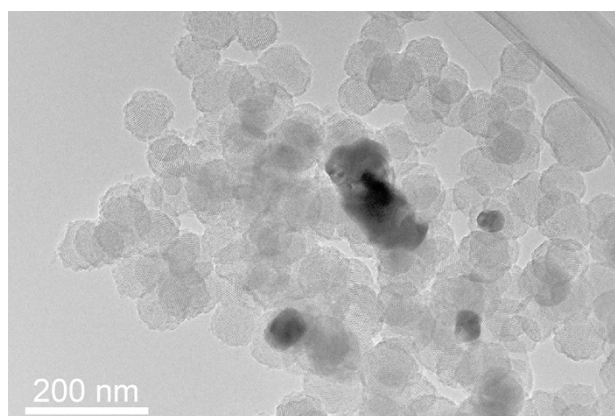


Fig. S6. The TEM image of the sample which synthesized by grafting Pd to a pre-prepared MCM-41 with CTAB removed.

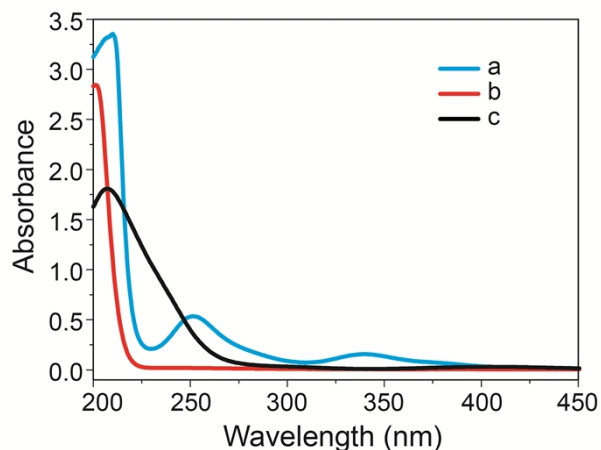


Fig. S7. The UV-vis spectra of different solutions: (a) the mixed solution of aqueous $(\text{NH}_4)_2\text{PdCl}_4$ and CTAB; (b) CTAB solution; (c) the aqueous $(\text{NH}_4)_2\text{PdCl}_4$ solution. The CTAB solution did not show obvious adsorption in the UV-vis range and the $(\text{NH}_4)_2\text{PdCl}_4$ solution showed one at 210 nm. For the mixture of CTAB and $(\text{NH}_4)_2\text{PdCl}_4$, two new bands around 250 nm and 340 nm were observed, probably due to the ligand exchange of CTAB and $(\text{NH}_4)_2\text{PdCl}_4$ which formed the palladate-CTAB which played a critical role in the grafting of Pd precursor.²

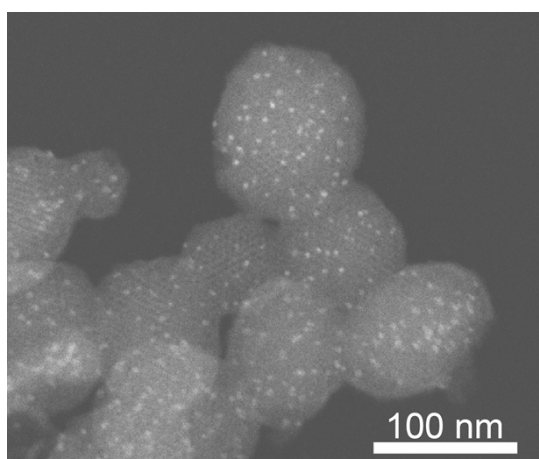


Fig. S8. The STEM image of the 1.1 wt% Pd/MCM-41 sample which has been used for the Suzuki reaction for 4 continuous runs. No obvious aggregation of Pd nanoparticles happened due to the protection of the MCM-41 channels.

References

- 1 W. Stober, A. Fink and E. Bohn, *J. Colloid Interface Sci.*, 1968, **26**, 62-69.
- 2 B. Veisz and Z. Kiraly, *Langmuir*, 2003, **19**, 4817-4824.