Electronic Supplementary Material (ESI) for RSC Advances.

Pd nanoparticles embedded in the outershell of mesoporous core-shell catalyst for phenol hydrogenation in pure water

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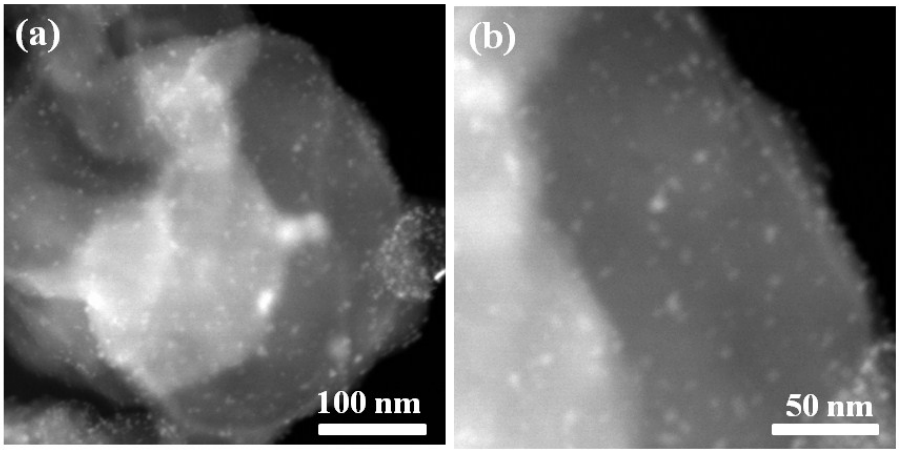

Figure S1 (a) HAADF-STEM of Pd/MCN@MS-NH_2 catalyst and (b) the magnified image.

The high-angle annular dark-field scanning transmission electron microscope (HAADF-STEM) analytical technique was used to determine the distribution of Pd NPs for the Pd/MCN@MS-NH_2 catalyst. As can be seen from Figure S1a, the STEM showed that the Pd NPs were distributed uniformly throughout the whole surface of the catalyst. Figure S1b represent the local magnified micrograph of Pd/MCN@MS-NH_2 catalyst. It is clearly observed that a plenty of tiny and bright Pd NPs located on the out-shell of the as-prepared catalyst. Additionally, the TEM image of Figure S2a also demonstrated that the vast majority of Pd NPs supported on the outershell of the catalyst.

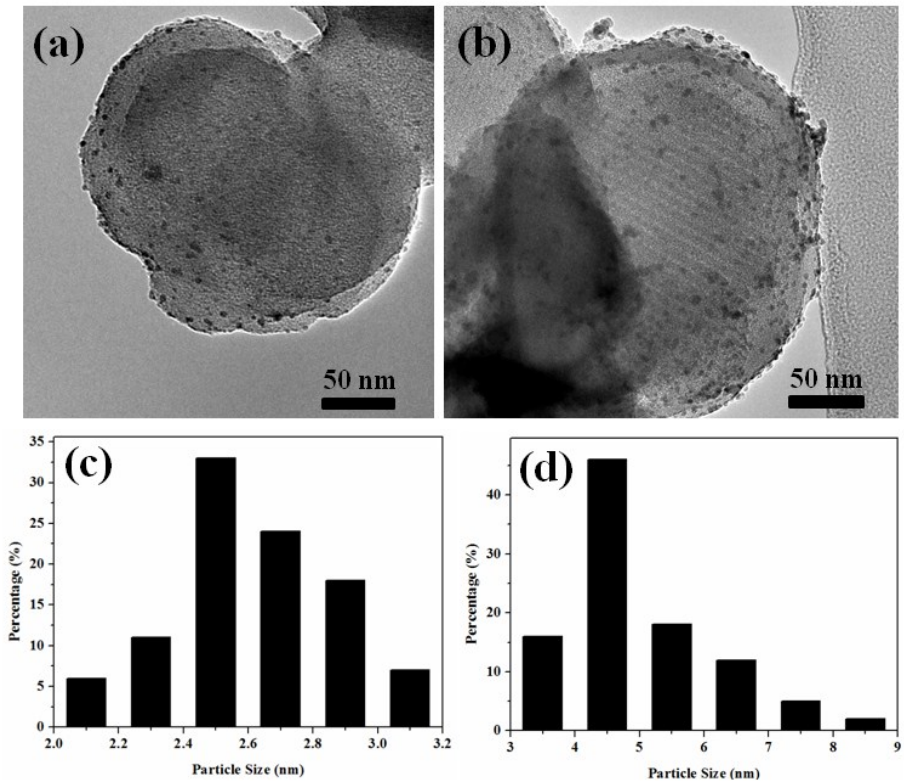

Figure S2 (a) and (b) the TEM image of Pd/MCN@MS-NH_2 catalyst before and after reaction, (c) and (d) the corresponding diameter distribution.

The particle size distribution of Pd NPs in the core-shell structured Pd/MCN@MS-NH_2 catalyst was systematically measured by HRTEM. The TEM image of catalyst and the corresponding diameter distribution of Pd NPs are provided in Figure S2, which suggested that the particle sizes are mainly centered at 2.5 nm. In order to observe the change for the catalyst after reaction, the reused catalyst was further characterized by TEM analysis. As can be seen from the TEM image of the recycled catalyst, the morphology of the catalyst is almost not changed significantly, but the Pd NPs tend to be assemble into larger aggregates and the particle sizes increased from 2.5 nm to 4.5 nm.

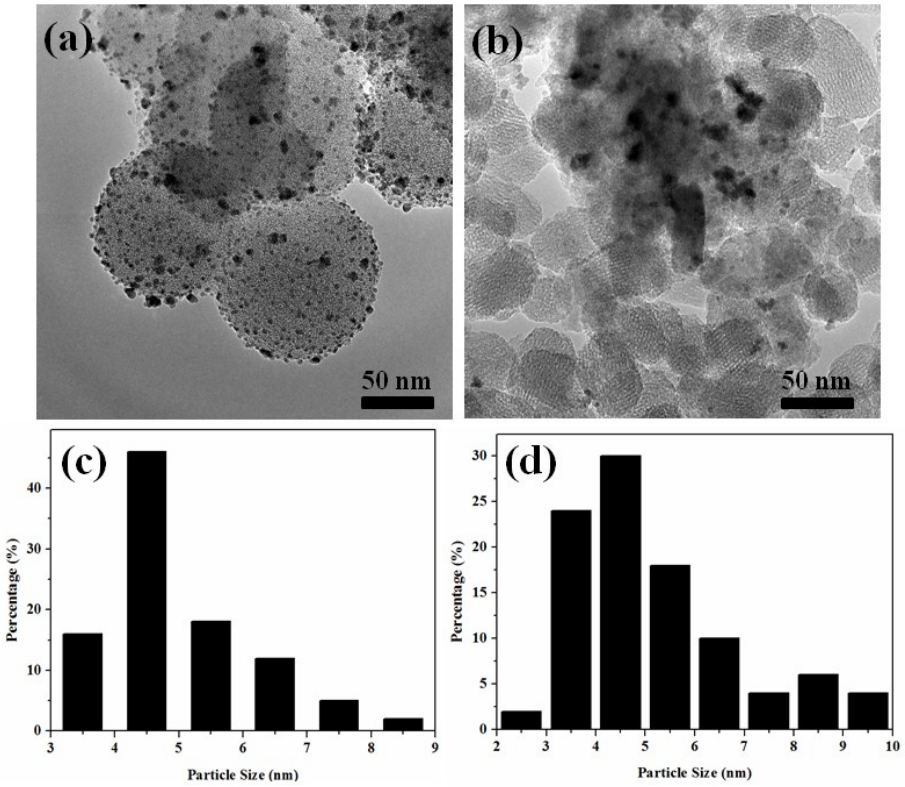

Figure S3 (a) and (b) the TEM image of Pd/MCN and Pd/MS-NH_2 catalyst, (c) and (d) the corresponding diameter distribution.

The TEM images and particle size distribution of Pd/MCN and Pd/MS-NH_2 catalysts are shown in Figure S3. As can be seen from Figure S3a and S3c, the Pd NPs are distributed evenly throughout the surface of spherical MCN and the average size of the Pd NPs is 4.5 nm, which is larger than the mean size of Pd NPs of MCN@MS-NH_2 catalyst (2.5 nm). The TEM image of Pd/MS-NH_2 catalyst revealed that the Pd NPs are somewhat aggregated into larger sizes during the preparation process and the mean diameter of Pd NPs is about 4.5 ± 1.0 nm.

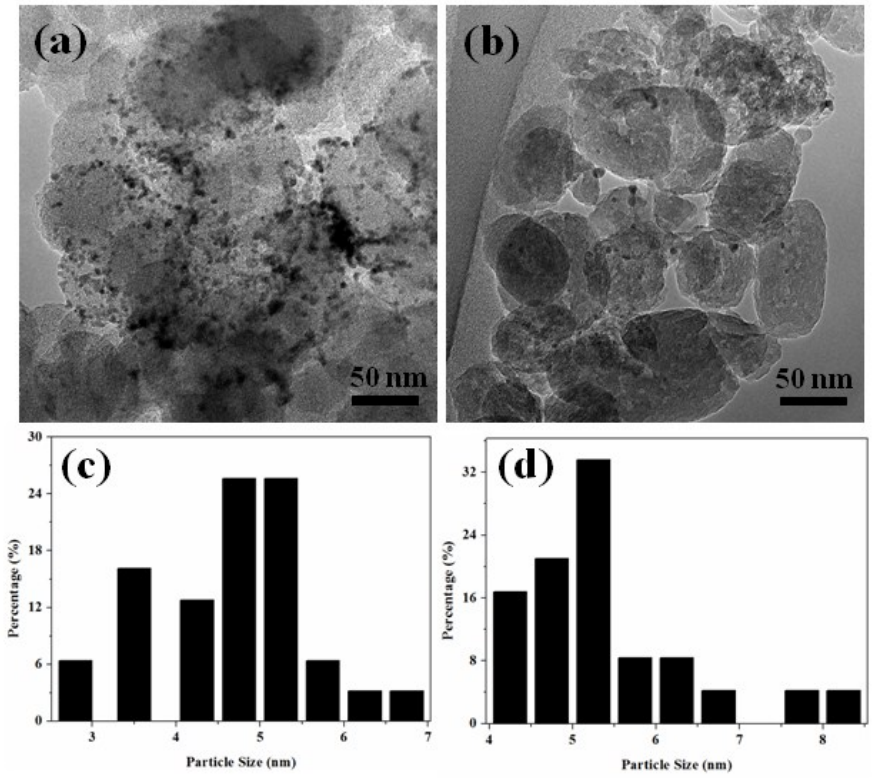

Figure S4 (a, b) TEM image of Pd/MCN and Pd/MS-NH_2 catalyst, (c, d) Diameter distribution of Pd/MCN and Pd/MS-NH_2 catalyst after reaction

After the phenol hydrogenation, the particle size distribution of Pd NPs on the recycled Pd/MCN and Pd/MS-NH_2 catalyst was also measured by HRTEM. TEM images of the two catalysts and the corresponding diameter distribution of Pd NPs are provided in Figure S4. As can be seen from Figure S4a and S4c, the Pd NPs are gathered together with each other throughout the spherical MCN surface and the average size of the Pd NPs is centered at 4.8 ± 0.5 nm after reaction, which is larger than the mean size of Pd NPs of fresh Pd/MCN catalyst (4.5 nm). Similarly, the TEM image of Pd/MS-NH_2 catalyst showed that the mean diameter of Pd NPs with a slight increase (4.75 ± 0.5 nm) after the phenol hydrogenation and no obvious aggregation phenomena are taken place for the Pd NPs.

The ICP-OES analysis results showed that the leaching of Pd NPs from the surface of Pd/MCN catalyst was about 0.13 wt%, while the leaching of Pd NPs was below 0.01 wt% for Pd/MS-NH_2 catalyst. That is to say, the Pd NPs dissolved in the aqueous solution will not have a great effect on the phenol hydrogenation.

Table S1 The catalytic performance of different catalysts for phenol hydrogenation [a].

Catalyst	T (^{o}C)	t (h)	Yield (%)	TON	TOF (h^{-1})
Pd/MCN	80	3	81.1	16.2	5.41
Pd/MS-NH_2	80	3	77.9	15.6	5.19
Pd/MCN@MS-NH_2	80	3	99	19.8	6.60

[a] Reaction conditions: 0.5 mmol of phenol, 80 mg catalyst (5.0 mol%) and 3.0 mL of H_2O under 1 atm of H_2. TON = the number of product moles/the number of Pd moles, TOF = the number of product moles/[the number of Pd moles • h].

As shown in Table S1, the yields of cyclohexanone for hydrophobic Pd/MCN and hydrophilic Pd/MS-NH_2 catalyst were 81.1% and 77.9%. By contrast, the yield of cyclohexanone for hydrophobic carbon core/hydrophilic silica shell structured Pd/MCN@MS-NH_2 catalyst can reached up to 99%. It is observed that the combination of the hydrophobicity/hydrophilicity can obviously improved the catalytic performance for Pd-based catalyst. The TOF value of Pd/MCN@MS-NH_2 catalyst was 1.22 and 1.27 times relative to Pd/MCN and Pd/MS-NH_2 catalyst, respectively. More recently, Chia-Min Yang et al. also demonstrated that the introduction of hydrophobic alkyl groups can enhanced the catalytic activity for aqueous-phase phenol hydrogenation[1].

Table S2 Leaching test during the washing process for Pd/MCN@MS-NH_2 catalyst.

Washing times	Pd leaching content (μg)	Pd leaching content (wt%)
1	0.328	0.014
2	0.048	0.002
3	<detection limit	—
4	< detection limit	—
5	< detection limit	—
6	0.045	0.0019

After each reaction, the Pd/MCN@MS-NH_2 catalyst was washed two times with deionized water under ultrasonic condition and then merged together to determine the content of Pd NPs in the washing liquid. As seen in Table S2, the Pd leaching content was 0.014 wt%, 0.002 wt% and 0.0019 wt% for the first, second and sixth recycle, respectively. And the Pd content in the 3-5 recycle cannot be detected in the washing liquid. Therefore, the leaching amount of Pd NPs from the catalyst surface was still at very low levels. On the whole, the MCN@MS-NH_2 supported Pd NPs catalyst displayed high stability in the phenol hydrogenation and leaching during washing.

Reference

1. C.-J. Lin, S.-H. Huang, N.-C. Lai and C.-M. Yang, *ACS Catal.*, 2015, **5**, 4121-4129.