Electronic Supplementary Information (ESI):

New Understanding and Controllable Synthesis of Silica Hollow Microspheres with Size-tunable Penetrating Macroporous Shells as A Superior Support of Macromolecular Polymer Hydrogenation Catalysts

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Supplementary Methods

1. Materials

Polystyrene (M_w = 250000) was purchased from Sigma-Aldrich (USA). SPs with different average molecular weights (M_w = 4000, 8000, 9600 and 30000) and sodium silicate solution (SiO_2, 26 wt.%) were purchased from Beijing Hongxing Chemical Company, Ltd. (P. R. China). Span 80, Tween 80, n-hexane, cyclohexane, tetrahydrofuran, chloroform, $PdCl_2$, HCl (36.5 wt.%) and NH_4HCO_3 were obtained from Beijing Modern Eastern Fine Chemicals Company, Ltd. (P. R. China). All of the chemicals were used as purchased without further purification.

2. Synthesis of SHMs

The ternary W/O/W emulsion systems used for synthesizing SHMs involves the following three solutions: the IWP, which is an W/O emulsion prepared using sodium silicate solutions of different concentrations (36 mL; 22.6 wt.% for SHM-(1-7), 17.4 wt.% for SHM-8, and 11.3 wt.% for SHM-9) and 0-0.8 g of SP; the OP, which is a solution (72 mL) of Tween 80 (0.75 g) and Span 80 (0.75 g) in n-hexane for stabilizing the IWP; and the OWP, which is a 2 M

NH_4HCO_3 solution (100 mL) used as a precipitant.

A typical synthesis procedure is described as follows: first, the OP and IWP are emulsified using a homogenizer operated at 10000 rotations per minute (rpm) for 1 min; then, the resultant mixture is added into the OWP to form a W/O/W emulsion system; after that, the W/O/W emulsion system is agitated for several minutes, producing some white solids, and aged for another 2 h at room temperature with vigorous stirring; finally, the resultant white precipitate is filtered, washed with deionized water and ethanol for several times, and dried at 120 ^{o}C for 6 h. The surface morphologies of the SHMs can be easily controlled by adding SPs with different dosages and molecular weights into the IWP. The experimental parameters are listed in Table 1. SHM-1, SHM-2, SHM-3 and SHM-4 were prepared by adding 0, 0.2, 0.5 and 0.8 g SP (M_w = 8000), respectively; SHM-5, SHM-6 and SHM-7 were made by using the SPs of the molecular weights of 4000, 9600 and 30000, respectively, at the same dosage (0.5 g); and SHM-8 and SHM-9 were obtained by controlling the contents of Na_2SiO_3 in the IWP at 17.4 wt.% and 11.3 wt.%, respectively, and using SP of the same molecular weight (M_w = 30000).

3. Preparation of supported Pd catalysts over SHMs

A series of supported Pd catalysts over SHMs were prepared by the conventional incipient wetness impregnation method. Before impregnation, SHM-3, SHM-5, SHM-6 and SHM-9 were treated at 800 ^{o}C for 3 h under hydrothermal conditions to remove small pores that may exist in them, because these small pores are unfavorable for macromolecule diffusion and may cause the entrapment of macromolecules in them. A typical preparation procedure is described as follows: 0.82 g of $PdCl_2$ and 5 mL of HCl (36.5 wt.%) are added into 30 mL of deionized water and stirred for 5 h to form a homogeneous solution; then, one of the SHMs (10 g) prepared above is added into the solution for impregnating Pd, and the resulting solids are first dried at room temperature, then calcined in air at 773 K (1.2 ^{o}C min^{-1}, 3 h), and finally reduced in a H_2 flow at 120 ^{o}C for 2 h and stored in a nitrogen glove box until use.

Seven samples of the prepared SHMs with different surface morphologies (SHM-1, SHM-2 and SHM-7 without hydrothermal treatment and SHM-3, SHM-5, SHM-6 and SHM-9 with hydrothermal treatment) were chosen as supports and the corresponding catalysts were named as S1-Pd/SHMs, S2-Pd/SHMs, S3-Pd/SHMs, S5-Pd/SHMs, S6-Pd/SHMs, S7-Pd/SHMs, and S9-Pd/SHMs, respectively.

4. Hydrogenation of polystyrene

The hydrogenation reaction was carried out in an agitated autoclave reactor of total volume of 500 mL. In a typical experiment, 0.5 g of one catalyst to be assessed, 2.0 g of polystyrene, and 100 mL of a 10 v% tetrahydrofuran/90 v% cyclohexane mixture were first put into the reactor, then the reactor was sealed and flushed with N_2 to remove air and then with H_2 to remove N_2. During the reaction, the system temperature and pressure were maintained at 150 ^{o}C and 7.0 MPa, respectively, and the agitation was kept at 1200 rpm. After reaction for 10 h, the hydrogenated polystyrene solution was centrifuged to separate the catalyst from the system. The final hydrogenated product was extracted with ethanol and then dried in a vacuum oven at 70 ^{o}C for 8 h. Furthermore, to evaluate the activity stability of the catalyst (S9-Pd/SHMs), the catalytic performance of the recycled catalyst, which was obtained by washing with acetone several times and drying under vacuum at room temperature, was assessed under the same reaction conditions.

5. Adsorption measurements of polystyrene

The adsorption of PS was studied in the similar manner as used for the hydrogenation reaction except without inputting hydrogen into the system. After contacting a catalyst (1.0 g) with the PS solution (0.2 g PS, 10 mL tetrahydrofuran and 90 mL cyclohexane solution) for a given period of time (1-15 h) at 150 ^{o}C, the adsorption experiment was stopped and the PS solution was filtered to remove the catalyst and the PS concentration in the solution was measured with a ultraviolet and visible light (UV-VIS) spectrophotometer.

6. Characterizations

The morphology and structure of the particles were characterized *via* **SEM** and **TEM** on a Quanta 200F electron microscope (FEI, Holland) and a JEM 2100 LaB6 machine (JEOM, Japan) operated at 200 kV. Prior to TEM observation, the sample to be observed was dispersed in ethanol and a droplet of the resultant suspension was deposited onto a carbon-coated Cu grid. **N_2 adsorption-desorption measurements** of the samples were performed on an ASAP 2020 instrument (Micromeritics, USA). The samples to be measured were firstly degassed at 250 ^{o}C under a vacuum of 10^{-5} Torr for 15 h and then switched to the analysis station for adsorption-desorption at liquid nitrogen temperature. **FTIR spectra** were collected on a Nexus 470 instrument (Nicolet, USA). For each measurement, 64 scans were made at a resolution of 4 cm^{-1} over the wavenumber range of 400-4000 cm^{-1}. **Average macropore diameters** (*AMD*) of SHMs were calculated by counting more than 100 SHMs from the SEM images and the calculation formula is $AMD = (\sum_{i=1}^{n} x_i D_i)/(\sum_{i=1}^{n} x_i)$, where D_i is macropore diameter , x_i is the number of macropores within a given diameter interval. **Relative viscosity** of the IWP was measured with a Ubbelohde viscometer at room temperature. **The concentration of aromatic rings** in the PS solutions was measured at 261.5 nm using a TU-1810 UV-VIS spectrophotometer (Pgeneral, China). A calibration absorption curve was drawn with several PS solutions of known concentrations. The concentration of aromatic rings after hydrogenation can be obtained by comparing the measured absorption and the calibration curve. The degree of hydrogenation (HD), which is an index to express the conversion of aromatic rings, was calculated by $HD = 1\text{-}C_A/C_{A0}$, where C_A is the concentration of aromatic rings after hydrogenation and C_{A0} is the initial concentration of aromatic rings. The concentrations of aromatic rings after adsorption were obtained through the same method. **The size of PS** in the tetrahydrofuran/cyclohexane mixtures was determined *via* the dynamic light scattering (DLS) method on a Zetasizer Nano S90 (Malvern, UK). The **chemical**

compositions of the different catalysts were determined by X-ray fluorescence (XRF) conducted on a Bruker S4 Explorer instrument.

Supplementary Table

Table S1 Chemical compositions of S*x*-Pd/SHMs.

Component, wt.%	Na_2O	MgO	Cl	CaO	K_2O	SiO_2	Pd
S1-Pd/SHMs	0.21	0.14	0.16	0.13	0.12	94.20	5.04
S2-Pd/SHMs	0.21	0.12	0.10	0.14	0.14	95.23	5.06
S3-Pd/SHMs	0.23	0.12	0.11	0.15	0.11	94.28	4.98
S5-Pd/SHMs	0.26	0.12	0.13	0.17	0.19	94.12	5.01
S6-Pd/SHMs	0.25	0.17	0.12	0.15	0.21	93.99	5.11
S7-Pd/SHMs	0.23	0.16	0.17	0.22	0.12	94.15	4.95
S9-Pd/SHMs	0.26	0.13	0.15	0.16	0.18	94.06	5.06

Supplementary Figures

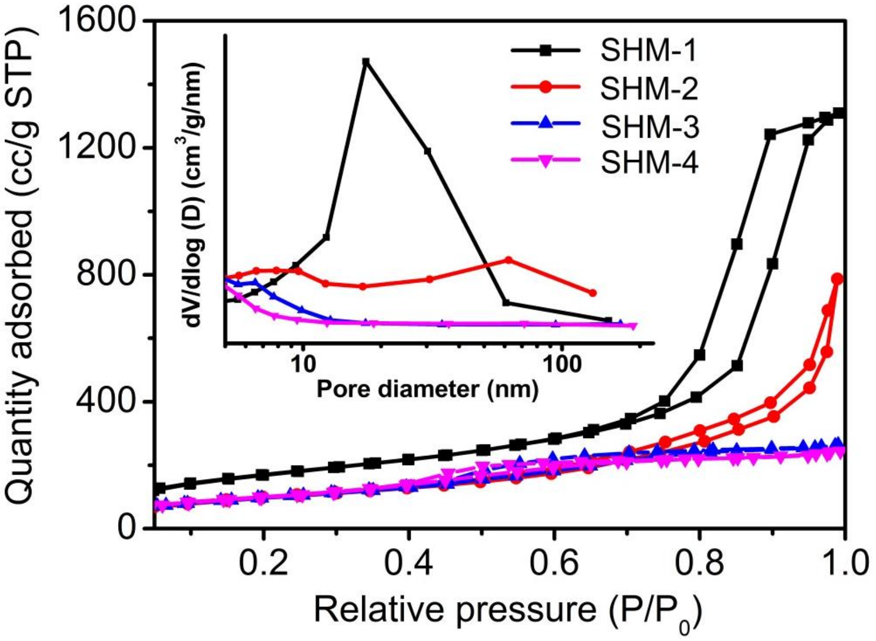


Fig. S1. Nitrogen adsorption-desorption isotherms and pore diameter distribution curves of SHM-1, SHM-2, SHM-3 and SHM-4 prepared by adding different amounts of SP (0, 0.2, 0.5, and 0.8 g, respectively) with the same molecular weight of 8000.

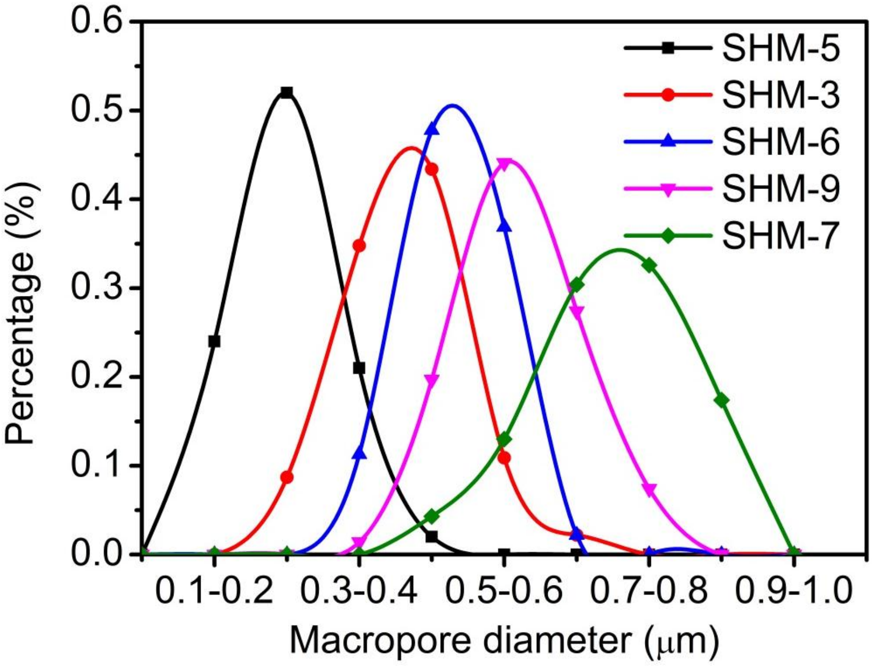


Fig. S2. Macropore diameter distributions of SHMs obtained by counting more than 100 SHMs from SEM images.

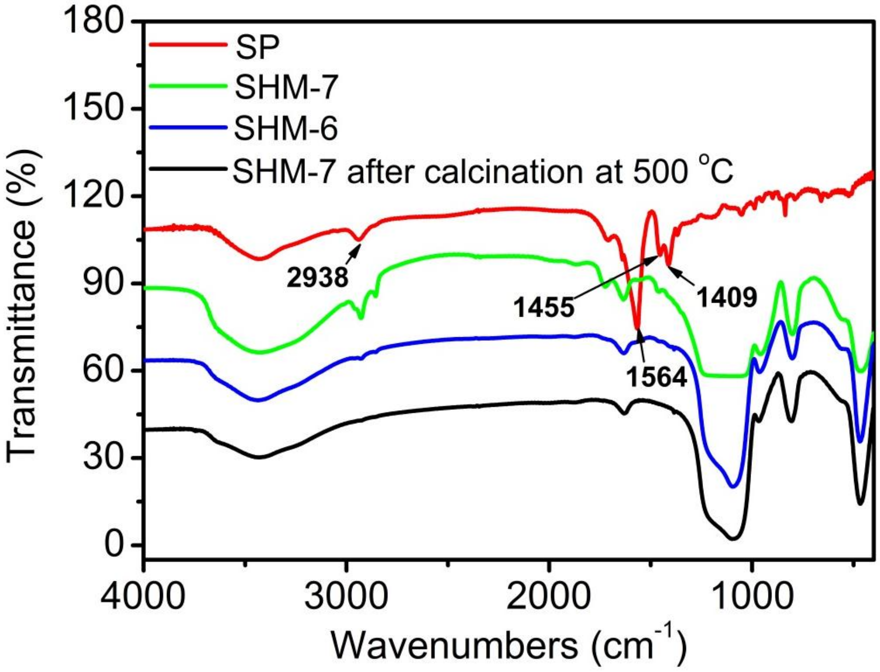


Fig. S3. FTIR spectra of SP and SHMs.

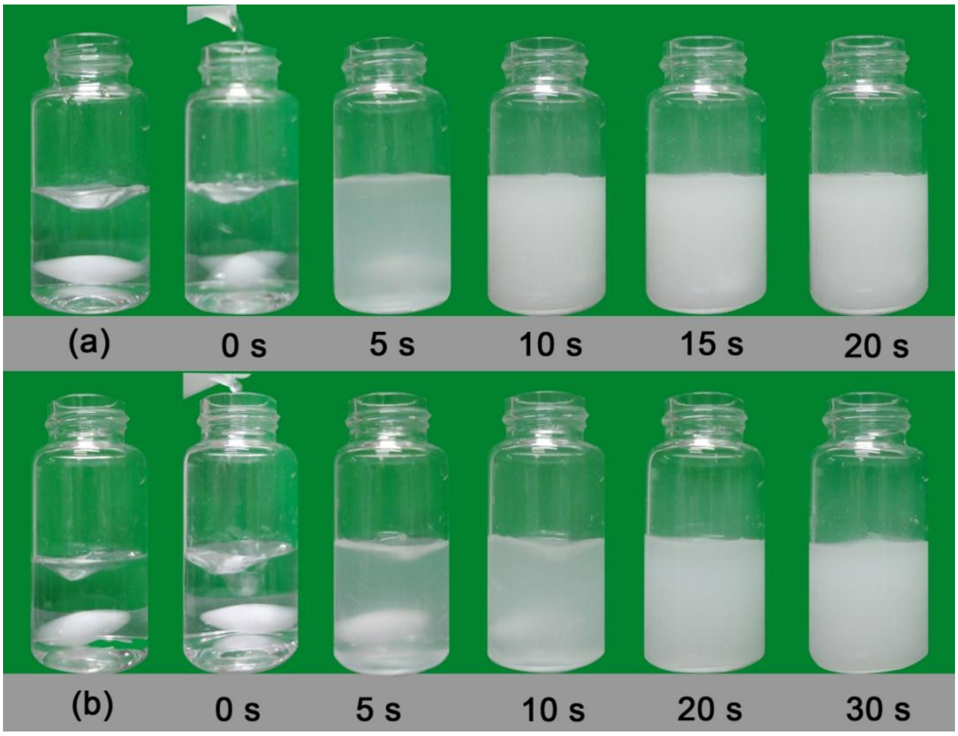


Fig. S4. Photographs showing the reaction phenomena with IWPs of different relative viscosities. (a) are the photographs of SHM-6 (*RV* = 4.83) and (b) are those of SHM-7 (*RV* = 6.52).

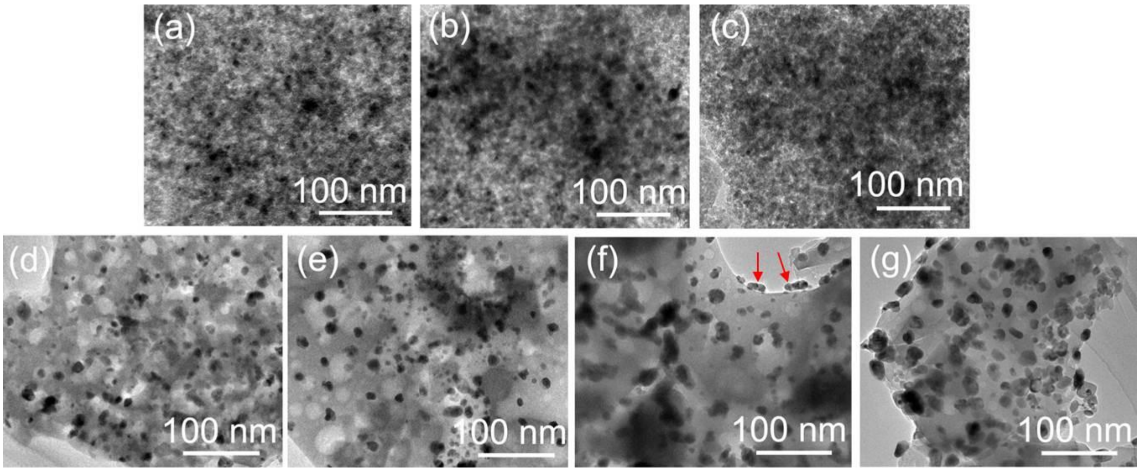
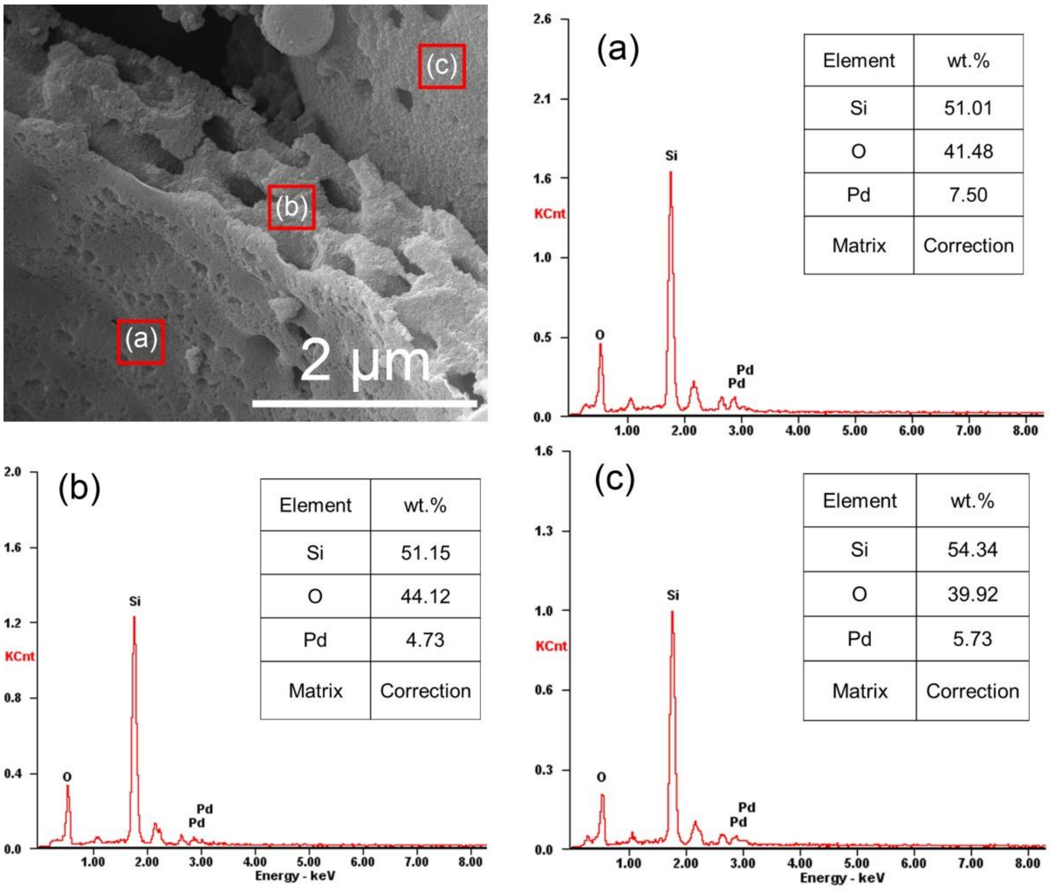


Fig. S5. TEM images of different catalysts. (a) S1-Pd/SHMs; (b) S2-Pd/SHMs; (c) S7-Pd/SHMs; (d) S3-Pd/SHMs; (e) S5-Pd/SHMs; (f) S6-Pd/SHMs; (g) S9-Pd/SHMs.



(a)

Element	wt.%
Si	51.01
O	41.48
Pd	7.50
Matrix	Correction

(b)

Element	wt.%
Si	51.15
O	44.12
Pd	4.73
Matrix	Correction

(c)

Element	wt.%
Si	54.34
O	39.92
Pd	5.73
Matrix	Correction

Fig. S6. SEM-EDS analysis of S9-Pd/SHMs at different positions. (a) Inner surface; (b) wall of macropores; (c) outer surface.

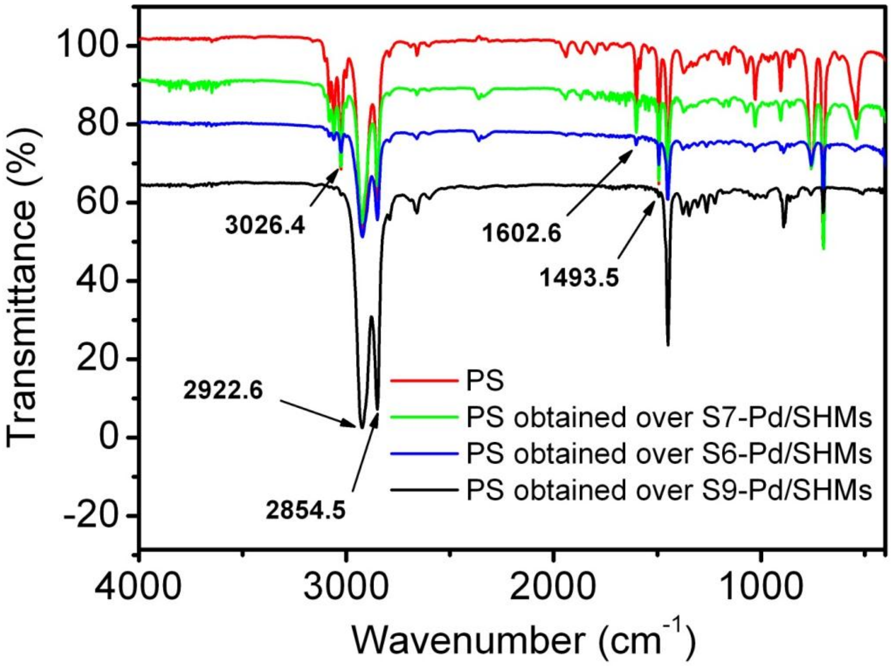


Fig. S7. FTIR spectra of PS and hydrogenated PSs obtained over the different catalysts.

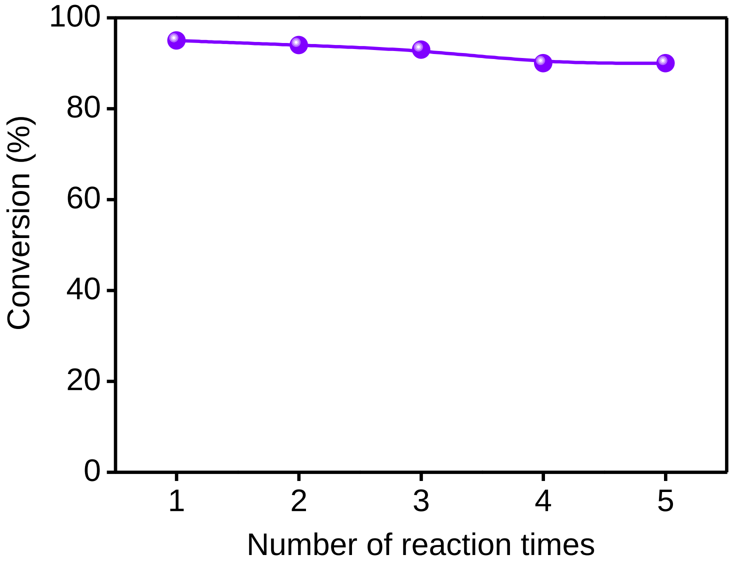


Fig. S8. The catalytic results obtained over S9-Pd/SHMs in five cycles of reaction.