

## Electronic Supplementary Information

# Synthesis of Yolk-Shell HPW@Hollow Silicalite-1 for Esterification Reaction

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## 1. Synthesis of parent silicalite-1

Silicalite-1 was synthesized from the clear solution method<sup>1</sup>. Typically, 15.4 ml of tetraethyl orthosilicate (TEOS) was mixed with a given amount of tetrapropylammonium hydroxide (TPAOH) solution. The molar composition of the synthesis mixture was  $1\text{SiO}_2 : 0.27\text{TPAOH} : 4\text{EtOH} : 46\text{H}_2\text{O}$ . After stirring for 5 h at 308 K, the gel was transferred into a 100 ml Teflon-lined steel autoclave and crystallized at 443 K for 3 days. The product was recovered by centrifugation and dried overnight at 373 K. Finally, the template was removed by calcination in static air at 813 K for 6h.

[1] C. Y. Dai, A. F. Zhang, L. L. Li, K. K. Hou, F. S. Ding, J. Li, D. Y. Mu, C. S. Song, M. Liu, and X. W. Guo, Chem. Mater., 2013, 25, 4197.

## 2. Synthesis of hollow silicalite-1

Hollow silicalite-1 was synthesized by the alkaline treatment method. In a typical experiment, 4 g of zeolite was added to 40 ml 0.3 M tetrapropylammonium hydroxide (TPAOH) solution. The mixture was mixed and heated in an autoclave at 443 K under stirring conditions for 72 h. Afterwards, the resulting solid was recovered by centrifugation, washed with distilled water, and dried overnight at 373 K. Finally, the template was removed by calcination in static air at 813 K for 6 h.

## 3. Synthesis of HPW@Hollow silicalite-1

HPW@Hollow silicalite-1 was synthesized by the ship-in-bottle approach. In a typical experiment, 1 g zeolite, 0.72 g  $\text{Na}_2\text{HPO}_4$  and 3.96 g  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  was added to 10 ml  $\text{H}_2\text{O}$ . The

mixture was mixed and heated in a flask at 40 °C under stirring conditions for 40 h. Afterwards, 3.5 mL HCl was added into the solution. The reaction mixture was heated at 95 °C under stirring conditions for 3 h. The formed HPW@Hollow S-1 was separated by centrifugation and washed 6-10 times with distilled water in order to completely remove the HPW anions formed on the external surface of hollow silicalite-1. Finally, HPW@Hollow S-1 was dried at 100 °C overnight and calcined at 250 °C for 3 h.

#### **4. Synthesis of HPW/Hollow silicalite-1**

HPW/Hollow silicalite-1 was prepared by the method of impregnation. Hollow silicalite-1 was added to a solution of HPW in deionized water and the mixture was dried at 100 °C overnight and calcined at 250 °C for 3 h.

#### **5. Characterization**

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max 2400 diffractometer, using nickel-filtered CuK $\alpha$  X-ray source at a scanning rate of 0.02 over the range between 5 ° and 50 °.

Transmission electron microscopy (TEM) images were taken on Tecnai G2 20 S-twin instrument (FEI Company) with an acceleration voltage of 200 kV. The samples for TEM analysis were prepared by dipping the carbon-coated copper grids into the ethanol solutions of the samples and drying at ambient condition;

Scanning electron microscopy (SEM) images were obtained on a Hitachi S-5500 instrument with an acceleration voltage of 3 kV and 10 kV. Some samples were sputtered with a thin film of gold.

Ar isotherms at 87 K were measured in a Quantachrome autosorb-iQ<sub>2</sub> gas adsorption analyzer.

Prior to the measurement, the samples were degassed in vacuum at 573K for 10h. The Brunauer-Emmett-Teller (BET) method was applied to calculate the total surface area, while the t-plot method was used to discriminate between micro- and mesoporosity. In the t-plot, the reported mesopore surface area ( $S_{\text{meso}}$ ) consists of contributions from the outer surface of the particles as well as mesopores and macropores.

Ammonia temperature programmed desorption ( $\text{NH}_3$ -TPD) of the sample was measured by heating the sample from 100 to 720 °C at a rate of 10 °C/min. Each sample was first treated at 300 °C in Ar flow for 1 h, and then cooled to room temperature. The effluent stream was monitored continuously with a thermal conductivity detector (TCD) to determine the rate of ammonia desorption.

Fourier transform infrared (FT-IR) spectra were recorded on an EQUINOX55 infrared spectrometer (Bruker Corp.) at 4  $\text{cm}^{-1}$  resolution. The sample used for IR was finely ground and pressed into a self-supporting wafer (8-10  $\text{mg}/\text{cm}^2$ , diameter 15 mm).

The solid state NMR experiments were performed on a Bruker Avance III 600 spectrometer equipped with a 14.1 T wide-bore magnet. The resonance frequency was 242.9 MHz.  $^{31}\text{P}$  MAS NMR experiments were performed on a 4 mm MAS probe with a spinning rate of 12 kHz.  $^{31}\text{P}$  MAS NMR spectra were recorded using high-power proton decoupling. A 2400 scans were accumulated with a  $\pi/4$  pulse width of 2.25  $\mu\text{s}$  and a 4 s recycle delay. Chemical shifts were referenced to 85%  $\text{H}_3\text{PO}_4$  at 0 ppm.

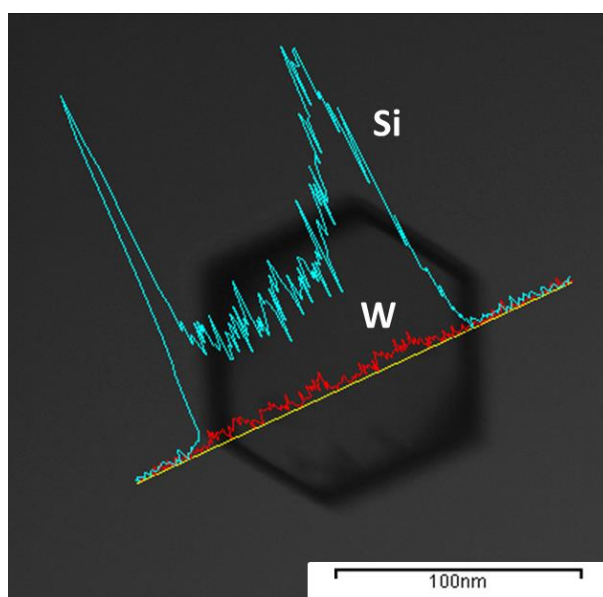
The elemental analysis of catalysts was conducted on a Perkin Elmer OPTIMA 2000DV ICP Optical Emission Spectrometer.

## 6. Catalytic testing

All reactions were conducted in a 50 mL tubular flask equipped with a magnetic stirring bar. In a typical procedure, 1 g of catalyst, 0.1 mole of acetic acid and 0.2 mole of ethanol were added to the flask. The mixture was stirred at 110 °C for 6 h under reflux conditions. After reaction, the product was analyzed by GC. For the catalyst recycling experiments, the used catalyst was dried at 100 °C overnight and used in the next run.

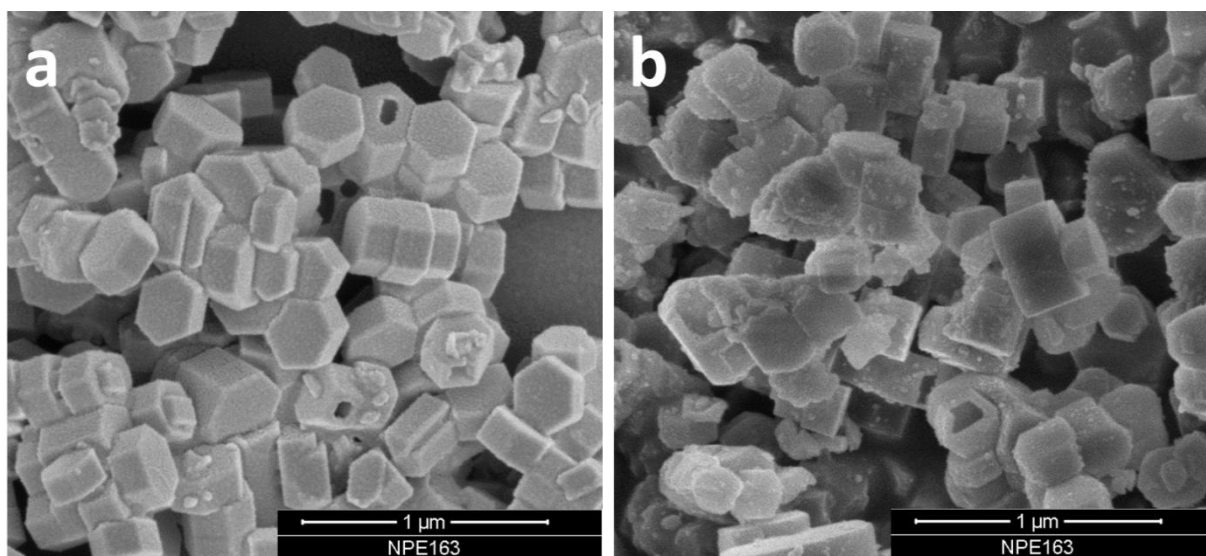
The catalytic performance of pure HPW: The amount of HPW is 0.03 g, and the catalytic testing procedure for HPW is the same as that with HPW/Hollow S-1 or HPW@Hollow S-1.

## 7. Electronic image and compositional line profiles of HPW@Hollow S-1



**Figure S1** Electronic image and compositional line profiles for HPW@Hollow S-1.

## 8. SEM images of the HPW@Hollow S-1 and HPW/Hollow S-1



**Figure S2** SEM images of the a) HPW@Hollow S-1 and b) HPW/Hollow S-1.

The images show that there are few HPW nanoparticles on the outer surface of hollow S-1 HPW@Hollow S-1 due to the 6-10 times washing after encapsulation. By contrast, it is clear that HPW nanoparticles distributed on the outer surface of HPW/Hollow S-1.

## 9. Ar adsorption isotherms

**Table S1** Results of porosity analysis

Sample	Area <sup>a</sup> (BET)/m <sup>2</sup> g <sup>-1</sup>	Total pore <sup>b</sup> volume/cm <sup>3</sup> g <sup>-1</sup>	Micro-pore <sup>c</sup> volume/cm <sup>3</sup> g <sup>-1</sup>	Micro-pore <sup>c</sup> area/m <sup>2</sup> g <sup>-1</sup>
Solid Silicalite-1	480	0.41	0.14	370
Hollow Silicalite-1	452	0.46	0.14	373
HPW@Hollow Silicalite-1	389	0.49	0.11	302

<sup>a</sup> Calculated from the Ar adsorption branch using the BET method.

<sup>b</sup> Estimated from the single-point amount adsorbed at P/P<sub>0</sub>=0.99.

<sup>c</sup> Calculated from the Ar adsorption branch using the t-plot method.

## 10. X-ray powder diffraction

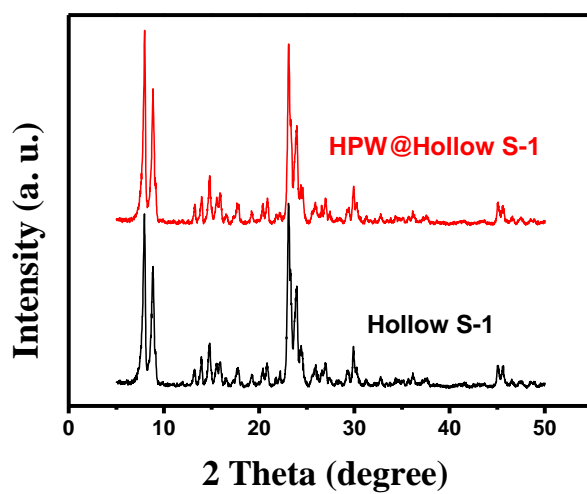


Fig. S3 XRD patterns of hollow silicalite-1 and HPW@Hollow S-1.

## 11. NH<sub>3</sub>-TPD

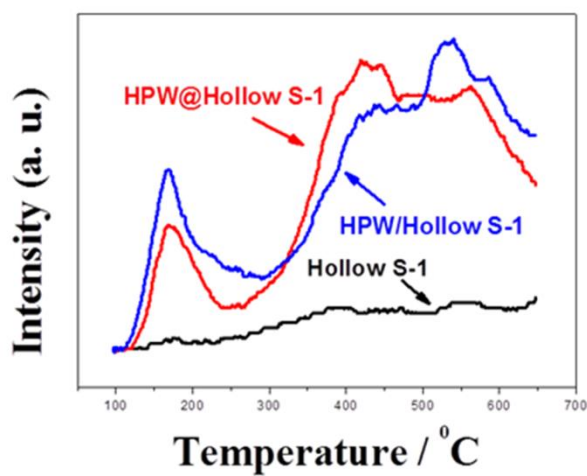


Fig. S4 NH<sub>3</sub>-TPD profiles of hollow silicalite-1, HPW@Hollow S-1 and HPW/Hollow S-1.

## 12. FT-IR

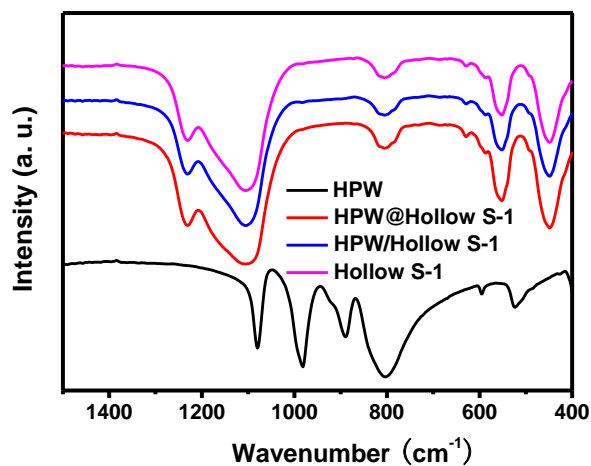


Figure S5 FT-IR spectra of pure HPW, HPW@Hollow S-1, HPW/Hollow S-1 and Hollow S-1.

## 13. Solid-state <sup>31</sup>P MAS NMR

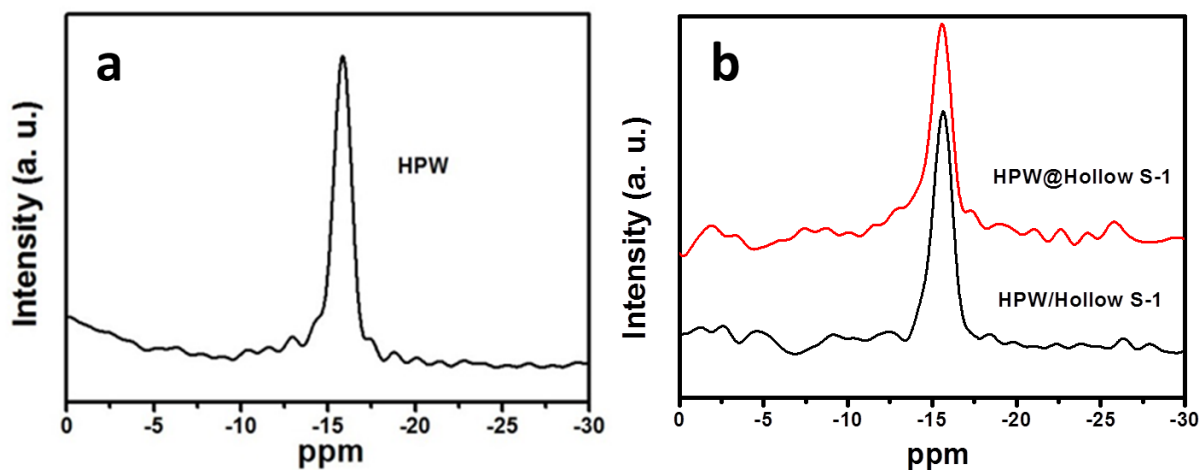


Fig. S6 Solid-state <sup>31</sup>P MAS NMR spectra of a) pure HPW, b) HPW/Hollow S-1 and HPW@Hollow S-1.



#### 14. Elemental analysis after recycle runs

The elemental analysis after recycle runs has been added in **Table S2**. The HPW loss of the HPW/Hollow S-1 samples is 89% due to the leaching occurs during the catalytic process. In contrast, the HPW loss of the HPW@Hollow S-1 samples is 11%.

**Table S2** Tungsten contents of the catalysts before and after running 6 times.

<b>Sample</b>	<b>Tungsten contents</b>	<b>Tungsten contents</b>
	<b>before running<sup>a</sup></b>	<b>after running 6 times<sup>a</sup></b>
<b>HPW/Hollow S-1</b>	1.96 wt%	0.21 wt%
<b>HPW@Hollow S-1</b>	2.09 wt%	1.86 wt%

a measured by inductively coupled plasma mass spectrometer (ICP)