Supporting information

Preparation of asphalt-based microporous organic polymers catalyzed by heteropoly acids

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Experimental Procedures

Chemicals and Materials

The asphalt with a softening point of 270 °C measured according to Chinese national standard (GB/T4507-2014) is provided by Jining Carbon Group Co., Ltd, and it is a mixture which consists of 81.4 % asphaltenes (As), 4.6 % saturates (S), 10.8 % aromatics (Ar) and 2.2 % resins (R), determined by the method described in Chinese national standard (GB/T0618-1993). Elemental combustion analysis (%) of asphalt afford: C: 94.43 %, H: 6.65 %, S: 0.51 %, C/H = 1.18. More details about the asphalt were described in our previous work.[1] Formaldehyde dimethyl acetal (FDA, 98 %) was purchased from Aladdin Chemical Industry Co., Ltd. Phosphotungstic acid 44-hydrate (HPW, 98%) was purchased from J&K Scientific Co., Ltd. Tungstosilicic acid 26-hydrate (HSiW, 98%) and phosphomolybdic acid x-hydrate (HPMo, 98%) were purchased from Shanghai Macklin Biochemical Co., Ltd (Shanghai, China). Before using, HPW and HSiW were dehydrated at 240 °C for 3h, HPMo was dehydrated at 130 °C for 2h according to the TGA profiles (Fig. S2). Methanol, 1, 2-dichloroethane (DCE) were obtained from Sinopharm chemical reagent Co., Ltd (Shanghai, China). DCE was dried over night with CaH_2 and then distilled. Unless specifically noted, all the chemical reagents were analytical grade and used as received without further purification.

Instruments

The infrared spectra were recorded on a Fourier transform infrared (FTIR) spectrometer (NICOLET iS10). The ^{13}C cross-polarization magic angle spinning (CP/MAS) NMR spectra were obtained on a WB 400 MHz BRUKER AV III spectrometer. Measurements were made with a 4 mm MAS probe spinning at 12 kHz. TGA curves were obtained from a NETZSCH-TG209F1 under air, 5 °C min^{-1}. Elemental analysis was performed by using an Elementar Vario EL III elemental analyzer. Powder X-ray diffraction (XRD) was performed on a Bruker D8 Advance X-ray diffractmeter. The morphologies of the samples were observed by scanning electron microscopy (SEM) (SU-70, Hitachi) under an electron beam with an accelerating voltage of 15 kV and a working distance of 15 mm. The high-resolution transmission electron microscopy (HRTEM) images were observed by JEM-2100 (JEOL) with an acceleration voltage of 200 kV. Nitrogen adsorption/desorption isotherms at 77.3 K were obtained using a Micromeritics TriStar II 3020 static volumetric analyzer. The N_2 adsorption isotherms were measured at 77.3 K up to 1.0 bar. Prior to adsorption measurements, the samples were degassed for 12 h at 100 °C ensuring that the residual pressure fell below 10 mbar. The Brunauer–Emmett–Teller surface area was calculated within the relative pressure range of 0.05 to 0.2. The total volume

was calculated at $P/P_0 = 0.99$. The CO_2 adsorption isotherms were measured at 273 K and 298 K up to 1.0 bar using a Micromeritics TriStar II 3020 static volumetric analyzer. The H_2 adsorption isotherms were measured using a Micromeritics ASAP 2020 static volumetric analyzer at 77.3 K up to 1.13 bar.

Synthetic procedures

Synthesis of PW-HCP-1 and **Recovery of HPW-1** Typically, asphalt (0.3040 g) and FDA (0.9120 g) were dissolved in 10 mL dried DCE under nitrogen atmosphere, then 2.880 g dehydrated HPW (hexahydrate, denoted as HPW-1) was added to the homogeneous solution. Subsequently the reaction was allowed to proceed at 80 °C for 18h. After the reaction, the resultant mixture was filtrated with methanol to recover the catalyst. Then the filter cake was further extracted in Soxhlet extractor with methanol and DCE, and finally dried under vacuum at 80 °C for 24 h. The product (denoted as PW-HCP-1) was obtained as dark brown powder (0.4655g, yield=104%, Equation S1). The methanol filtrate was dried by rotary evaporation at 50 °C under reduced pressure, then the gray white powder was collected, dried at 80 °C for 3h and recycled for the next polymerization (denoted as HPW-2, 2.8317g, recovery yield=98%).

Control experiment Control experiment was conducted following the same procedures as PW-HCP-1 unless the as-received phosphotungstic acid 44-hydrate was used directly without dehydration. The product was obtained as dark powder (0.3842g, yield=86%). Similarly, the employed catalyst was recovered with a recovery yield of 83% (2.3895g).

Synthesis of SiW-HCP-1 Synthesis of SiW-HCP-1 was followed the same procedures as PW-HCP-1 unless as dehydrated HSiW was used. The product (denoted as SiW-HCP-1) was obtained as dark powder (0.4755g, yield=106%, Equation S1).

Synthesis of PMo-HCP-1 Synthesis of PMo-HCP-1 was followed the same procedures as PW-HCP-1 unless as dehydrated HPMo was used. The product (denoted as PMo-HCP-1) was obtained as dark brown powder (0.4605g, yield=103%, Equation S1).

Synthesis of $FeCl_3$-HCP Synthesis of $FeCl_3$-HCP was followed the same procedures as PW-HCP-1 unless $FeCl_3$ was used. The product (denoted as $FeCl_3$-HCP) was obtained as dark brown powder (0.4301g, yield=96%).

Recycle experiments The recycle experiments were performed taking the synthesis of PW-HCP as an example. Similar to the synthesis of PW-HCP-1, HPW-2 (2.736g) was employed for the next synthesis (0.2888g asphalt and 0.8664g FDA in 10ml DCE) to afford PW-HCP-2 (0.4207g, yield=99%). And HPW-2 was recovered with a recovery yield of 95% (2.6034g, denoted as HPW-3).

HPW-3 (2.544g) was employed for the next synthesis (0.2686g asphalt and 0.8058g FDA in 10ml DCE) to afford PW-HCP-3 (0.3862g, yield=98%). And HPW-3 was recovered with a recovery yield of 95% (2.4264g, denotes as HPW-4).

HPW-4 (2.366g) was employed for the next synthesis (0.2500g asphalt and 0.7500g FDA in 10ml DCE) to afford PW-HCP-4 (0.2652g, yield=72%). And HPW-4 was recovered with a recovery yield of 97% (2.3160g, denotes as HPW-5).

HPW-5 (2.2004g) was employed for the next synthesis (0.2325g asphalt and 0.6975g FDA in 10ml DCE) to afford PW-HCP-5 (0.3298g, yield=96%). And HPW-5 was recovered with a recovery yield of 95% (2.0920g, denotes as HPW-6).

HPW-6 (2.0244g) was employed for the next synthesis (0.2139g asphalt and 0.6417g FDA in 10ml DCE) to afford PW-HCP-6 (0.1401g, yield=45%). And HPW-6 was recovered with a recovery yield of 97% (1.9580g, denotes as HPW-7).

HPW-7 (1.8827g) was employed for the next synthesis (0.1989g asphalt and 0.5967g FDA in 10ml DCE) to afford PW-HCP-7 (0.2558g, yield=87%). And HPW-7 was recovered with a recovery yield of 94% (1.7731g, denotes as HPW-8).

HPW-8 (1.6944g) was employed for the next synthesis (0.1790g asphalt and 0.5370g FDA in 10ml DCE) to afford PW-HCP-8 (0.2366g, yield=90%). And HPW-8 was recovered with a recovery yield of 93% (1.5702g, denotes as HPW-9).

HPW-9 (1.5588g) was employed for the next synthesis (0.1647g asphalt and 0.4941g FDA in 10ml DCE) to afford PW-HCP-9 (0.2064g, yield=85%). And HPW-9 was recovered with a recovery yield of 96% (1.5025g).

Computational methods

Equation S1

$$\textbf{Yield\%} = \frac{\mathbf{m_1(g)}}{\mathbf{m_2(g)}} \times \mathbf{100\%}$$

The yield estimation of products are followed the Equation S1. Where m_1 is the real weight of the resulting product measured after vacuum drying; m_2 is the ideal weight including the weight of asphalt and equimolar CH_2 groups from FDA. A small quantity of unreacted methoxy groups will cause m_1 higher than m_2. Thus the yields over 100% of PW-HCP-1, SiW-HCP-1 and PMo-HCP-1 are attributed to the unreacted methoxy groups.[2]

Equation S2

$$\textbf{Recovery yield}(\%) = \frac{\mathbf{m_1(g)}}{\mathbf{m_2(g)}} \times \mathbf{100\%}$$

The recovery yields estimation of HPW-x are followed the Equation S2. Where m_1 is the weight of the employed HPW; m_2 is the weight of the recovered HPW.

Results and Discussion

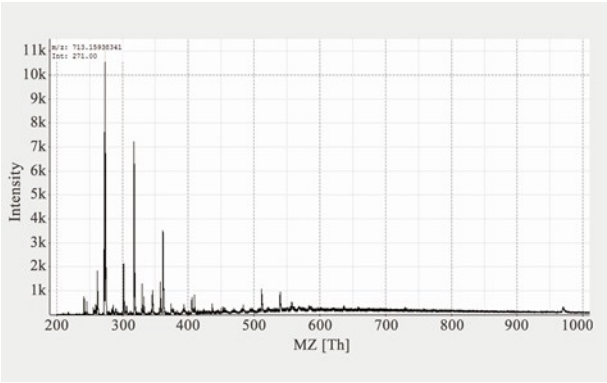

Fig. S1 MALDI-TOF-MS spectrum of the employed asphalt.

As shown in Fig. S2, the mass loss is obviously divided into three steps.[3-5] In the TGA curve of the as received HPW, the first step before 80 °C corresponds to the loss of adsorbed moisture, and the second step between 140 °C and 240 °C is caused by the loss of crystallization water. Subsequently, a plateau is observed between 240 °C and 330 °C. With the continuously increasing temperature, the HPW loses the structure water molecules and finally decomposes. Considering that the stable structure of catalyst is important for recycling, thus the HPW was dehydrated at 240 °C for 3h to afford HPW with the most stable structure, according to the region of the plateau. Similarly, the HSiW is also dehydrated at 240 °C for 3h. While due to the relatively poor thermal stability of the HPMo, the plateau appears between 130 °C and 280 °C. Consequently, the HPMo was dehydrated at 130 °C for 2h.

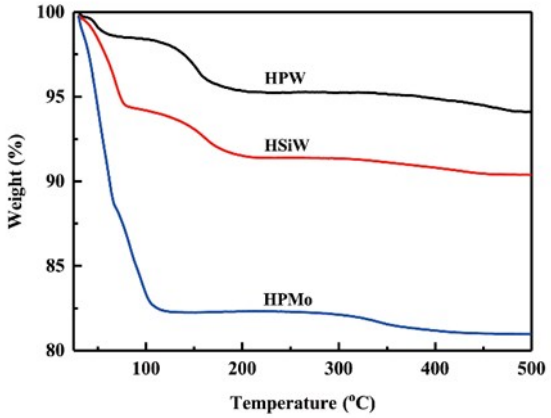

Fig. S2 TGA curves of the as-received HPW, HSiW and HPMo.

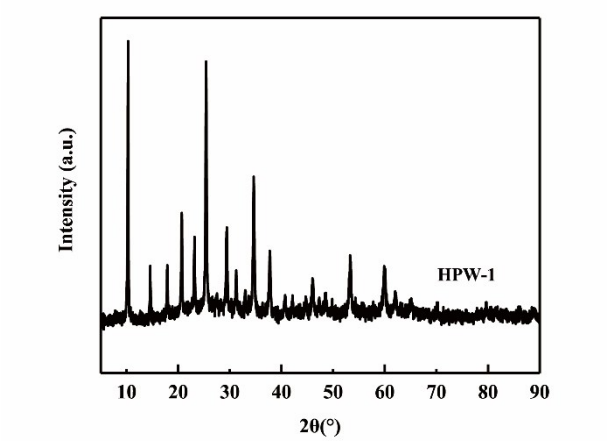

Fig. S3 XRD pattern of the as dehydrated HPW (denoted as HPW-1), which is indexed to the crystal phase of HPW•6 H_2O (JCPDS 50-0304).

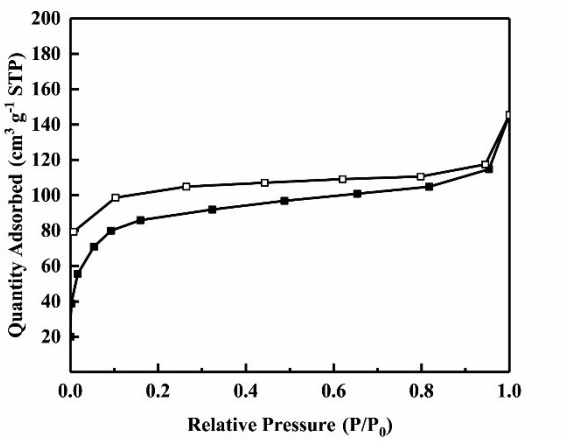

Fig. S4 Nitrogen sorption isotherm of MOP catalyzed by the as-received HPW•44 H_2O at 77.3 K.

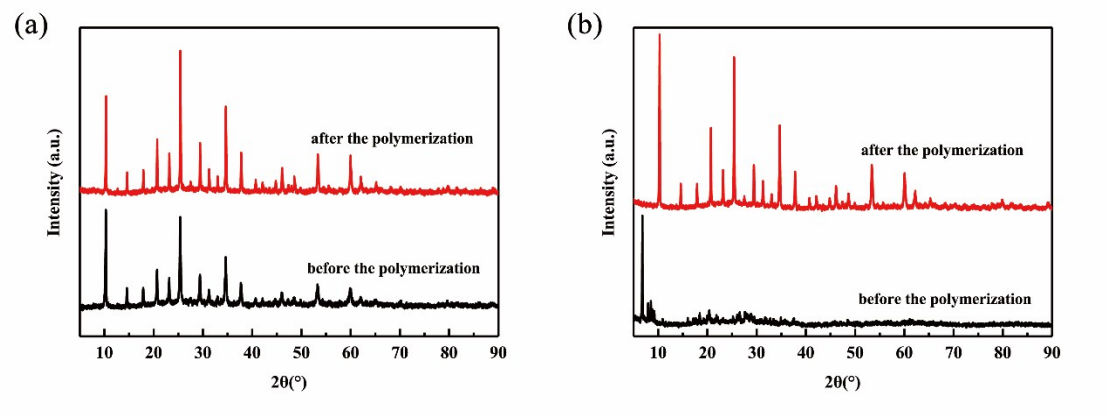

Fig. S5 (a) XRD patterns of the HPW•6 H_2O (HPW-1) before and after the first polymerization. (b) XRD patterns of the as-received HPW•44 H_2O before and after the first polymerization.

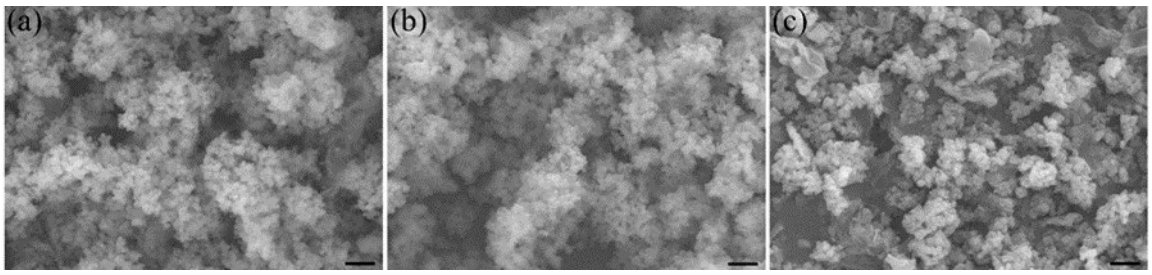

Fig. S6 SEM images of PW-HCP-1(a), SiW-HCP-1(b) and PMo-HCP-1(c). The scale bars: 2 μm.

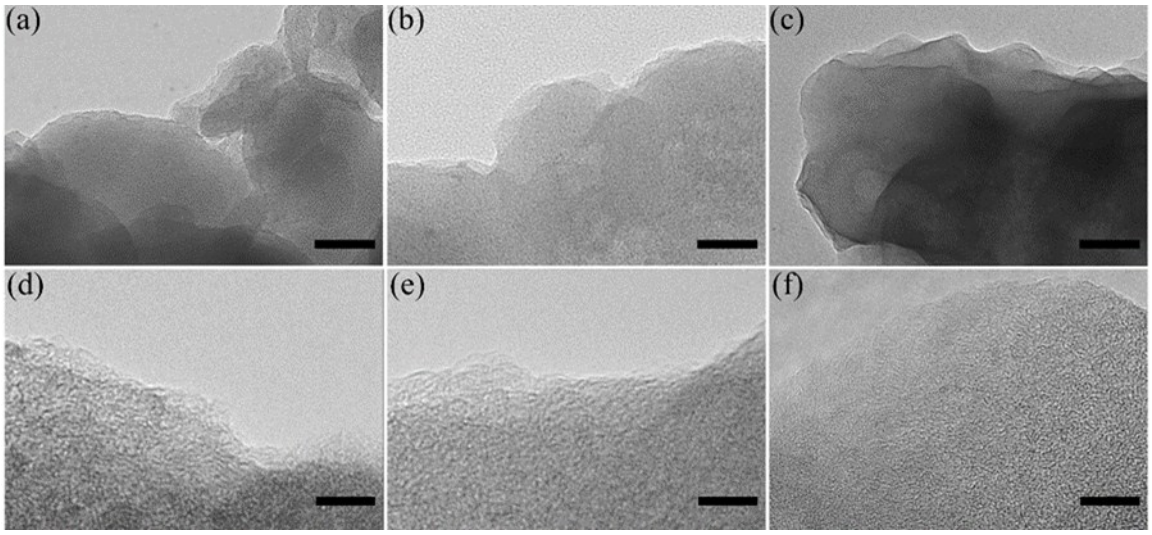

Fig. S7 HR-TEM images of PW-HCP-1(a, d), SiW-HCP-1(b, e) and PMo-HCP-1(c, f). The scale bars: 50 nm (a, b and c), 5 nm (d, e and f), respectively.

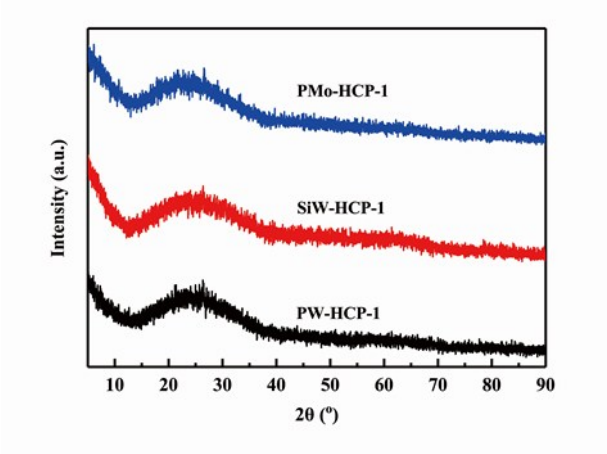

Fig. S8 XRD patterns of PW-HCP-1, SiW-HCP-1 and PMo-HCP-1.

Both SiW-HCP-1 and PMo-HCP-1 show isosteric enthalpy (Q_{st}) values for CO_2 of 28.7-28.2 kJ mol^{-1} and 28.0-27.2 kJ mol^{-1}, respectively.

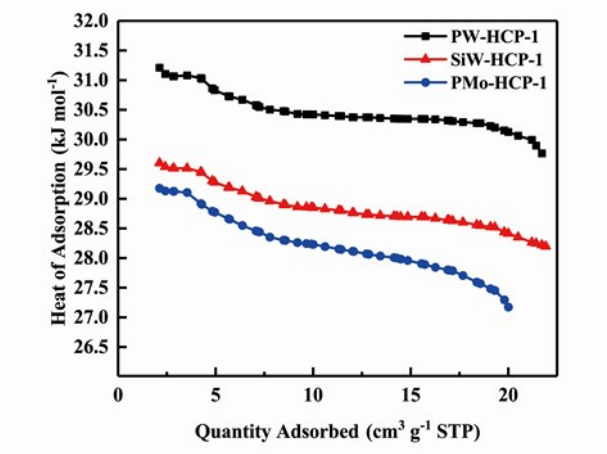

Fig. S9 Isosteric heat of adsorption for PW-HCP-1, SiW-HCP-1 and PMo-HCP-1 determined from CO_2 adsorption isotherms at 273 K and 298 K.

The CO_2/N_2 selectivity of SiW-HCP-1 and PMo-HCP-1 calculated from the initial slope method is 31 and 35, respectively.

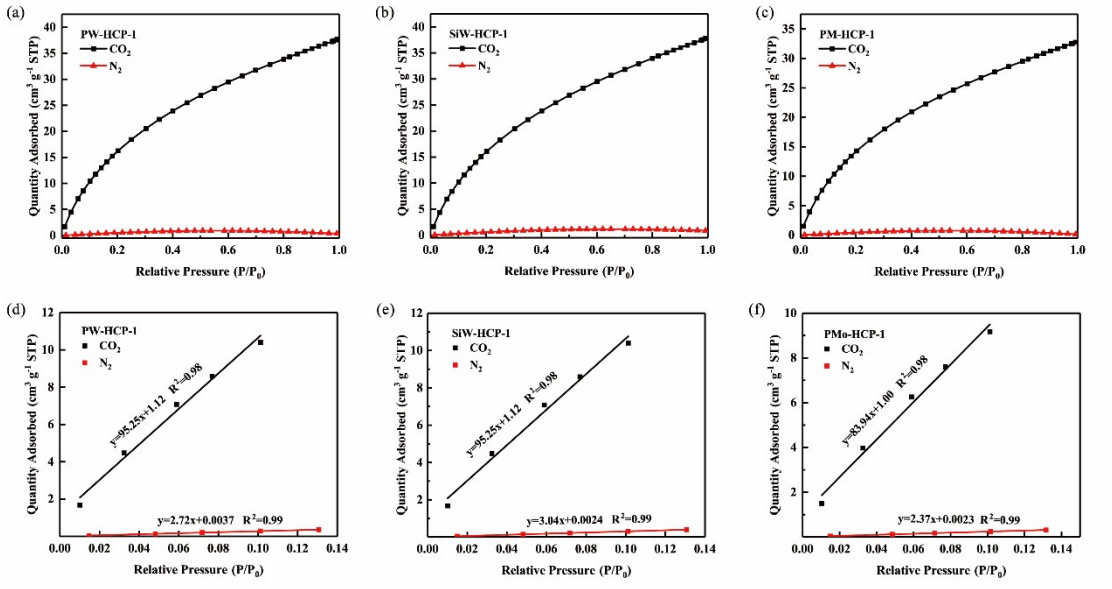

Fig. S10 Adsorption isotherms of CO_2 and N_2 at 273 K for PW-HCP-1 (a), SiW-HCP-1 (b) and PMo-HCP-1 (c). Adsorption selectivity of CO_2 over N_2 for PW-HCP-1 (d), SiW-HCP-1 (e) and PMo-HCP-1 (f) derived from the initial slope method at 273 K.

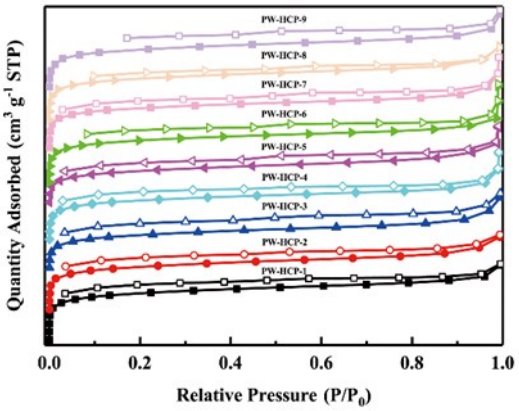

Fig. S11 Nitrogen sorption isotherms of PW-HCP-x at 77.3 K.

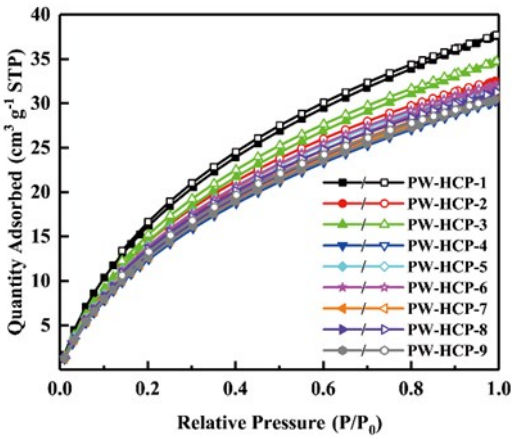

Fig. S12 CO_2 adsorption (filled) and desorption (empty) isotherms of PW-HCP-x up to 1.0 bar at 273 K.

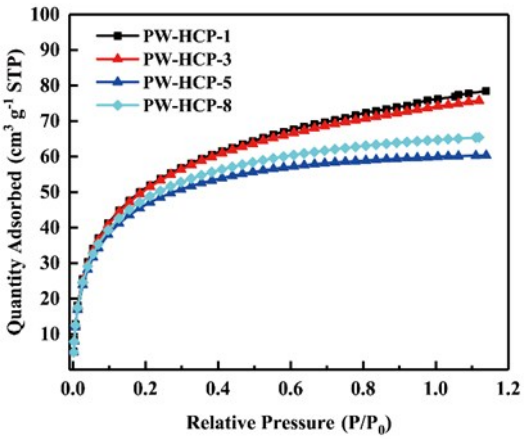

Fig. S13 H_2 adsorption isotherms of PW-HCP-x up to 1.13 bar at 77.3 K.

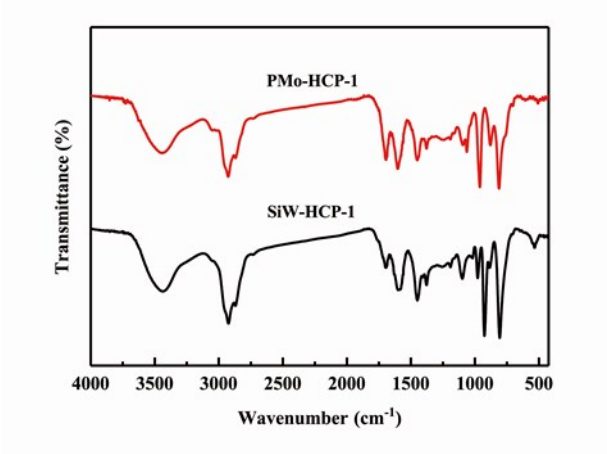

Fig. S14 FT-IR spectra of SiW-HCP-1 and PMo-HCP-1.

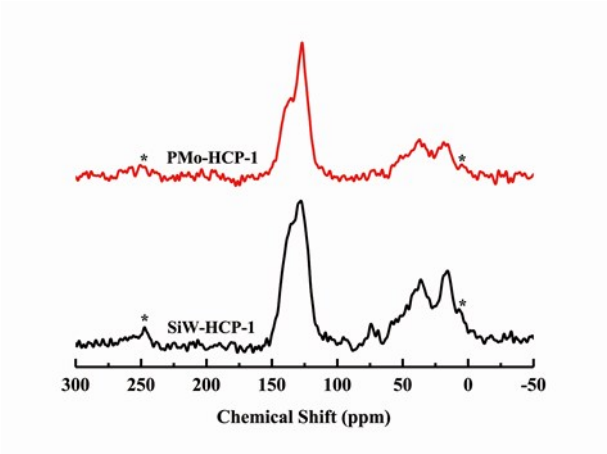

Fig. S15 Solid state ^{13}C cross-polarization nuclear magic-angle spinning (CP/MAS) NMR spectra of SiW-HCP-1 and PMo-HCP-1. Asterisks denote the spinning sidebands.

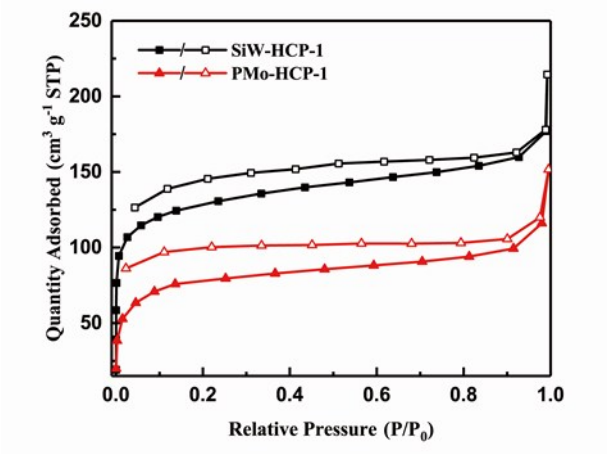

Fig. S16 Nitrogen sorption isotherms of SiW-HCP-1 and PMo-HCP-1 at 77.3 K.

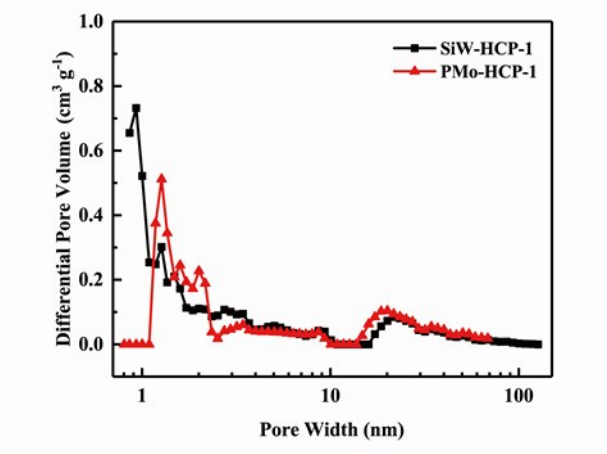

Fig. S17 Pore size distribution curves (calculated using DFT methods) of SiW-HCP-1 and PMo-HCP-1.

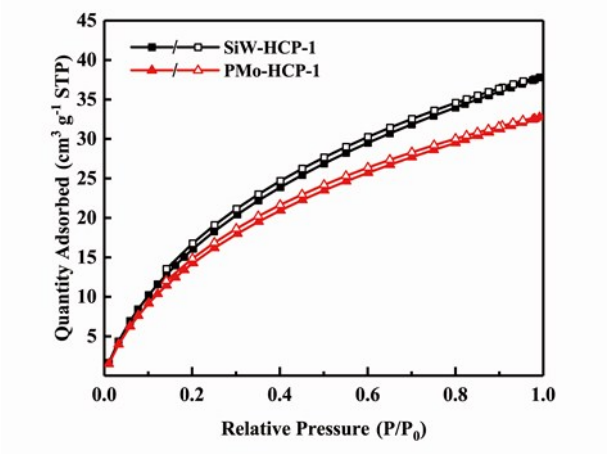

Fig. S18 CO_2 adsorption (filled) and desorption (empty) isotherms of SiW-HCP-1 and PMo-HCP-1 up to 1.0 bar at 273 K.

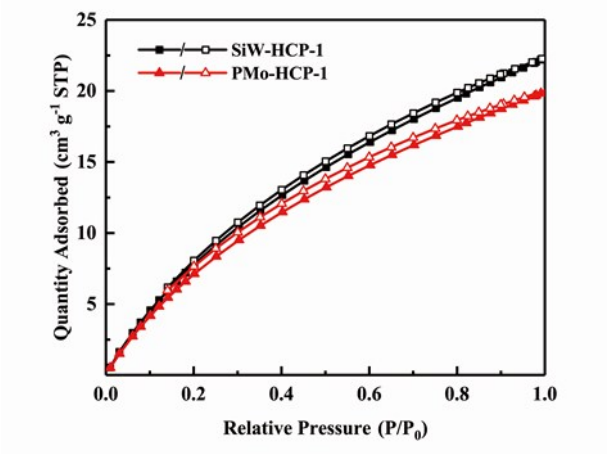

Fig. S19 CO_2 adsorption (filled) and desorption (empty) isotherms of SiW-HCP-1 and PMo-HCP-1 up to 1.0 bar at 298 K.

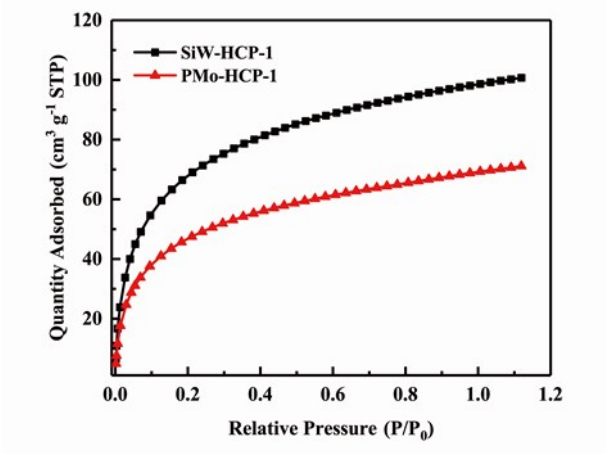

Fig. S20 H_2 adsorption isotherms of SiW-HCP-1 and PMo-HCP-1 up to 1.13 bar at 77.3 K.

References

[1] H. Gao, L. Ding, H. Bai, A. Liu, S. Li, L. Li, *J. Mater. Chem. A* 2016, **4**, 16490-16498.

[2] L. Tan, B. Li, X. Yang, W. Wang, B. Tan, *Polymer* 2015, **70**, 336-342.

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