Supporting Information

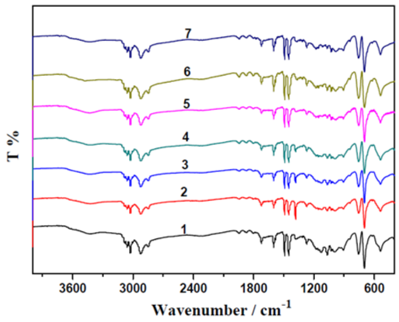

Fig. S1 FT-IR spectra of CaPS-PVPA 1-7

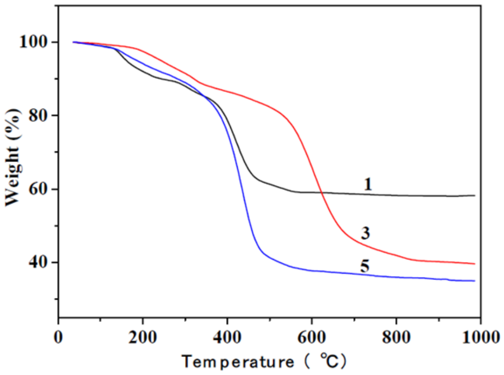

Fig. S2 TG curves of CaPS-PVPA 1, 3, 5.

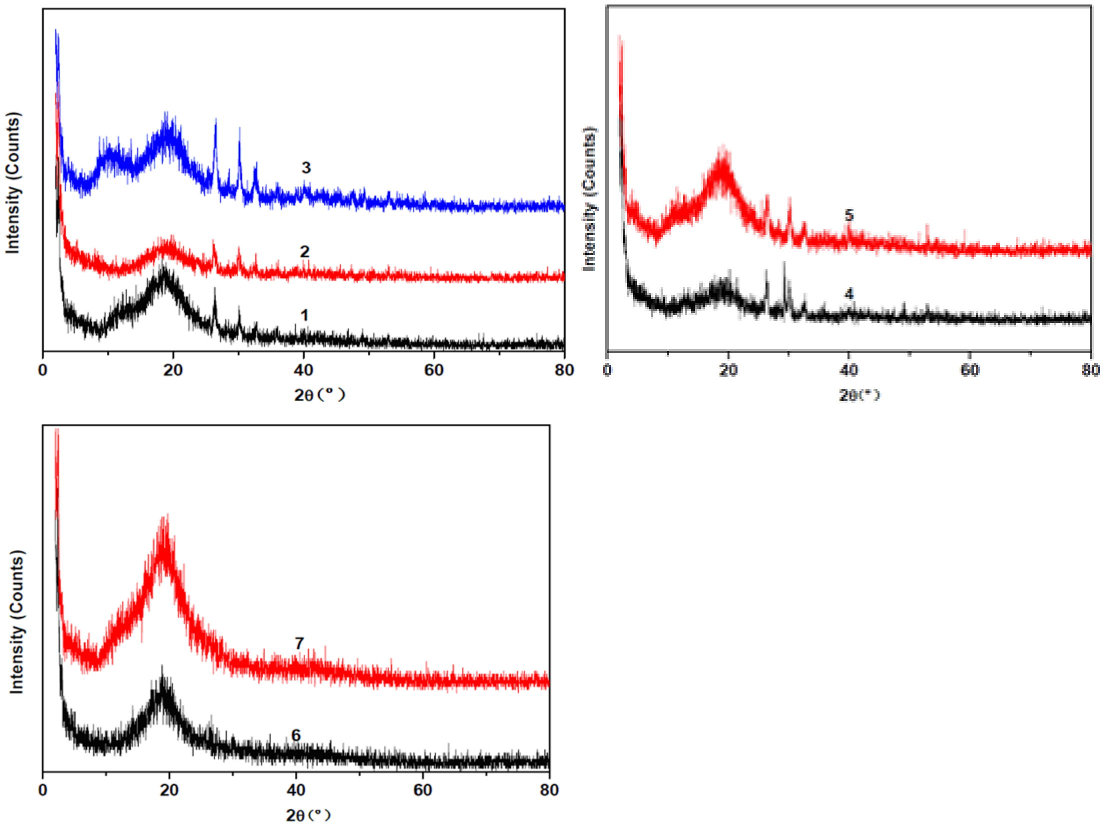

Fig. S3 XRD of CaPS-PVPA 1-7

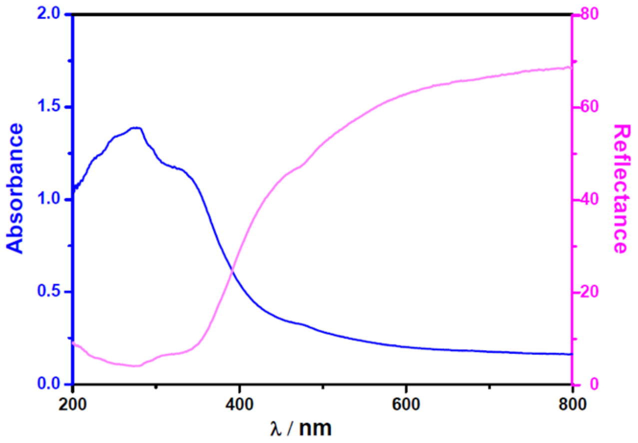

Fig. S4 UV-vis spectrum and diffuse reflectance UV-vis spectrum of CaPS-PVPA 3

Calcium poly(styrene-phenylvinylphosphonate)-phosphate 1.
0.95g, in 56% yield. IR (KBr): vmax/cm^{-1} 3059, 3025, 2922 (CH), 1601, 1493, 1452, 756, 698 (-C_6H_5), 1026 (P=O).

Calcium poly(styrene-phenylvinylphosphonate)-phosphate 2.
1.2g, in 74% yield. IR (KBr): vmax/cm^{-1} 3059, 3025, 2922 (CH), 1601, 1493, 1452, 755, 697 (-C_6H_5), 1027 (P=O).

Calcium poly(styrene-phenylvinylphosphonate)-phosphate 3.
1.3g, in 90% yield. IR (KBr): vmax/cm^{-1} 3059, 3025, 2922 (CH), 1601, 1493, 1452, 756, 697 (-C_6H_5), 1027 (P=O).

Calcium poly(styrene-phenylvinylphosphonate)-phosphate 4.
1.2g, in 76% yield. IR (KBr): vmax/cm^{-1} 3059, 3025, 2921 (CH), 1601, 1493, 1452, 756, 697 (-C_6H_5), 1027 (P=O).

Calcium poly(styrene-phenylvinylphosphonate)-phosphate 5.
1.1g, in 80% yield. IR (KBr): vmax/cm^{-1} 3059, 3025, 2921 (CH), 1601, 1493, 1452, 754, 697 (-C_6H_5), 1026 (P=O).

Calcium poly(styrene-phenylvinylphosphonate)-phosphate 6.
1.1g, in 85% yield. IR (KBr): vmax/cm^{-1} 3059, 3025, 2921 (CH), 1601, 1493, 1452, 756, 697 (-C_6H_5), 1027 (P=O).

Calcium poly(styrene-phenylvinylphosphonate)-phosphate 7.
1.1g, in 91% yield. IR (KBr): vmax/cm^{-1} 3059, 3025, 2921 (CH), 1601, 1493, 1452, 756, 697 (-C_6H_5), 1027 (P=O).

Materials Characterization

FT-IR spectra were recorded with KBr pellets using a Bruker RFS100/S spectrophotometer (USA) and diffuse reflectance UV-vis spectra of the solid samples were examined with an integrating sphere using BaSO4 as the standard. 1H NMR and 31P NMR were performed with AV-300 NMR instrument at ambient temperature at 300 and 121 MHz, respectively. All of the chemical shifts were reported downfield in ppm relative to the hydrogen and phosphorus resonance of TMS and 85% H_3PO_4, respectively. Number- and weight-average molecular weights (Mn and Mw) and polydispersity (Mw/Mn) were estimated by Waters1515 gel permeation chromatograph (GPC; against polystyrene standards) using THF as an eluent (1.0 mL min−1) at 35 ℃. X-ray photoelectron spectrum were recorded on ESCALab250 instrument. The interlayer spacings were obtained on DX-1000 automated X-ray power diffractometer, using Cu Kα radiation and internal silicon powder standard with all samples. The patterns were generally measured between 3.00º and 80.00º with a step size of 0.02º min-1 and X-ray tube settings of 36 kV and 20 mA. C, H and N elemental analysis was obtained from an EATM 1112 automatic elemental analyzer instrument (Thermo, USA). TG analyses were performed on a SBTQ600 thermal analyzer (USA) with the heating rate of 20 ℃ min−1 from 25 to 1000 ℃ under flowing N2 (100 mL min−1). The Mn contents of the catalysts were determined by a TAS-986G (Pgeneral, China) atomic absorption spectroscopy. The FE-SEM were obtained from a JEOL (JSM-6700F) microscope at an acceleration voltage of 5 kV and a working distance of about 8 mm. TEM were obtained on a TECNAI10 (PHILIPS, Holland) apparatus. Nitrogen adsorption isotherms were measured at 77 K on a 3H-2000I (Huihaihong, China) volumetric adsorption analyzer with BET method. The racemic epoxides were prepared by epoxidation of the corresponding olefins by 3-chloroperbenzoic acid in CH2Cl2 and confirmed by NMR (Bruker AV-300), and the gas chromatography (GC) was calibrated with the samples of n-nonane, olefins and corresponding racemic epoxides. The conversions (with n-nonane as internal standard) and the ee values were analyzed by gas chromatography (GC) with a Shimadzu GC2010 (Japan) instrument equipped using a chiral column (HP19091G-B213, 30 m×30 m×0.32 mm×0.25 μm) and FID detector, injector 230 ℃, detector 230 ℃. Ultrapure nitrogen was used as the carrier (rate 34 mL/min) with carrier pressure 39.1kPa and the injection pore temperature was set at 230 ℃. The column temperature for indene, α-methylstyrene and styrene was programmed in the range of 80-180 ℃.

Hypothesized structure of the copolymer

There is another factor for CaPS-PVPA as excellent catalyst support which is bound up with the structure of the copolymer. The hypothesized structure of the copolymer is shown in Fig. S3. In the experiment, the content of PVPA in the copolymer is dealt with the amount of initiator and the ratio of PVPA to St. In general, the main segments of the molecule chain are $-(St)_{m1}-(PVPA)_{r1}-(St)_{m2}-(PVPA)_{r2}-(St)_{m3}-$ in the copolymer, here r1, r2… are usually 1 and seldom more than 2. Although the ratio of PVPA to St in the experiment is 1:8, the content ratio of PVPA to St in the copolymers are found practically in the range of 1:6-9 by virtue of the relative reactivities in the copolymerization for PVPA and St. On account of this, it can be deduced that a great deal of hydrophobic segments of polystyrene can form half or part of holes and cavums with different volumes and shapes for which the content of hydrophobic segments of polystyrene in the copolymer are much more than that of hydrophilic segments of PVPA in the copolymer. Meanwhile, many hydrophilic-PO_3H_2 groups may gather together. The largest surface area with the ratio of organic phosphonate to phosphate is 1:2 for hybrid zirconium phosphonate-phosphate,18 and the similar phenomenon happened to hybrid calcium phosphonate-phosphate. During the synthesis of CaPS-PVPA, nearly all of phosphate in the reactive system take part in the formation of it. While for the organic phosphoric acid in copolymer, the majority participate in preparing or getting into CaPS-PVPA and a small quantity cover on the surface of CaPS-PVPA. Simultaneously, hydrophobic segments of polystyrene in the copolymer which generate half or part of holes and cavums with different volumes and shapes are covered on the surface of CaPS-PVPA. And the two neighboring -PO3H2 groups in the copolymer may be in the same or in a different particle, which will aggregate into larger particles of CaPS-PVPA. Apart from this, the hydrophobic parts of polystyrene and the hydrophilic parts of phosphate contribute to CaPS-PVPA with dual properties for instance hydrophobic and hydrophilic. In other words, CaPS-PVPA may be reacted with other complexes, either in aqueous solution or in organic solvent, even in mixed solvent, which is the character that many other materials cann’t compare with.