

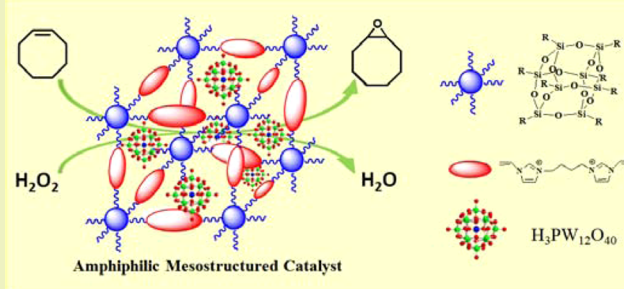
POSS-Derived Mesostructured Amphiphilic Polyoxometalate-based Ionic Hybrids as Highly Efficient Epoxidation Catalysts

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Supporting Information

ABSTRACT: Novel amphiphilic mesostructured polyoxometalate-based ionic hybrids have been successfully synthesized through designing new POSS-derived mesoporous poly(ionic liquids) (POSS-BM_x) to interact with Keggin-type phosphotungstic acid (PW). The obtained ionic hybrids POSS-BM_x-PW have good thermal stability, adjustable pore structure and surface wettability. Catalytic tests for H₂O₂-based epoxidation of cyclooctene, along with comparisons to various counterparts, well demonstrate that POSS-BM_x-PW ($x = 8, 11$) exhibit high activity and selectivity, coupled with convenient recovery and steady reuse. The unique mesoporous structure and the amphiphilic catalyst surface are revealed to be responsible for the catalyst's excellent performances in epoxidation reaction with H₂O₂.

KEYWORDS: Mesoporous material, amphiphilic catalyst, poly(ionic liquids), polyhedral oligomeric silsesquioxanes (POSS), polyoxometalates (POMs)



INTRODUCTION

Polyoxometalates (POMs) are well-known transition metal oxygen clusters and have been widely used in the catalytic field.^{1,2} Particularly, POMs proved to be highly efficient homogeneous catalysts for H₂O₂-based epoxidation of olefins.^{3,4} To recover the catalysts, many efforts have been made to prepare heterogeneous POM-based catalysts. The traditional method is immobilization of POMs on various porous silica and zeolite supports,^{5,6} which favors higher surface areas and adjustable porous structures to accelerate the mass transfer. However, the hydrophilic inorganic frameworks largely influence their catalytic activities because of the low accessibility of the active sites for hydrophobic reactants. Recently, assembling of POMs with appropriate organic counteranions is revealed to be a successful example for preparing heterogeneous POM catalysts,^{7–9} which is beneficial for adjusting the solubility, redox properties, and surface micro-environment of POM. However, these catalysts still suffer from inferior catalytic performance because they are always non-porous. Therefore, it is necessary to develop new strategies to generate suitable micro/mesostructures on these POM hybrid catalysts.

Ionic liquids (ILs) have been extensively investigated as alternative solvents and catalysts for chemical reactions owing to their negligible volatility, remarkable solubility, and potential recyclability.^{10–12} By varying the cations and/or anions with specific functions that constitute IL's structure, it is possible to

design abundant ILs with required functionalities.^{13,14} Indeed, POMs have been used as the counteranions for preparing "task-specific" ionic hybrids,^{15,16} including our recent work on POM-paired hybrid catalysts for heterogeneous organic transformations, and most of them exhibit superior catalytic performance in H₂O₂-based liquid-phase organic oxidation reactions.^{17–19} On the other hand, poly(ionic liquids) (PILs) resulting from the polymerization of ionic liquids (IL) monomers or copolymerization of ILs with other monomers have attracted great research interest owing to their advantages of both ILs and polymers.^{20–22} A topic of interest in this context is the design of mesoporous PILs (MPILs),^{23–26} and many efforts have been devoted to controlling the pore structure, morphology, chemical composition, and surface functionality for various MPIL materials. For example, Yuan et al.^{27–29} prepared a series of porous PIL materials with high surface areas via self-complexation of IL copolymers and carboxylic acid units, and the resulting PIL materials offer great potential applications in catalysis, absorption, and separation. Nevertheless, the properties and function of POM-based porous PIL hybrids have attracted somehow rare attention, possibly due to the extreme difficulty in designing suitable PILs

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that can self-assemble with POM anions to create and control the porosity.

Polyhedral oligomeric silsesquioxanes (POSS), an intriguing class of organic–inorganic hybrid materials, possess a cubic structure represented by the formula $R_8Si_8O_{12}$, in which the central hydrophobic inorganic core (Si_8O_{12}) is surrounded by organic moieties at the eight vertices.^{30–32} Their unique star-shaped nanostructures and chemical properties, such as facile chemical modification, good pH tolerance, high temperature and oxidation resistance properties, make POSS an excellent building block for constructing multifunctional materials.^{33–35} The recent studies have shown that the incorporation of POSS into organic or inorganic polymer could create a micro/mesoporous matrix without using a template.^{36,37} The high surface area provided by the porous polymer network and the functionality of the POSS can be synergistically combined in such a structure configuration, which representing a promising pathway to amplify material functions. In spite of this, so far there are no reports on the preparation of POSS-derived micro/mesoporous PILs by copolymerization of POSS units with ILs.

Herein, we demonstrate a successful preparation of mesoporous POM-based ionic hybrids with amphiphaticity by copolymerization of dicationic imidazole IL (BM) with octa(*N*-vinylimidazole silsesquioxane) POSS without using any templates, followed by ion exchange with the Keggin-type $H_3PW_{12}O_{40}$. The POSS unit is introduced to control the pore structure and wettability of the obtained POSS-BM_x-PW hybrids. Catalytic tests for H_2O_2 -based epoxidation of cyclooctene, along with comparisons to various counterparts, have shown that this newly designed catalysts exhibit high activity and selectivity, coupled with easy recovery and steady reuse.

EXPERIMENTAL SECTION

Reagents and Analysis. All chemicals were analytical grade and used as received. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 360 FT-IR instrument (KBr discs) in the 4000–400 cm^{-1} region. 1H NMR and ^{29}Si NMR spectra were measured with a Bruker DPX 400 spectrometer at ambient temperature in D_2O or $CDCl_3$ using tetramethylsilane (TMS) as the internal reference. Thermogravimetric (TG) analysis was carried out with a STA409 instrument in dry air at a heating rate of 10 $^{\circ}C/min$. Nitrogen adsorption/desorption were measured at liquid nitrogen temperature, using an ASAP 2020 gas sorption analyzer (Micromeritics, USA). Before analysis, the samples were degassed under vacuum condition at 120 $^{\circ}C$ for 3 h. The Brunauer–Emmett–Teller (BET) surface areas were calculated based on the linear part of the BET plot ($P/P_0 < 0.30$). The total pore volumes were estimated according to nitrogen uptake at a relative pressure (P/P_0) of ca. 0.99. The pore size distribution was derived from the desorption branch of N_2 isotherms using Barrett–Joyner–Halenda (BJH) method. Water repellency was checked by the contact angle of a pure water droplet using a contact angle meter of OCA 40. Scanning electron microscopy (SEM) images were performed on a HITACHI S-4800 field-emission scanning electron microscope. Transmission electron microscopy (TEM) images were obtained with JEOL JEM-2100 electron microscope operated at 200 Kv. The amount of leached tungsten species in the filtrate was measured using a Jarrell–Ash 1100 ICP-AES spectrometer. The CHN elemental analysis was performed on an elemental analyzer Vario EL cube.

Preparation of Catalysts. *Synthesis of IL 1,1-(Butane-1,4-diyl)-bis(3-vinylimidazolium)]Br₂ (BM).* The dicationic imidazole IL 1,1-(butane-1,4-diyl)-bis(3-vinylimidazolium)]Br₂ was prepared according to our previous report.³⁸ In detail, *N*-vinylimidazole (18.84 g, 0.20 mol) and 1,4-dibromobutane (21.59 g, 0.10 mol) were dissolved in isopropyl alcohol (50 mL) with stirring at 80 $^{\circ}C$ for 24 h under

nitrogen atmosphere. On completion, the white solid of BM was obtained after the removing of solvent and washing with tetrahydrofuran (THF). 1H NMR (400 MHz, D_2O , TMS) δ (ppm) = 2.00 (s, 2H, CH_2), 4.34 (s, 2H, CH_2), 5.44 (d, 1H, CH), 5.86 (d, 1H, CH), 7.18 (m, 1H, CH), 7.63 (s, 1H, CH), 7.81 (s, 1H, CH), 9.11 (s, 1H, CH) (see the Supporting Information, Figure S1).

Synthesis of Octa(3-chloropropyl silsesquioxane) (POSS-Cl). Octa(3-chloropropyl silsesquioxane) was prepared according to the previous literature.³⁹ Typically, methanol (150 mL) and concentrated hydrochloric acid (5 mL) were added into a 250 mL flask. Then, (3-chloropropyl)trimethoxysilane (15 g) was added dropwise into the above solution with vigorous stirring. After 48 h of stirring, di-*n*-butyltin dilaurate (0.15 g, 0.24 mmol), as a condensation catalyst, was added into the above mixture, followed by 48 h reaction. The formed white crystalline precipitate product POSS-Cl was filtered and washed with methanol for three times, and dried in vacuum at 80 $^{\circ}C$ for 24 h. 1H NMR (400 MHz, $CDCl_3$, TMS) δ (ppm) = 0.82 (t, 16H, $SiCH_2$), 1.90 (m, 16H, CH_2), 3.57 (t, 16H, CH_2Cl) (see the Supporting Information, Figure S2). ^{29}Si NMR (400 MHz, $CDCl_3$, TMS) δ (ppm) = 67.08 (s, O–Si–O) (see the Supporting Information, Figure S3). Elemental analysis for POSS-Cl calcd (wt %): C, 27.80; H, 4.67. Found: C, 27.72; H, 4.77.

Synthesis of Octa(N-vinylimidazole silsesquioxane) (POSS-IM). Octa(*N*-vinylimidazole silsesquioxane) was prepared as follows: POSS-Cl (2 mmol) and *N*-vinylimidazole (16 mmol) were dissolved in toluene (50 mL). The reaction mixture was vigorously stirred at 80 $^{\circ}C$ for 48 h under nitrogen atmosphere. On completion, toluene was removed by distillation, and the residue was washed with ethanol for three times and dried under vacuum to afford POSS-IM. 1H NMR (400 MHz, $CDCl_3$, TMS) δ (ppm) = 0.83 (t, 16H, $SiCH_2$), 1.90 (m, 16H, CH_2), 3.56 (t, 16H, CH_2Cl), 4.93 (d, 16H, CH), 5.32 (d, 16H, CH), 6.93 (m, 16H, CH), 7.16 (d, 32H, CH_2), 7.67 (s, 16H, CH) (see the Supporting Information, Figure S4).

Synthesis of Ionic Copolymer POSS-BM_x. POSS-BM_x (*x* stands for the molar ratio of BM with POSS) copolymers were synthesized through free radical polymerization of POSS-IM with BM. As a typical run for the synthesis of POSS-BM₈, the obtained POSS-IM (1.79 g, 1 mmol), BM (3.23 g, 8 mmol), and azodiisobutyronitrile (AIBN, 0.12 g) were dissolved in a mixture solvent (anhydrous dimethylformamide 15 mL and anhydrous ethanol 15 mL). Then the solution was stirred at 80 $^{\circ}C$ for 24 h. On completion, the above mixture was added dropwise into ethyl acetate (200 mL) to afford a light yellow solid. The solid product POSS-BM₈ was filtered, washed with ethanol, and dried under vacuum. The other ionic copolymers POSS-BM₂, POSS-BM₄, POSS-BM₆, and POSS-BM₁₁ were prepared by similar procedures.

Synthesis of PW-based Ionic Hybrids POSS-BM_x-PW. Ionic hybrids POSS-BM_x-PW were prepared from the reaction between POSS-BM_x and $H_3PW_{12}O_{40}$ (PW). The starting molar ratio of POSS-BM_x to PW was 1:(8 + 2*x*)/3 (8 stands for the positive number of POSS; 2 stands for positive number of BM; 3 stands for negative number of PW). POSS-BM_x and PW were dissolved in dimethylformamide (DMF, 20 mL) and deionized water (20 mL), respectively. Then the aqueous solution of PW was added into the POSS-BM_x solution, followed by stirring at room temperature for 24 h. The white solid products (POSS-BM_x-PW) were filtered, washed with ethanol and deionized water for three times, and dried under vacuum. The ionic hybrid BM-PW was prepared accordingly.

Catalyst Test. Cyclooctene (1 mmol), solvent (5 mL), and catalyst (5.56 μ mol), were loaded into a 25 mL round-bottom flask and then H_2O_2 (30 wt %, 3 mmol) was added dropwise into the mixture. The reaction was vigorously stirred at 70 $^{\circ}C$ for 6 h. After reaction, the product mixture was analyzed by gas chromatography (GC). For a four-run operation of the epoxidation of cyclooctene to test the catalytic stability of POSS-BM₈-PW, the catalyst was recovered by a filtration or centrifugation after reaction, followed with washing with ethanol and vacuum drying.

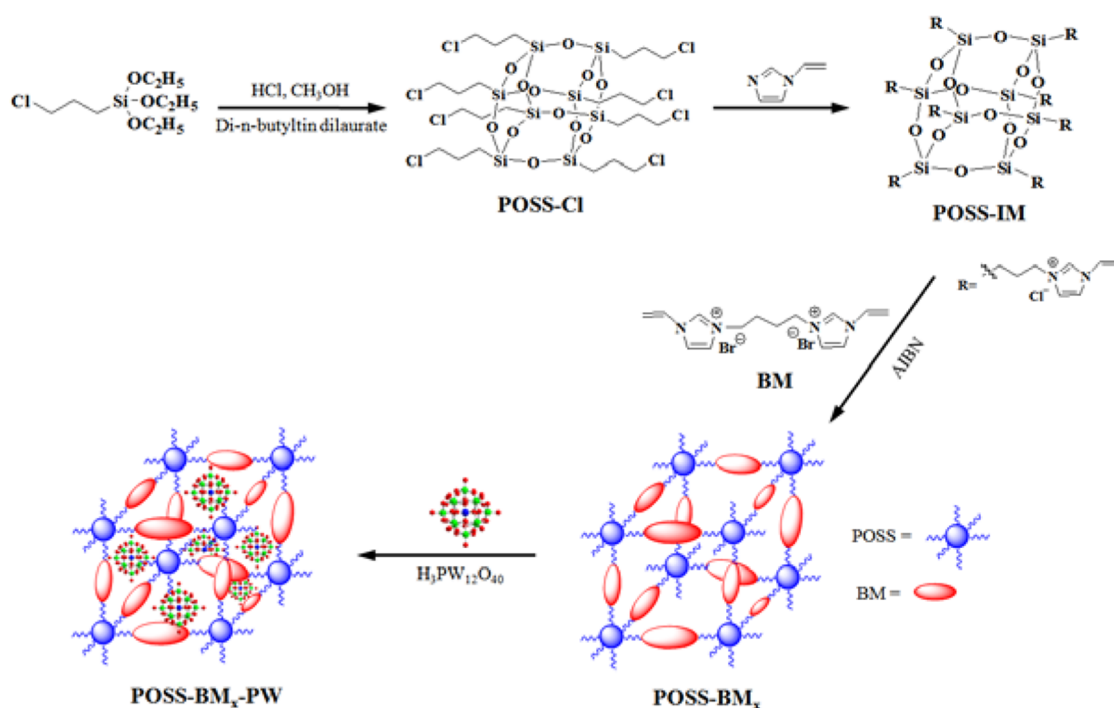


Figure 1. Schematic illustration outlining the preparation and structure for the ionic hybrids POSS-BM_x-PW.

RESULTS AND DISCUSSION

Preparation and Characterization of POSS-BM_x-PW.

The preparation of the POM-based ionic hybrids was carried out according to the procedures shown in Figure 1. A POSS precursor, octa(3-chloropropyl silsesquioxane) POSS-Cl was first prepared by hydrosilylation of octachloropropyl POSS with triethoxysilane. Then, the vinyl imidazole was tethered onto the POSS-Cl via nucleophilic substitution reaction to give POSS-IM, which was characterized by ¹H NMR (see the Supporting Information, Figures S2 and S4). The PILs POSS-BM_x were synthesized by free radical copolymerization of POSS-IM and BM using AIBN as the initiator. By varying the molar ratio of the BM to POSS-IM, a series of ionic copolymers POSS-BM_x could be prepared in the same way. Afterward, H₃PW₁₂O₄₀ was anion-exchanged into the POSS-BM_x polymeric framework to provide the final catalysts POSS-BM_x-PW, which were fully characterized by nitrogen sorption, TG, TEM, SEM, FT-IR, XRD, and contact angle. The TG patterns (see the Supporting Information, Figure S5) for the obtained POSS-containing hybrids shows a high thermal stability up to ca. 300 °C, which is higher than that of the conventional organic polymers. Moreover, ionic hybrids POSS-BM_x-PW are insoluble in most common solvents, including water, acetonitrile, methanol, ethyl acetate, DMF, DMSO, and acetic acid, and thus can be used as the heterogeneous catalysts.

Figure 2 illustrates the FT-IR spectra of ionic hybrid POSS-BM₈-PW and its intermediate products PW, POSS-Cl, and POSS-BM₈. Four characteristic vibration bands for the Keggin structure of PW₁₂O₄₀³⁻ anion are observed for PW at 1080, 985, 891, and 804 cm⁻¹ (Figure 2, curve b), assignable to the stretching vibration of the central oxygen ν(P—O_a), terminal oxygen ν(W=O_t), interoctahedral oxygen ν(W—O_b—W), and intraoctahedral oxygen ν(W—O_c—W), respectively. The FT-IR spectrum of POSS-BM₈ (Figure 2, curve c) shows the band at 1110 cm⁻¹ assigned to asymmetric vibration of Si—O—Si and the characteristic bands (1160, 1400–3140 cm⁻¹)

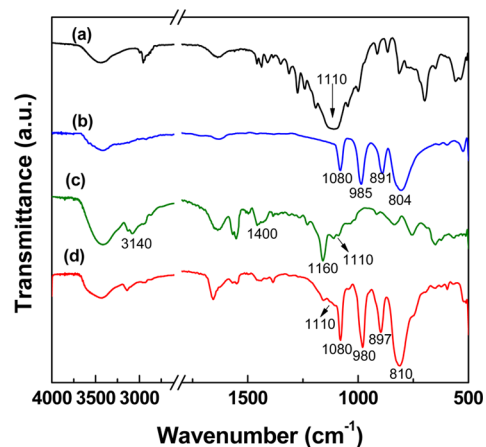


Figure 2. FT-IR spectra of (a) POSS-Cl, (b) H₃PW₁₂O₄₀, (c) POSS-BM₈, and (d) POSS-BM₈-PW.

for organic groups, indicating the presence of both POSS and BM. For POSS-BM₈-PW (Figure 2, curve d), the four Keggin peaks also appeared, with the simultaneous occurrence of the characteristic peaks for POSS-BM₈. Further, two of the vibrations for Keggin structure at 985 and 891 cm⁻¹ shifted to 980 and 897 cm⁻¹, respectively, mostly due to the strong ionic interactions between IL cations and PW anions.

Figure 3 presents the TEM images of POSS-BM₈ and POSS-BM₈-PW. Nanoparticles with small size of 10–15 nm are clearly seen for the POSS-BM₈ (Figure 3A), demonstrating the existence of POSS unites. Meanwhile, the TEM image of POSS-BM₈ shows random meso/micropores in the primary particles. In the TEM image of POSS-BM₈-PW (Figure 3B), the observed dark micelles indicates that the introduced PW has been uniformly dispersed in the PIL network. X-ray diffraction measurements (XRD) (see the Supporting Information, Figure S6) were performed to characterize the solid

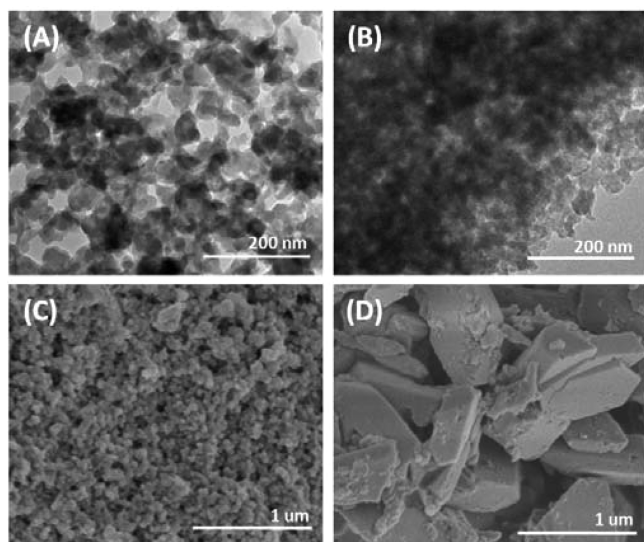


Figure 3. TEM images of (A) POSS-BM₈ and (B) POSS-BM₈-PW, and SEM images of (C) POSS-BM₈-PW and (D) BM-PW.

structures. The diffraction curve of POSS-BM₈-PW has lost the sharp characteristic crystalline peaks of H₃PW₁₂O₄₀, which is most likely originate from some disordering of the amorphous material structure by cross-linked copolymerization of the POSS and BM. The SEM image indicates that the primary particles of POSS-BM₈-PW (Figure 3C) have irregular fluff coral-shaped morphology with micrometer size and nanoscale hollow structure. However, in the case of BM-PW without

bearing POSS units in the polymeric cations, the morphology changed to angular blocks with a smooth surface (Figure 3D).

The surface area and pore structure are examined by nitrogen sorption measurements. As shown in Figure 4A, the isotherm of POSS-BM₈ is type IV with a clear H1-type hysteresis loop at a relatively higher partial pressure region of $P/P_0 = 0.9-1.0$, reflecting the existence of mesopores. Curve a in Figure 4B gives the pore size distribution of POSS-BM₈ calculated by the Barrett–Joyner–Halenda method, which shows a wide pore size distribution with the most probable pore size of 30.5 nm. Table 1 lists the surface areas, pore volumes, and average pore sizes. The results indicate that POSS-BM₈ has a moderate BET surface area of 42.2 cm²/g and pore volume of 0.21 cm³/g (Table 1, entry 1). For the POM-based ionic hybrid, POSS-BM₈-PW also shows a type-IV nitrogen sorption isotherm with H1-type hysteresis loop in a partial pressure range of $P/P_0 = 0.8-1.0$, which corresponds to the most probable pore size of 13.6 nm (Figure 4A,B, curve b). Thus, the as-synthesized POSS-BM₈-PW catalyst maintained the mesoporous nature with a reasonable specific surface area of 38.7 cm²/g and pore volume of 0.11 cm³/g, respectively (Table 1, entry 4). In contrast, POSS-free ionic hybrid BM-PW is a nonporous material with a surface area of only 3.4 cm²/g (curve c in Figure 4A,B, and Table 1, entry 8), even lower than that of PW (Table 1, entry 2). These results demonstrate that the POSS is significant for the formation of mesostructures.

We further studied the effects of the molar ratio of BM to POSS on the POSS-BM_x-PW's ($x = 2-11$) porous structures, with the nitrogen sorption isotherms and pore size distribution curves for the resultant samples displayed in Figure 4C,D, respectively. Clearly, all the samples showed typical type-IV

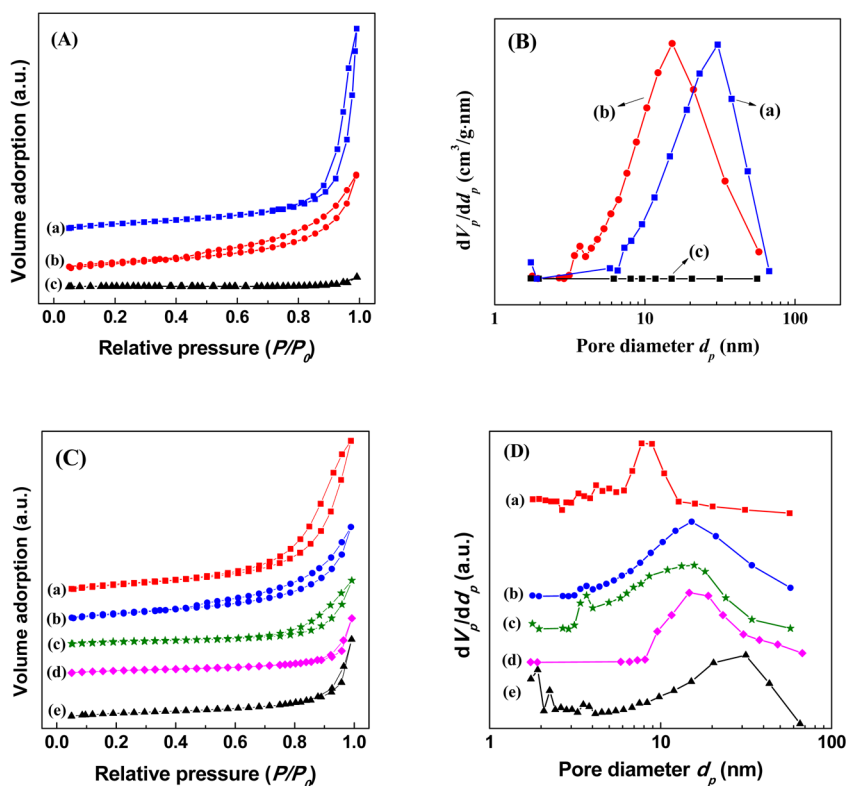


Figure 4. (A) N₂ sorption isotherm and (B) BJH pore size distributions of (a) POSS-BM₈, (b) POSS-BM₈-PW, and (c) BM-PW; (C) N₂ sorption isotherm and (D) BJH pore size distributions of (a) POSS-BM₁₁-PW, (b) POSS-BM₈-PW, (c) POSS-BM₆-PW, (d) POSS-BM₄-PW, and (e) POSS-BM₂-PW.

Table 1. Textural Properties and Catalytic Performances of Catalysts in the Epoxidation of Cyclooctene with H₂O₂^a

entry	samples	S_{BET}^b (m ² /g)	V_p^c (cm ³ /g)	D_{av}^d (nm)	solubility in reaction	con ^e (%)	sel ^f (%)
1	POSS-BM ₈	42.2	0.21	33.1	insoluble		
2	PW	5.4			soluble	26	81
3	POSS-BM ₁₁ -PW	42.0	0.16	9.5	insoluble	99	100
4	POSS-BM ₈ -PW	38.7	0.11	13.6	insoluble	99	100
5	POSS-BM ₆ -PW	26.2	0.10	14.1	insoluble	89	100
6	POSS-BM ₄ -PW	18.5	0.06	15.7	insoluble	55	100
7	POSS-BM ₂ -PW	15.6	0.06	21.4	insoluble	40	100
8	BM-PW	3.4			insoluble	42	100

^aReaction conditions: catalyst (5.56 μmol), cyclooctene (1 mmol), H₂O₂ (30%, 3 mmol), CH₃CN (5 mL), 70 °C, 6 h. ^bBET surface area. ^cTotal pore volume. ^dAverage pore diameter. ^eConversion of cyclooctene. ^fSelectivity for 1,2-epoxycyclooctane; byproducts: 2-cycloocten-1-ol, 2-cycloocten-1-one, and 1,2-cyclooctanediol.

isotherms, giving a steep increase at a relative pressure of $0.7 < P/P_0 < 1$, indicating the presence of mesoporosity. It is worth noting that the increase of the molar ratio of BM to POSS from 2 to 11 leads to continuous increase in BET surface areas and pore volumes, but causes continuous decline in pore sizes. The optimum specific surface 42.0 cm²/g and pore volume 0.16 cm³/g were obtained when the mole ratio of BM to POSS was 11:1 (Table 1, entry 1). However, an absence or rather high content of POSS evidently gives nonporous or less porous systems. The above results further confirm that the POSS plays an important role in the pore formation, and the surface area and pore structure can be adjusted flexibly through tuning the POSS content.

Catalytic Activity in the Epoxidation Reaction. The catalytic performances of various catalysts were assessed in the epoxidation of the probe substrate cyclooctene with aqueous H₂O₂ as oxidant and acetonitrile as solvent, and the results are shown in Table 1. The mesoporous PW-based ionic hybrid POSS-BM₈-PW is insoluble in the reaction and thus led to a liquid–solid heterogeneous system, exhibiting 100% selectivity with a high conversion of 99% (Table 1, entry 4, for the optimization of reaction conditions, see the Supporting Information, Figure S7). Besides, POSS-BM₈-PW also shows high conversions (>80%) with satisfying selectivity above 99% in other commonly seen solvents, such as in methanol, ethanol, and ethyl acetate (see the Supporting Information, Figure S8), but they are lower than that in acetonitrile solvent. Acetonitrile is an aprotic solvent; its inertness and weak alkalinity may be benefit for the epoxidation reaction and can prevent the ring-opening reaction of the epoxidation products. Further experiments in Table S1 (Supporting Information) demonstrate that this new hybrid catalyst POSS-BM₈-PW can be applied to different substrates such as styrene, cyclohexene, 1-octene, 1-hexene, *cis*-3-hexenol, and bipentene with good catalytic activities and selectivity.

In contrast to POSS-BM₈-PW, the ionic copolymer POSS-BM₈ is inactive and the homogeneous H₃PW₁₂O₄₀ only give a 26% conversion and 81% selectivity (Table 1, entries 1 and 2). The low selectivity is mostly due to the strong acidity of H₃PW₁₂O₄₀ that cause the ring-opening and deep oxidation of

the epoxidation product. The POSS-free counterpart BM-PW also shows a low conversion of 42% (Table 1, entry 8). The above special comparisons indicate that the POSS units are indispensable for the high activities of the target PW catalyst for epoxidation of cyclooctene with H₂O₂. Notably, ionic hybrids POSS-BM_x-PW with different molar ratios of BM to POSS cause desirable heterogeneous reactions as well, but they have quite different catalytic activities, the catalytic conversion decreased as the BM:PW molar ratio was decreased. This variation was also reflected in their surface area and pore structure, the POSS-BM₁₁-PW with a relative high surface area and large pore volume exhibits excellent conversions of 99% with 100% selectivity (Table 1, entry 3), which is similar to that of POSS-BM₈-PW. The hybrid POSS-BM₂-PW with a low surface area and small pore volume only offers 40% conversion (Table 1, entry 7). The above results demonstrate that the catalytic activities of POSS-BM_x-PW are reasonably related to its surface area and porous structure, and the comparatively high surface area and large pore volume favor higher activity.

More insight into the POSS-BM_x-PW-catalyzed epoxidation was gained by the contact angles (CAs) measurement of the PW-involved catalysts. When a droplet of cyclooctene was brought in contact with the surface of POSS-BM_x-PW ($x = 2-11$), the CAs were measured to be less than 5° for all samples (see the Supporting Information, Figure S9), demonstrating excellent surface wettability for reactant cyclooctene. With water as the testing droplet, the CAs increased as the POSS content increased (Figure 5), the enhanced hydrophobicity for

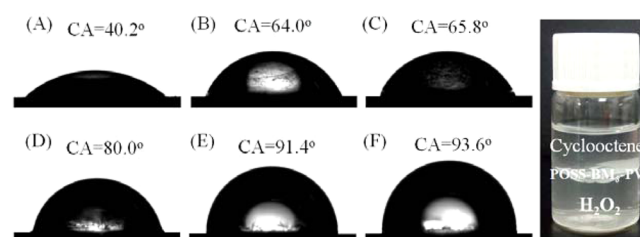


Figure 5. Water droplets on the surface of catalyst (A) BM-PW, (B) POSS-BM₁₁-PW, (C) POSS-BM₈-PW, (D) POSS-BM₆-PW, (E) POSS-BM₄-PW, and (F) POSS-BM₂-PW. Photographs of POSS-BM₈-PW appeared at the H₂O₂/cyclooctene interface.

POSS-BM_x-PW may be attributed to the hydrophobicity of the POSS monomer. It is well-known that the catalytic activity of solid catalysts on H₂O₂-based epoxidation of alkenes is significantly affected by its surface wettability, and constructing an amphiphilic substructure for a solid is one of the most effective solution to form highly reactive systems.^{40–43} In this case, the POSS-BM₈-PW and POSS-BM₁₁-PW with good wettability for both cyclooctene and water show much higher catalytic activities than that of hydrophobic POSS-BM₂-PW. We thus suggest that excellent catalytic activities of POSS-BM₈-PW and POSS-BM₁₁-PW for epoxidation of cyclooctene largely arise from their unique amphiphilic catalyst structure. Correspondingly, the dispersion property of the POSS-BM₈-PW in H₂O₂/cyclooctene biphasic media in Figure 5 shows that POSS-BM₈-PW could be well dispersed at the interface of the H₂O₂ and cyclooctene phases, which further confirms the amphiphilic nature of POSS-BM₈-PW. It is thus proposed that the amphiphilic catalyst structure should have supplied a unique microenvironment for the catalyst to involve both the hydrophobic alkene substrates and hydrophilic H₂O₂ molecules

during the epoxidation reaction, which allows PW species in the bulk of the catalyst give full play as active centers.

Catalyst Resuability. After reaction, the catalyst recovered by filtration was washed with ethanol, dried, and reused for the next run without adding any fresh catalyst. The catalytic reusability for POSS-BM₈-PW in epoxidation of cyclooctene was measured by four-run tests. The results in Figure 6 reveal

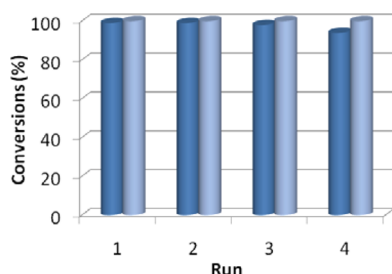


Figure 6. Catalyst recycling in epoxidation of cyclooctene with H₂O₂ over POSS-BM₈-PW.

quite a steady reusability for this hybrid catalyst, and in each run, only the corresponding epoxide was detected and no other ring-opening byproducts were found. To test the possible catalysis of the slightly leached metal species in the reaction solution from the catalyst, a hot-filtration experiment was carried out. Initially, the mixture of catalyst POSS-BM₈-PW and H₂O₂ in acetonitrile was stirred at 70 °C for 2 h. The catalyst was then removed and the reaction proceeded for another 4 h with the homogeneous filtrate. It can be seen in Figure S10 (Supporting Information) that no oxidation occurred. Furthermore, the concentration of W in the reacted filtrate was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) elemental analysis. The result shows that less than 1.1 wt % W in the catalyst leached into the reaction media, and this slight amount of leached W species have not taken a role of catalysis during the hot-filtration test. The above results strongly indicate the heterogeneous nature of the present catalyst POSS-BM₈-PW for the epoxidation reaction. The slight decrease of the activity in the fourth run is mostly due to the weight loss in the operation for recovering the catalyst. Furthermore, the IR spectrum for the recovered POSS-BM₈-PW in Figure S11 (Supporting Information) was well consistent with that of the fresh one, demonstrating a durable catalyst structure.

CONCLUSIONS

In summary, we have demonstrated the successful application of octachloropropyl-POSS as a building block for preparing amphiphilic mesoporous POM-based ionic hybrids POSS-BM_x-PW via free radical polymerization and ion exchange reaction. Particularly, the controllable introduction of POSS units into the polymeric IL cations favors the pore structure and surface wettability control of these POM-based ionic hybrids. The obtained hybrid materials were found to be highly efficient catalysts for epoxidation of cyclooctene with H₂O₂ as an oxidant. The overall superior catalytic activity, high selectivity, and excellent recyclability of POSS-BM_x-PW as a heterogeneous catalyst could be attributed to their unusual pore structure and the amphiphilic surface, which allow for a rapid diffusion of the reactants into the reactive PW centers. The approach in this work represents an ideal pathway for easy access to a series of porous, functionalizable hybrids with high

surface tailorability, which can be applied for catalytic applications and is also promising for a myriad of potential applications.

ASSOCIATED CONTENT

Supporting Information

¹H NMR spectra for dicationic imidazole IL, POSS-Cl, and POSS-IM, ²⁹Si NMR spectrum for POSS-Cl, TG patterns for POSS-BM₈-PW, POSS-Cl and POSS-BM₈, XRD patterns for H₃PW₁₂O₄₀ and POSS-BM₈-PW, the influence of different reaction conditions on conversion of epoxidation of cyclooctene over catalyst POSS-BM₈-PW with H₂O₂, the catalytic performances of catalysts in epoxidation of cyclooctene with H₂O₂ in different solvents, the cyclooctene droplets on the surface of catalysts, the kinetic profile of epoxidation of cyclooctene with H₂O₂ and leaching experiment of POSS-BM₈-PW, the FT-IR spectra of fresh and reused catalyst POSS-BM₈-PW, epoxidation of various alkenes with H₂O₂ catalyzed by POSS-BM₈-PW. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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